(War Research)

THE MECHANISM OF RDX FORMATION IN THE BACHMANN REACTION

A Thesis

by

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THE MECHANISM OF RDX FORMATION IN THE BACHMANN REACTION

The mechanism of RDX formation in the Bachmann reaction has been investigated from two distinct experimental points of view.

The first approach was made by substituting amine nitrates for the ammonium nitrate, by withholding the ammonium nitrate and by adding ammonium or amine nitrates in the later stages of the reaction. Ammonium nitrate is not unique in its function; nearly all amine nitrates generate some RDX when substituted for ammonium nitrate in the Bachmann reaction, although never in yields greater than one mole per mole of hexamine. The belated addition of an amine nitrate, unlike the belated addition of ammonium nitrate, does not give rise to RDX. These techniques were also applied to a study of the conversion of DNPT to HMX. Here, too, ammonium nitrate is not unique.

The second approach was made by studying the effect of many reaction variables on the yields of solid products, recovery of reagents from the mother liquor and material balances in the Bachmann reaction. It is believed that the equivalence between RDX production and ammonium nitrate consumption as determined by other researchers is invalid.

The results of these experiments may be successfully interpreted in terms of a mechanism involving the two processes of "catalysed nitrolysis" and "synthesis", while many data herein presented cannot be interpreted in terms of other mechanisms.

FOREWORD

Some explanation of the method used in this thesis in discussing the results of other investigators is necessary. Experiments which were carried out before this project was undertaken and experiments which are of general interest only are described in the Historical Introduction to this thesis. Experiments which were carried out concurrently and experiments which are of specific interest from a point of view of the problem are discussed, along with the author's own results, in the Experimental and Theoretical section of this thesis. It is considered that this procedure is justified from a standpoint of clarity and brevity. Very careful distinction has been made between the author's own results and those of other investigators.

With regard to etymology, two terms have been introduced which are not generally used. The term "researcher" corresponds to the more conventional "research worker" or "investigator". The term "inisolable" has been used in the sense of "unable to be isolated".

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GENERAL INTRODUCTION

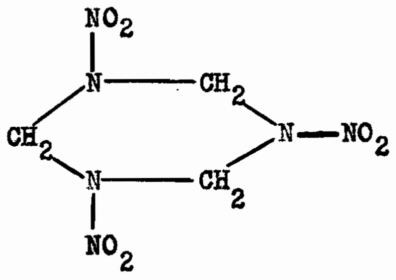
One of the most outstanding advances in organic chemistry during World War II has been the development of new methods for the preparation of cyclotrimethylenetrinitramine (RDX) on an industrial scale. Linstead has stated in his second monograph (1) that "RDX has indeed been organic chemistry's main contribution to the war effort and the war's main contribution to organic chemistry."

RDX was first prepared by Henning (2) in 1899 and was early recognized as an explosive of extraordinary power and brisiance. For many years, no successful industrial preparation of RDX was realized. One of the reasons for this was the fact that formaldehyde, a starting material, was available only in limited quantities. This barrier to the industrial preparation of RDX was removed in 1923 by the introduction of a method of preparing methanol (and hence formaldehyde) by the catalytic reduction of carbon monoxide (3). In 1932, the literature reported the existence of an RDX plant at Avigliana, Italy, which was operated by the Nobel Dinamite Company (4). During the past decade, the Research Department of the Royal Arsenal at Woolwich has carried out extensive investigations on the production of RDX and, at as early a date as 1938, a pilot plant was in operation (5).

When war broke out in September, 1939, research in the field of high explosives was stimulated in all countries. The result of these increased efforts was the discovery of a new and essentially different method of producing RDX (6) and the development of the older method to large-scale production.

In the early stages of World War II, RDX was available only in very limited quantities and found its greatest use as a special-purpose explosive. As the war progressed, RDX found increased use in mines, torpedoes, plastic explosive, high-explosive shells, aerial bombs and jet-propelled bombs. Some estimate of its importance is to be found in the fact that the allied nations now produce in the order of 5,000,000 tons of RDX annually - - a thousandfold increase in five years. This estimate is based on the rated capacity of the three principal RDX plants: Wabash, Indiana; Kingsport, Tennessee; Bridgewater, England. RDX has been found in German, Italian and Japanese high-explosive shells, and is known to be produced by these countries in at least two ways. (7)

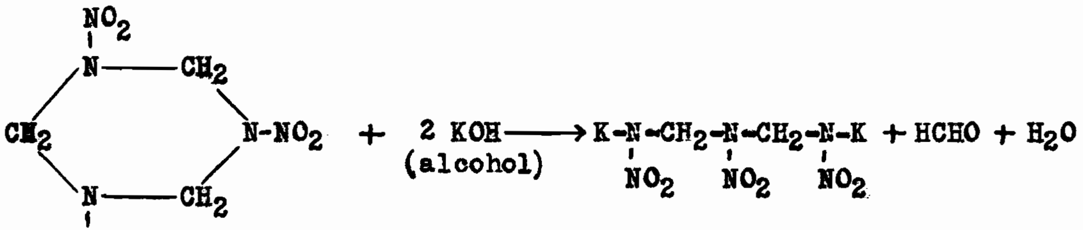
RDX is variously known a Hexonite (Henning). Hexogen (Germans, French and Swiss), T_4 (Italians) and Cyclonite or RDX (British and Americans). In Chemical Abstracts it is listed as Hexogen. Its chemical structure may be represented by the following formula:



Corresponding to this representation, RDX may be named

1,3,5-trinitrohexahydro-1,3,5-triazine, N-trinitrotrimethylenetriamine, cyclic trimethylenetrinitramine or 1,3,5-trinitro-1,3,5-triazacyclohexane.

The chemical structure of RDX has never been conclusively proved. The generally-accepted structure was postulated by von Herz (8) who called his product cyclotrimethylenetrinitramine. RDX undergoes no known chemical reactions other than complete degradation, with one possible exception. Ross and Boyer (9) have reported the isolation of a metallic derivative of an open-chain degradation product of RDX, the structure of which is uncertain. On the basis of a study of some straight-chain methylenenitramines, they believe that the reaction may be represented by the following equation:



- - - - - - - - - - 1.

This research has not been carried far enough, however, to admit it as evidence for the structure of RDX.

A chemical proof-of-structure of RDX lies in its preparation in yield from hexamethylenetetramine*(urotropine) by two separate and distinct methods (2, 6). Hexamine is believed to contain four

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* Hereinafter called hexamine.

six-membered rings (see Figure I), but its structure, too, is uncertain (10, 11). Another, and perhaps a better, chemical proof-of-structure of RDX is the preparation of RDX in yield by the low-temperature, nitric acid oxidation of 1,3,5-trinitrosohexahydro-1,3,5-triazine (11). The structure of the trinitroso compound is somewhat more certain than that of the trinitro compound since Duden and Scharff (10) have reduced the trinitroso compound to 1,3,5-triaminohexahydro-1,3,5-triazine (isolated as the salicylaldehyde derivative) which, in turn, was decomposed into three moles of hydrazine and three moles of formaldehyde on warming with dilute mineral acids.

In the end, however, it must be admitted that the weight of evidence for the triazine structure of RDX lies in such broad statements as "analytical results," "stability of RDX to concentrated nitric acid," the "symmetry of the X-ray pattern diagram," and the "evidence of the dipole moment." (5)

Industrially, RDX is produced by two different processes. These may be briefly represented by the following theoretical equations:

<u>Nitrolysis (Woolwich) Process:</u>

$$(CH_2)_6N_4 + 4HNO_3 \longrightarrow (CH_2)_3(N\text{-}NO_2)_3 + 3HCHO + NH_4NO_3$$

(Hexamine) (Nitric Acid) (RDX) (Formaldehyde) (Ammonium Nitrate)

----- 2.

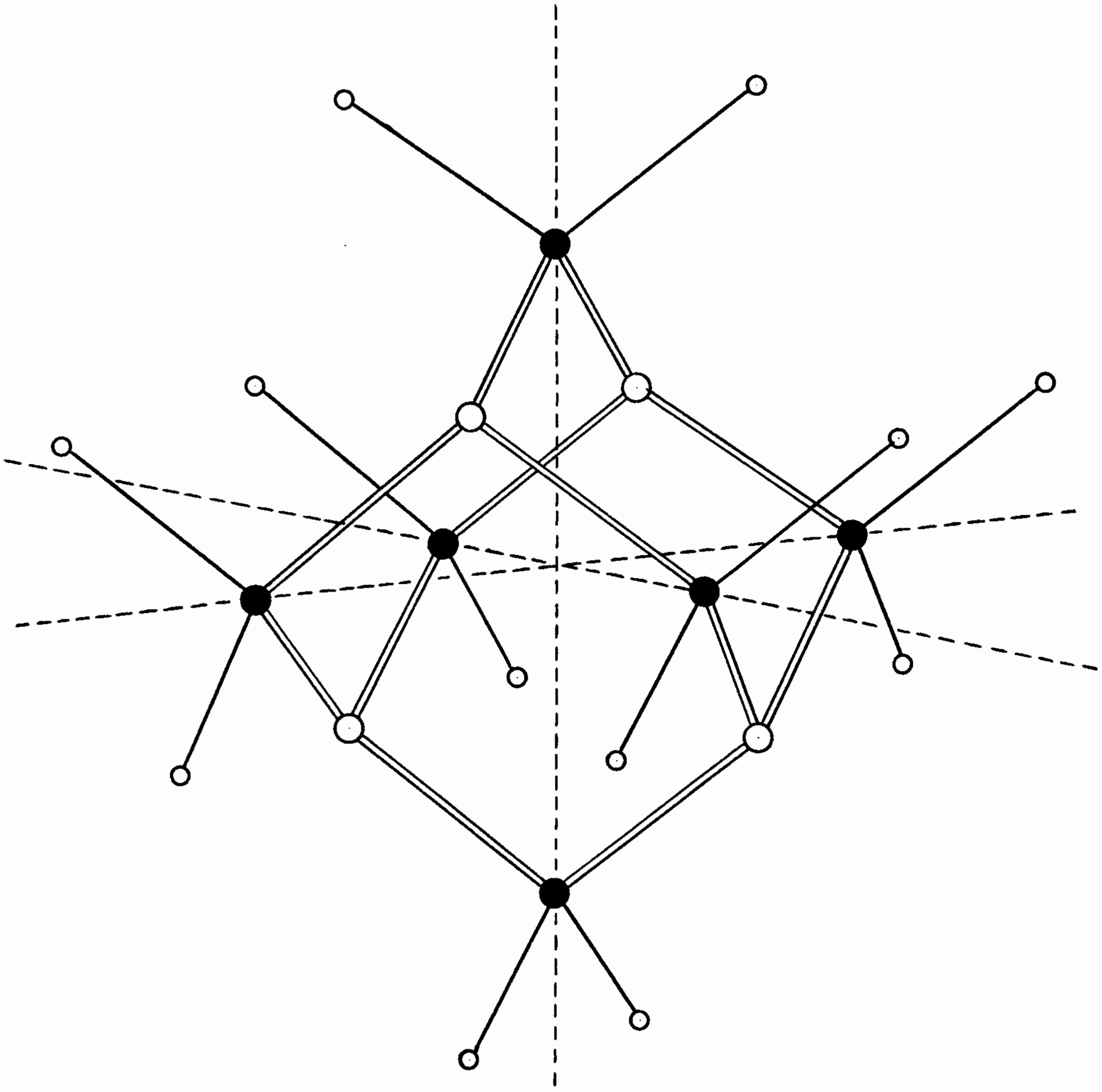

Figure No. 1

Molecular Model Hexamethylenetetramine

● Carbon Atom

○ Hydrogen Atom

◯ Nitrogen Atom

Bachmann (Combination) Process:

$$(CH_2)_6N_4 + 4\ HNO_3 + 2\ NH_4NO_3 + 6\ (CH_3CO)_2O \longrightarrow$$

(Hexamine) (Nitric Acid) (Ammonium Nitrate) (Acetic Anhydride)

$$\longrightarrow 2(CH_2)_3(N\text{-}NO_2)_3 + 12\ CH_3COOH \quad \text{-----} \quad 3.$$

(RDX) (Acetic Acid)

While the direct nitrolysis process is theoretically represented by equation 2, in actual practice it is more accurately represented as follows (12) :

$$(CH_2)_6N_4 + 15.60\ HNO_3{}^{*} \longrightarrow 2.9\ CO_2 + 11.60\ NO_2 + 1.40\ N_2 +$$

$$+ 0.20\ N_2O + 0.80\ (CH_2)_3(N\text{-}NO_2)_3 + 11.40\ H_2O +$$

$$+ 0.7\ CO_2\ \text{(unaccounted for)} \quad \text{------} \quad 4.$$

The yield of RDX on the basis of the formaldehyde content of the hexamine approximates forty percent and on the basis of the nitric acid, no higher than ten percent. In view of the low yields, of the fact that nitric acid of greater than eighty-nine percent and preferably of ninety-seven percent strength is required, and also of the serious danger of violent decomposition of the reaction mixture, extensive research was carried out with the purpose of finding a new process.

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* Actually 22 moles of nitric acid are required, but approximately 7 moles are recovered unchanged.

In 1940, Ross and Schiessler (13) succeeded in preparing RDX in yield by the interaction of paraformaldehyde (paraform) and ammonium nitrate in the presence of an excess of acetic anhydride. The reaction may be represented by the following theoretical equation:

$$\underset{\text{(Paraform)}}{3\,(CH_2O)_n} + \underset{\text{(Ammonium Nitrate)}}{3n\ NH_4NO_3} + \underset{\text{(Acetic Anhydride)}}{6n\ (CH_3CO)_2O} \longrightarrow$$

$$\underset{\text{(RDX)}}{n\ (CH_2)_3(N\text{-}NO_2)_3} + \underset{\text{(Acetic Acid)}}{12n\ CH_3COOH} \quad \text{-----} \quad 5.$$

The yield of RDX in this reaction approaches fifty-five percent on the formaldehyde basis and only slight excesses of ammonium nitrate and acetic anhydride are required. The reaction is characterized by an induction period (14), however, which is disadvantageous from an industrial point of view, and the reaction mixture is subject to violent decomposition (13). It is possible that further research will eliminate these difficulties, but up to the present time, the "McGill Process" has not advanced beyond the pilot plant stage. The main interest in the McGill Reaction lies in its theoretical implications and in the fact that it was the forerunner of the Bachmann process.

In 1941, Bachmann (6) found that by nitrating hexamine with a mixture of nitric acid and ammonium nitrate in the presence of acetic anhydride he could produce RDX in yields greater than one mole per mole of hexamine. Since this reaction (see equation 3) combined essential features of both the direct nitrolysis and McGill processes (the use of hexamine and nitric acid on the one hand and the use of ammonium nitrate and acetic anhydride on the other), he called it the "Combination Process." The yield of RDX in this case approximates eighty percent on the formaldehyde basis and only small excesses of nitric acid, ammonium nitrate and acetic anhydride are required. In addition to these attractive features, the introduction of acetic acid (15) as a solvent for the hexamine gave rise to simplicity of operation and ease of temperature control. The reaction was soon put on the basis of a continuous process and adapted to pilot-plant and plant scale operation.

The question of the mechanism of RDX formation has always been of interest; this interest has increased greatly corresponding to the new demands for RDX as a military explosive and the discovery of new methods for its preparation. In particular, the mechanism of RDX formation in the Bachmann reaction is of interest due to its pre-eminence among the industrial methods and to the fact that it combines features of both the direct nitrolysis and McGill reactions. This mechanism is, however, extremely complex of solution. *

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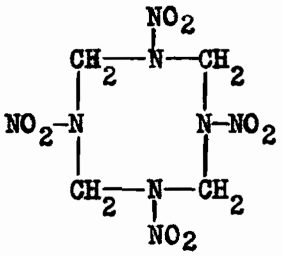
* The problem, "The Stepwise Elucidation of the Mechanism of RDX Formation," was assigned to this researcher by the Chairman of the Associate Committee on Research of the Explosives Committee of the National Research Council; XR - 42 (Jan. 1942).

The complexity of an investigation of the mechanism of the Bachmann reaction is due in part to the fact that the reaction mixture contains at least four reactants and produces at least three products. In this reaction, temperature, time and dilution play an important part in determining the yields (both absolute and relative) of the various reaction products as do the rates of addition of reagents (both absolute and relative) and concentrations of reagents (both absolute and relative). Furthermore, in discussing the mechanism of the Bachmann reaction, one must take into account those factors which it has in common with the direct nitrolysis and McGill reactions and also the dozens of allied reactions which have been elucidated during the past few years and which now constitute the field of chemistry of the polymethyleneamines and polymethylenenitramines.

Early in this investigation, it was decided that the best approach to the mechanism of RDX formation lay in an investigation of the function of the ammonium nitrate in the Bachmann reaction. The reason for this decision was threefold.

1. Ammonium nitrate is a necessary component of both the McGill and Bachmann reactions and, at the time that this investigation was started, it was thought to be unique in its function (16).

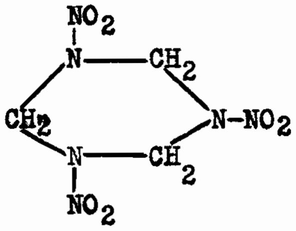
2. Ammonium nitrate seems to be, in some way, associated with the production of HMX, the most important by-product in the McGill and Bachmann reactions;



(HMX)

In the nitrolysis reaction, the yield of HMX relative to the yield of RDX is in the ratio of about 1:2500 (17). In both the McGill and Bachmann reactions, the ratio is of the order of 1:15 (18).

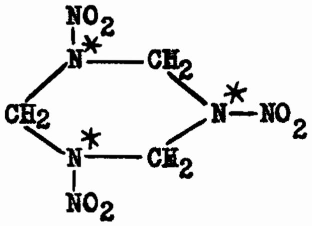
3. Since in the nitrolysis reaction, the hexamine molecule represents the only source of amino nitrogen, it is obvious that all of the nitrogen in the triazine ring of RDX must have originated in the hexamine molecule. The molecule of RDX produced in this way may be pictured as follows:



TYPE I RDX

In the idealized reaction (see equation 2) one mole of RDX is produced per mole of hexamine.

Similarly, in the McGill reaction, the ammonium nitrate is the only source of amine nitrogen atoms: thus it is obvious that all of the ring nitrogen in the RDX must have originated in the ammonium nitrate. A molecule of RDX produced in this manner may be represented as follows:

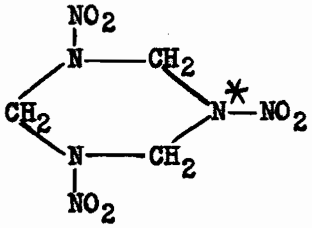


TYPE II RDX **

where N^* refers to an amino nitrogen atom which originated in the ammonium nitrate rather than in the hexamine. In the idealized reaction (see equation 5), one mole of RDX will arise from three moles of formaldehyde (paraform) and three moles of ammonium nitrate.

In the case of the Bachmann reaction, however, both the hexamine and the ammonium nitrate may act as sources of amino nitrogen. In view of this fact, two possible*** cases present themselves in dealing with an idealized Bachmann reaction (see equation 3):

Case I



(2 moles)

TYPE III RDX

This representation implies that the two moles of RDX arising from one

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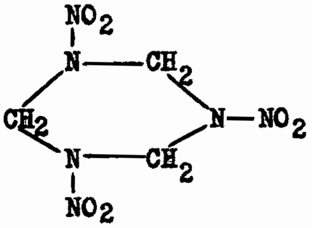
** It should be emphasized that the different "Types" of RDX are chemically and physically identical, differing only with respect to the "history" of their amino nitrogen atoms.

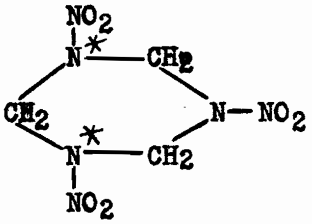
*** There is actually one other case corresponding to complete random distribution of amino nitrogen atoms, but the mechanism corresponding to this case is considered unlikely (see page 156 Ref.1).

mole of hexamine are identical, each containing two amino nitrogen atoms originating in the hexamine and one amino nitrogen atom originating in the ammonium nitrate.

Case II


(1 mole)

TYPE I RDX


(1 mole)

TYPE IV RDX

This representation implies that the first mole of RDX produced in the Bachmann reaction contains only amino nitrogens which had their origin in the hexamine. It is also implied that the triazine ring in this mole of RDX is one which existed in the hexamine, having survived the reaction conditions. In this case, it is necessary that the second mole of RDX have, on an average**, two amino nitrogen atoms which originated in the ammonium nitrate and only one in the hexamine.

** The second mole of RDX may well be composed of all four possible "Types", but in theory, the average structure must be Type IV.

Now, the existence of the two possibilities in the mechanism of the Bachmann reaction (as represented by Case I and Case II), presents to the researcher his first major problem in connection with the mechanism and yet, at the same time, opens to him three distinct experimental approaches to the solution of the mechanism. The problem is, obviously, to decide whether Case I or Case II represents the type of product produced. The experimental approaches may be summarized briefly as follows:

(a) The first method of attacking the problem is to attempt to "mark" or "label" the amino nitrogen atoms of either the hexamine or the ammonium nitrate in order that the "Types" of RDX may be differentiated by something more tangible than the mere "history" of a given nitrogen atom.

(b) The second experimental approach is based on the fact that if Case II is indicative of the mechanism of the reaction, the first mole of RDX (Type I) contains no amino nitrogen atoms which originated in the ammonium nitrate. Thus, with respect to the first mole of RDX, the function of the ammonium nitrate is purely catalytic. In this case, then, it may be possible to substitute some other catalyst for the ammonium nitrate and still obtain one mole of RDX. In Case I, however, the ammonium nitrate actually contributes to both moles of RDX and its function here is synthetic rather than catalytic. In this event, no other substance should be able to replace the ammonium nitrate.

(c) If Case I represents the reaction product, the molar consumption of ammonium nitrate should equal the molar production of RDX since each molecule of RDX contains one amino nitrogen atom which originated in a molecule of ammonium nitrate. In Case II, however, the ratio between ammonium nitrate consumption and RDX production is not necessarily equal to unity and would be expected to vary with changing reaction conditions. Thus, an investigation of the ammonium nitrate consumption constitutes a third experimental approach.

It was for these reasons that an investigation of the function of the ammonium nitrate in the Bachmann reaction was considered to be the most promising approach to the problem of the mechanism of RDX formation. The experimental procedures used and the results obtained in this investigation are considered in another section of this Thesis.

HISTORICAL INTRODUCTION

The (Direct) Nitrolysis Reaction

$$(CH_2)_6N_4 + 4HNO_3 \longrightarrow (CH_2)_3(N\text{-}NO_2)_3 + 3HCHO + NH_4NO_3 \text{ ------- } 2.$$

The majority of significant research carried out on the direct nitrolysis reaction has been reported by the following workers or groups of workers: Henning (2), von Herz (8), Hale at the Picatinny Arsenal (19), Roberts and co-workers at the Research Department* of the Royal Arsenal, Woolwich (1, 5), Whitmore at Pennsylvania State College (20), Wright at the University of Toronto (21), Winkler at McGill University (22), Hirst at the University of Bristol (1), and Linstead of the British Central Scientific Office (1, 5). It is not the purpose of this dissertation to abstract all of these series of papers, but it is intended to present in as brief and clear a manner as possible all experimental results believed to be significant from a point of view of the reaction mechanism and to deal concisely with all postulated mechanisms.

Experimental

It is proposed to discuss the experimental data of previous workers under the heading of the various reaction variables.** In cases where more than one worker has investigated the same phenomenum, the results of the most extensive investigation are used. In cases where the results of two investigations differ, the most widely-accepted results are reported unless the difference itself is of significance.

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* Hereafter designated as R.D. or A.R.D. (Armament Research Dept.).

** This method has also been used by Linstead (1).

1. Nitric Acid Strength

An extensive investigation of this phase of the nitrolysis reaction has been reported by Winkler (22). His investigations* were carried out in the region of 89 to 97 percent nitric acid. For a given nitric acid: hexamine ratio, the rate of RDX formation increases with increased acid strength. For a given ratio, the yield of RDX decreases with decreased acid strength unless the ratio is high (a value of 20 - 30 moles of nitric acid to one mole of hexamine is considered normal); if the ratio is high, however, the final yield of RDX is independent of the acid strength within the range of concentrations studied.

For acids of less than 89 percent, the yield falls off rapidly no matter how high the ratio of nitric acid to hexamine. Winkler reports a yield of 44 percent RDX (instead of 80 percent) at 86 percent acid. Hale (19) reports only a trace of RDX at 80 percent acid. All workers agree that no RDX is produced using 70 percent acid.

For acids of greater than 97 percent strength, there is some disagreement. The R.D. (23) reports that there is an optimum strength of nitric acid for a given nitric acid: hexamine ratio and for a given temperature. This optimum lies in the region 96 to 98 percent acid and about 82 percent RDX yield is obtained at the optimum.

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* While the experimental technique of various workers differs somewhat, their methods of carrying out batch nitrolysis reactions are essentially the same: hexamine is added slowly to cooled nitric acid and the reaction temperature is controlled by internal (dry ice) or external (dry ice-acetone) cooling; when the reaction is essentially complete, the mixture is sometimes heated briefly and is then diluted with water. For details of the experimental procedures see references 1,5,8,19,20,21,22.

Other workers (20,21) report that the yield of RDX increases right up to 100 percent acid. Wright has shown that 106 percent nitric acid (100 percent nitric acid fortified with nitrogen pentoxide) gives a yield of only 31 percent of RDX. (21).

2. Nitric Acid: Hexamine Ratio

Winkler (22) has shown that for nitric acid of 89 percent, 92 percent, 95 percent and 98 percent strength, the rate of RDX formation increases rapidly with an increase in the nitric acid: hexamine ratio. As regards total yield of RDX, no RDX was obtained for molar ratios below a value of ten to one. As the ratio is increased beyond this value, the yield increases rapidly to a maximum. This maximum is reached more slowly with lower concentrations of nitric acid. The maximum yield is independent of the acid strength provided that the ratio is sufficiently high.

The group at Bristol (24) have investigated the yield of RDX using 98 percent nitric acid and nitric acid : hexamine ratios between 10 and 150 at temperatures of 0°C. and 20°C. The results of this investigation were essentially the same as those obtained by Winkler. For the series of runs at 0°C., a flat maximum was reached in the region of 22 moles of nitric acid per mole of hexamine. At 20°C., however, the yield of RDX fell off from the maximum as large excesses of nitric acid were used. This decrease in yield was not due to solubility and it must be considered that RDX is destroyed by nitric acid at this temperature or, alternatively, the actual RDX production may be lower.

It has been emphasized by Winkler (22) that the nitric acid strength factor and the nitric acid:hexamine ratio factor are in a sense complementary. Within limits, low nitric acid strength may be compensated for by use of large excesses of nitric acid. Further, in his rate studies, Winkler found that the initial rate of RDX formation is proportional to the number of moles of nitric acid in excess of a given minimum.

3. Temperature (25)

Below 30°C., the temperature of the reaction has little effect on the final yield of RDX but it influences the rate of RDX formation to a very great extent. The rate of RDX formation increases greatly with increased temperature. For example, the nitration of hexamine with 26 moles of 98 percent nitric acid showed that at 0°C., nitration is complete in eighty minutes while at 10°C., nitration is complete in twenty minutes. At temperatures above 30°C., there is a definate decrease in yield with an increase in temperature.

During the reaction, about 70 kcals. of heat are immediately evolved per mole of hexamine. This is followed by a slow evolution of heat amounting to about 14 kcals. per mole, this value being smaller at low temperatures. This secondary evolution of heat is considered to be due to oxidative decomposition (26).

4. Time

In this discussion time has been considered as a dependent variable.

5. Diluents and Catalysts (1)

Apart from chloroform and nitromethane, which do not seem to affect the yield, solvents decrease the yield of RDX.

Acetic acid, acetic anhydride, nitrous acid, mineral acids (other than nitric acid), phosphorus pentoxide, nitrogen pentoxide, sulphur dioxide and iodine depress the yield of RDX. Whitmore (20) and Wright (21) have found that inorganic salts are ineffective in small concentrations and are deleterious in larger amounts.

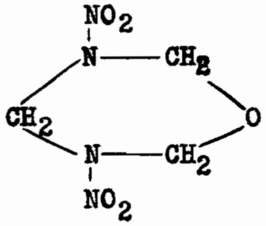
The history of the use of ammonium nitrate in the reaction mixture is an interesting one. The R.D. (25) reported that the addition of ammonium nitrate to the nitrolysis reaction mixture in equal weight to the weight of hexamine used had a slight beneficial effect when the reaction mixture was held at 50°C. for about thirty minutes before dilution. Whitmore (20) and Wright (21), however, reported that the addition of ammonium nitrate was either without effect (at 100 percent nitric acid strength) or was decidedly detrimental (at lower concentrations of nitric acid). In June, 1944, it was disclosed that workers in England (27) had achieved great increases in yield by the addition of large amounts of ammonium nitrate to the reaction mixture after the initial nitrolysis was complete and by heating this mixture to 90°C. for about thirty minutes. The effect was most pronounced when the ammonium nitrate: nitric acid ratio was two to one and when large excesses of this complex were used. Yields up to 135 percent (on the basis of one mole of RDX from one mole of hexamine) have now been obtained. At the same time it was reported that formaldehyde and many compounds containing the methylene group yielded RDX when subjected to this same treatment. These results have been confirmed and extended by Wright (34). This research constitutes one of the major advances in RDX chemistry since the discovery of the Bachmann reaction.

6. Products, By-Products and Intermediates

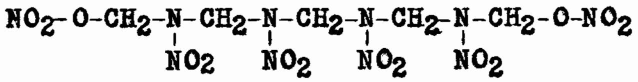
RDX is the principle product of the nitrolysis reaction and is obtained in better than 80 percent yield under optimum conditions. By-products in the reaction are HMX, cyclonite oxide, 106, P_1,P_2 and a precursor of DNPT.

HMX:- The presence of HMX (cyclotetramethylenetetranitramine) in the liquors of the nitrolysis reaction was established by Wright (28) and has already been mentioned (see Page 10). This by-product is produced in extremely small quantities and is of little but theoretical importance in the nitrolysis reaction.

Cyclonite oxide:- The compound cyclonite oxide was reported by the R.D. (29) to occur in the crude nitrolysis product in small quantities. It has been assigned the structure of 3,5-dinitro-1-oxa-3,5-diazacyclohexane:



106:- Wright (21) has isolated very small quantities of 1,9-diethoxypentamethylene-2,4,6,8-tetranitramine after fractional recrystallization of a crude nitrolysis product. This is believed to have arisen from the 1,9-dinitroxy derivative ("106") after alcohol recrystallization.



$$NO_2\text{-}O\text{-}CH_2\text{-}\underset{NO_2}{\underset{|}{N}}\text{-}CH_2\text{-}\underset{NO_2}{\underset{|}{N}}\text{-}CH_2\text{-}\underset{NO_2}{\underset{|}{N}}\text{-}CH_2\text{-}\underset{NO_2}{\underset{|}{N}}\text{-}CH_2\text{-}O\text{-}NO_2$$

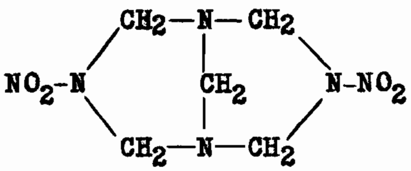
("106")

P_1 and P_2:- When the undiluted nitrolysis mixture is extracted with carbon tetrachloride, fairly large quantities of a liquid product are obtained in the extract. This liquid may be separated into high-boiling and low-boiling fractions which have been named P_1 and P_2 respectively. These products are believed to represent the fate of the formaldehyde liberated in equation 2. While their structures are uncertain, they have been assigned the following formulae* (5):

$$NO_2\text{-}CH(OH)\text{-}O\text{-}NO_2 \qquad (P_1)$$

$$NO_2\text{-}CH(OH)\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}NO_2 \qquad (P_2)$$

DNPT:- On neutralization of the diluted mother liquor, a small quantity of DNPT is produced (21). Wright has postulated the structure for DNPT as (bicyclo)-dinitropentamethylenetetramine:



This substance is not believed to exist as such in either the undiluted or unneutralized reaction liquors but is thought to arise from a precursor upon neutralization. In view of recent work it seems that this precursor is 1,3-hydroxymethylenenitramine (21) or its nitrate:

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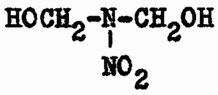
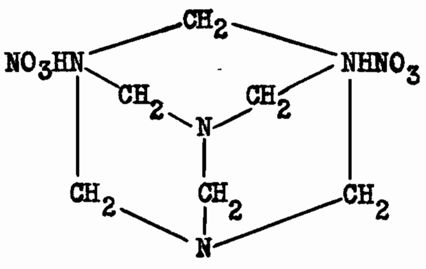
* See also p. 27



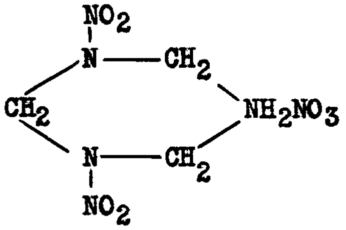
$$HOCH_2-\underset{\displaystyle NO_2}{\underset{|}{N}}-CH_2OH$$

Three compounds, hexamine dinitrate, PCX and PCX-A, have been isolated in modified nitrolysis reactions and may be intermediates in the production of RDX by the direct nitrolysis reaction.

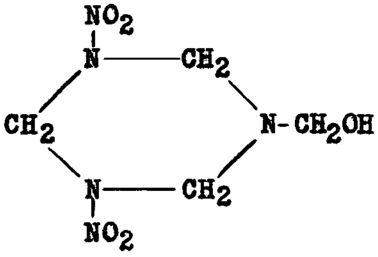
Hexamine Dinitrate:- If hexamine is added to a solution of concentrated nitric acid in chloroform, hexamine dinitrate is precipitated momentarily and is then dissolved as the reaction goes on to give RDX (30). Furthermore, if hexamine dinitrate is used in the nitrolysis reaction instead of hexamine, the yield of RDX (30), the rate of RDX formation (22), the heat of formation of RDX (31), and the energy of activation of the reaction (22) are the same as when hexamine is used. It is generally agreed that at least some hexamine mono-, di- and trinitrate are formed when hexamine is added to the concentrated nitric acid (32), but there is general disagreement as to how much of each is formed and as to which one, if any, represents the general course of the reaction. The formula for hexamine dinitrate is as follows:



PCX:- PCX was first prepared by Winkler (22) by dissolving hexamine dinitrate in an excess of 89 percent nitric acid at low temperatures (-40°C) and by diluting this reaction mixture with chipped ice after a few minutes' standing. The precipitate, PCX, was obtained in good yield. It may be converted to RDX in almost theoretical yield by the action of eight moles of strong nitric acid. Winkler believes that the conversion of PCX to RDX represents the rate-controlling step in the nitrolysis reaction and states that the activation energy of the nitrolysis reaction approximates that of the PCX-RDX conversion. The researchers at the Armament Research Department (A.R.D.) (33) have suggested that PCX is not a true intermediate but is formed through a hydrolysis reaction. The generally-accepted formula is that of 3,5-dinitrohexahydro-1,3,5-triazine nitrate-(1):



PCX-A:- When the A.R.D. (33) attempted to prepare PCX by drowning the reaction liquor with ether instead of water, they obtained a small yield of an ethoxy derivative of PCX-A after recrystallization of the crude product from alcohol. Winkler does not believe that this compound is a true intermediate and has shown that PCX-A can be obtained from PCX in the presence of formaldehyde. The generally-accepted structure of PCX-A is 1-methylol-3,5-dinitrohexahydro-1,3,5-triazine:



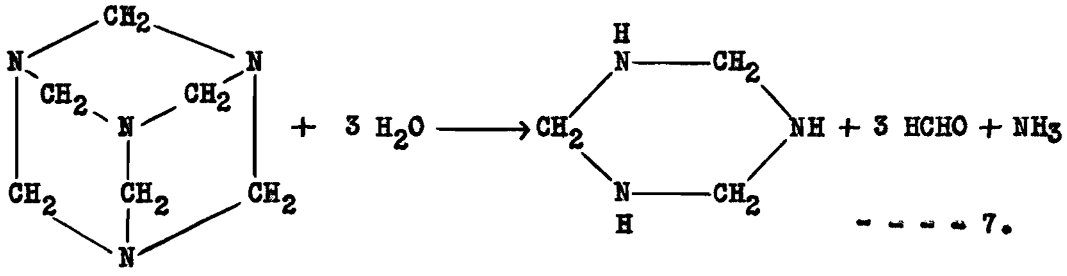
(PCX-A)

The question as to whether the three compounds mentioned here are true intermediates or not is discussed further in the next section.

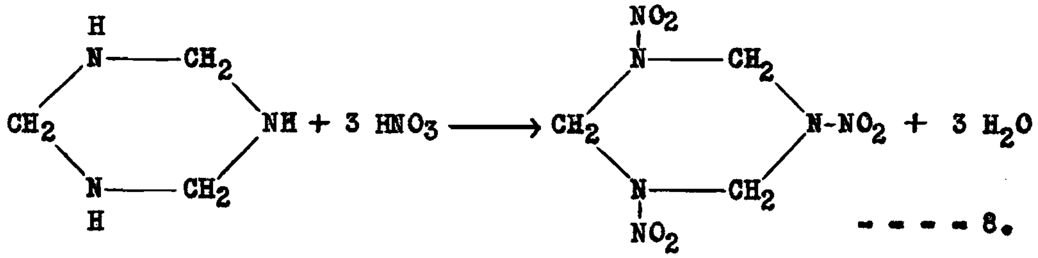
Theoretical

1. The Mechanism of von Herz (8)

Von Herz postulated a simple decomposition of hexamine to hexahydro-1,3,5-triazine and subsequent nitration of this hypothetical intermediate.



- - - - 7.



- - - - 8.

There is no experimental evidence for this mechanism and it is of little but historical interest.

2. The Mechanism of Hale (19)

Hale postulated the existence of three competing reactions:

$$(CH_2)_6N_4 + 4HNO_3 \longrightarrow 3HCHO + (CH_2)_3(N\text{-}NO_2)_3 + NH_4NO_3 \quad \text{-----} \quad 9.$$

$$(CH_2)_6N_4 + 6H_2O + 4HNO_3 \longrightarrow 6HCHO + 4NH_4NO_3 \quad \text{-----} \quad 10.$$

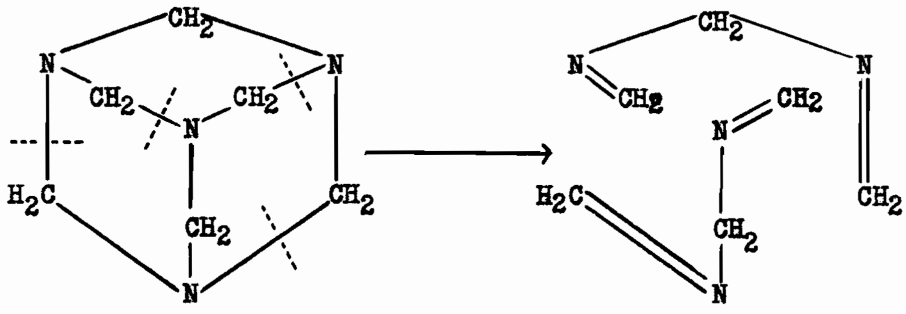
$$(CH_2)_6N_4 + 2HNO_3 \longrightarrow (CH_2)_6N_4 \cdot 2HNO_3 \quad \text{-----} \quad 11.$$

Hale supposed that the decomposition represented by equation 10 represented the course of the reaction in 70 percent nitric acid, that in 80 - 85 percent acid, reactions 10 and 11 predominated, and that only in the region of 95 - 100 percent acid did reaction 9 take place to any appreciable extent. His postulation of equation 10 was based on the fact that in 70 percent acid, no RDX is produced and that in more concentrated acids, no great build-up of water is observed in spite of the fact that water must be produced by the nitration of formaldehyde. It is interesting to note that Hale considered the formation of hexamine dinitrate as a reaction competing with RDX formation. He arrived at this conclusion on the basis of the fact that after his nitrolysis reactions, he was able to precipitate hexamine dinitrate as a double salt of mercuric chloride.

3. The R.D. Mechanism (5)

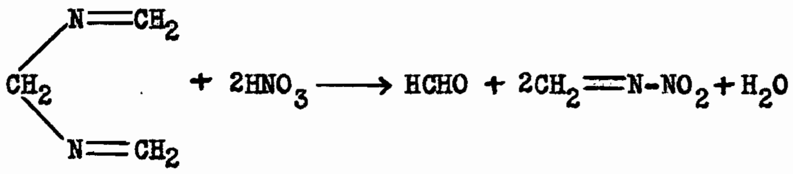
The R.D. postulated an initial depolymerization of hexamine to hemi-hexamine which was decomposed by nitric acid to methylenenitramine; this compound was supposed to trimerize to RDX.

(a) Depolymerization



----- 12.

(b) Nitration



$CH_2(N{=}CH_2)_2 + 2HNO_3 \longrightarrow HCHO + 2CH_2{=}N\text{-}NO_2 + H_2O$ ----- 13.

(c) Polymerization

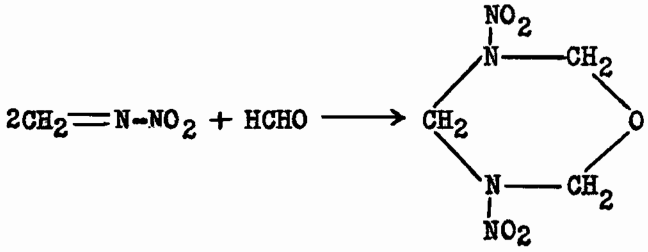
$2CH_2{=}N\text{-}NO_2 \longrightarrow (CH_2)_2(N\text{-}NO_2)_2$ ----- 14.

$3CH_2{=}N\text{-}NO_2 \longrightarrow (CH_2)_3(N\text{-}NO_2)_3$ ----- 15.

(RDX)

$4CH_2{=}N\text{-}NO_2 \longrightarrow (CH_2)_4(N\text{-}NO_2)_4$ ----- 16.

(HMX)



(cyclonite oxide)

----- 17.

(d) Side Reactions

$$5HCHO + 6HNO_3 \longrightarrow 2\underset{(P_1)\ *}{NO_2\text{-}O\text{-}CH_2\text{-}O\text{-}NO_2} + \underset{(P_2)\ *}{NO_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}NO_2} + 3H_2O$$

----- 18.

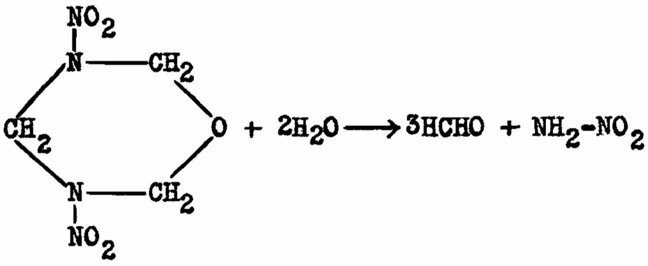
(e) Decomposition

$$HCHO + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 3H_2O \qquad \text{----- 19.}$$

$$CH_2{=}N\text{-}NO_2 + H_2O \longrightarrow HCOOH + N_2 \qquad \text{----- 20.}$$

$$(CH_2)_2(N\text{-}NO_2)_2 + 2H_2O \longrightarrow 2HCHO + 2NH_2\text{-}NO_2 \qquad \text{----- 21.}$$

$$NH_2\text{-}NO_2 \longrightarrow N_2O + H_2O \qquad \text{----- 22.}$$



----- 24.

---

* These are alternate structures for P_1 and P_2.

Linstead (5) has criticized the mechanism on the following grounds:

(a) There is no advantage to introducing the concept of the dimer. There is no evidence for its existence and all experimental evidence can be explained without it;

(b) The mechanism does not account for the production of nitrogen very well;

(c) Formaldehyde does not condense with nitramide to give cyclonite;

(d) Hemi-hexamine has never been shown to exist, and the concept of the depolymerization is very artificial;

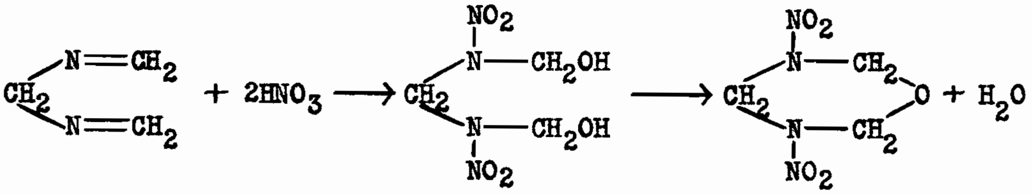
(e) "On general grounds the formation of unsaturated intermediates from the action of nitric acid on hexamine is not to be expected, and the simultaneous attack on four separate bonds of the molecule is theoretically unacceptable," and

(f) If hemi-hexamine does exist, it is likely that it is the precursor of cyclonite oxide.

On the basis of his criticisms, Linstead has proposed a modification of the original R.D. mechanism. This modification may be summed up by equations 12, 13, 15, 16, 18, 19, 22, and the following:

$$CH_2{=}N{-}NO_2 + H_2O \longrightarrow HCHO + NH_2{-}NO_2 \qquad \text{-----} \quad 25.$$

$$2NH_2{-}NO_2 \longrightarrow 2N_2 + O_2 + 2H_2O \qquad \text{-----} \quad 26.$$



----- 27.

The mechanism has been criticized by Winkler (22) who points out that it does not take the intermediate PCX into account. A further criticism is that, theoretically, more than one mole of RDX may be obtained from one mole of hexamine. This has never been observed in the simple nitrolysis reaction.

4. The Mechanism of Linstead I (5)

In his first monograph, Linstead introduced* the mechanism based on the preservation of one of the six-membered rings present in hexamine. This mechanism is characterized by the stepwise degradation of the hexamine molecule. The methyleneamine linkages in the hexamine molecule are supposed to undergo nitrolysis in the following manner:

$$-CH_2-N\langle + HO-NO_2 \longrightarrow -CH_2OH + NO_2-N\langle \qquad \text{----- } 28.$$

The methylol groups may or may not be esterified in the following manner:

$$-CH_2OH + HO-NO_2 \longrightarrow -CH_2-O-NO_2 + H_2O \qquad \text{----- } 29.$$

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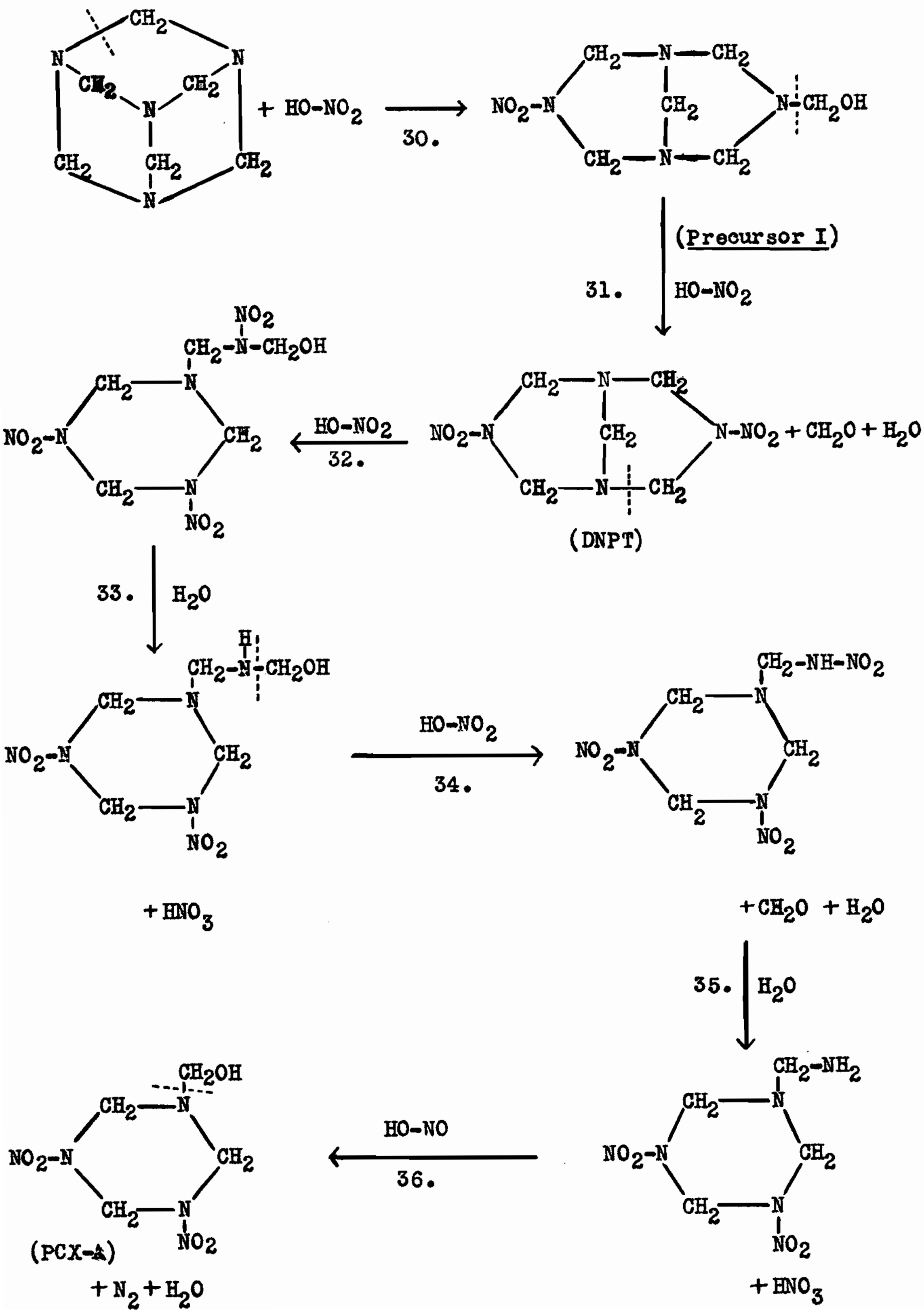
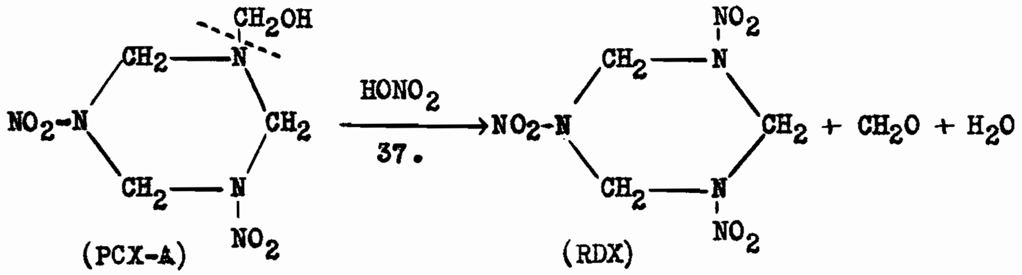
* In March, 1941, Wright (35) speaks of the "trihydroxytrimethylamine fragment" -- this is seven months before Linstead postulated this mechanism in his first monograph.


+ HO-NO2
30.
(Precursor I)
31.
HO-NO2
+ CH2O + H2O
(DNPT)
HO-NO2
32.
33.
H2O
+ HNO3
HO-NO2
34.
+ CH2O + H2O
35.
H2O
+ HNO3
HO-NO
36.
(PCX-A)
+ N2 + H2O



In this mechanism, the by-product formaldehyde is supposed to be converted to P_1 and P_2. The mechanism is weak in that DNPT is known to be converted into HMX by the action of nitric acid (21). It accounts particularly well for the production of nitrogen and has this advantage over the older R.D. mechanism. On the basis of this mechanism, the equation of the combined nitrolysis and fume-off is as follows:

$$(CH_2)_6N_4 + 14HNO_3 \longrightarrow (CH_2)_3(N\text{-}NO_2)_3 + 3CO_2 + 10NO_2 + N_2 + 10\ H_2O \text{ ----- } 38.$$

The actual figures as determined by the R.D. (12) are

$$(CH_2)_6N_4 + 15.6HNO_3 \longrightarrow 0.8(CH_2)_3(N\text{-}NO_2)_3 + 2.9CO_2 + 11.6NO_2 + 1.4N_2 +$$

$$+ 11.4H_2O + 0.2\ N_2O + 0.7CO_2 \quad \text{(unaccounted for)}$$

----- 4

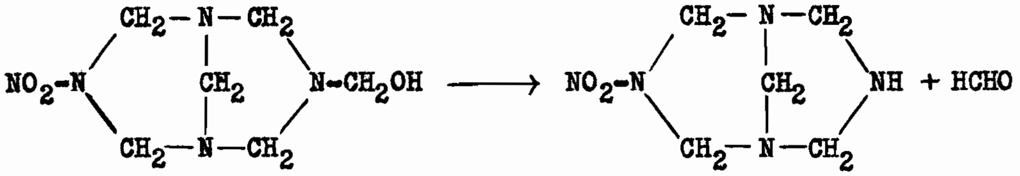
The presence of cyclonite oxide is not accounted for by this mechanism. Linstead believed that the low yield of RDX in dilute acids could be explained by the competing reaction of hexamine nitrolysis (see equation 10).

The discovery of PCX and PCX-A (whether they be true intermediates or not) supports Linstead's concept of stepwise degradation of the hexamine molecule.

5. The Mechanism of Connor, Davy, et al (16)

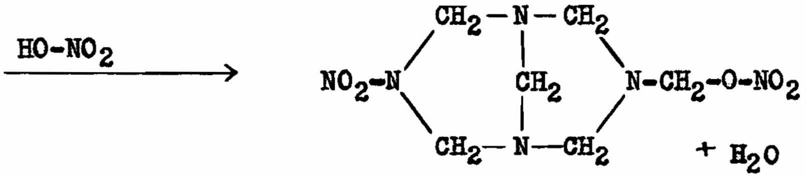
In February, 1943, an informal document entitled "Mechanism of the Reaction of Hexamine and Related Compounds with Nitric Acid, Acetic Anhydride and Ammonium Nitrate" was distributed by the N.D.R.C. While it dealt primarily with the mechanism of the reactions between hexamine and acetyl nitrate and the mechanism of the Bachmann reaction, at least one new idea concerning the mechanism of the nitrolysis reaction was put forward.

It was postulated that Linstead's first intermediate, "Precursor I," could either lose formaldehyde or undergo nitration:



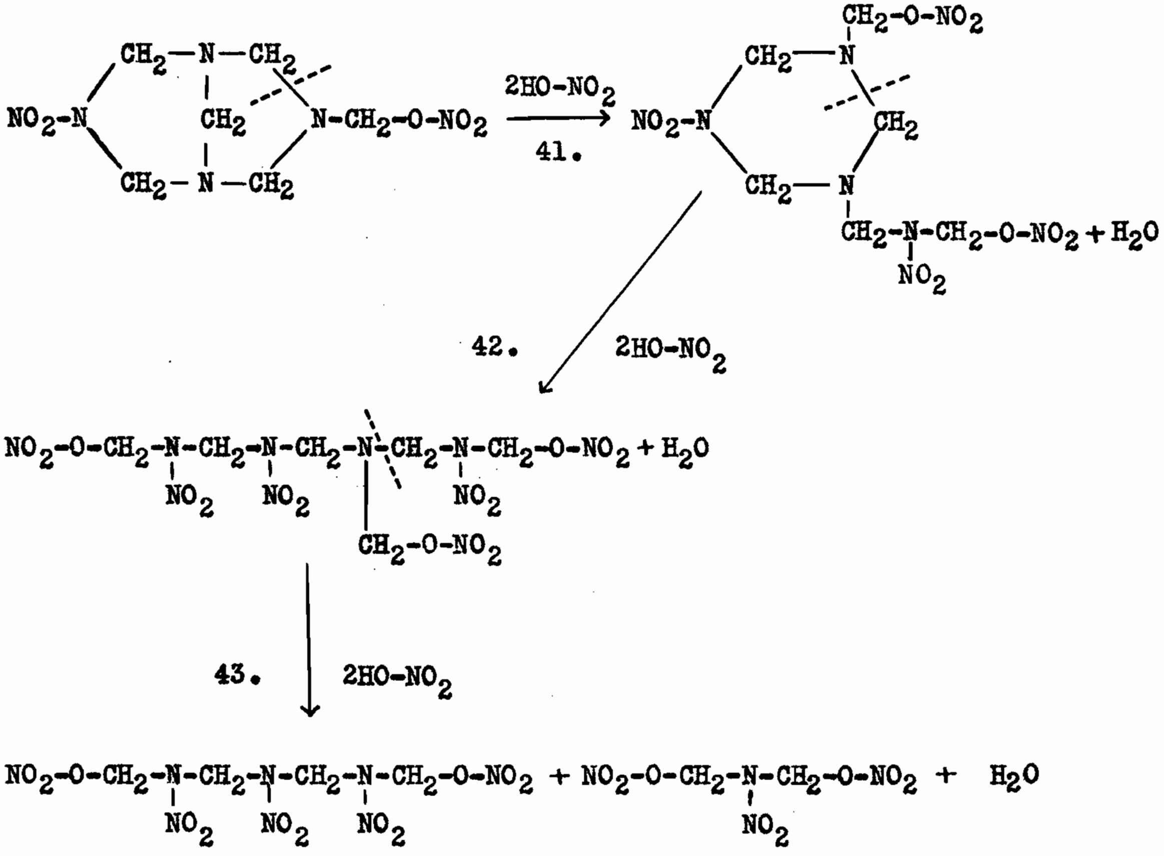
(Precursor I)

----- 39.



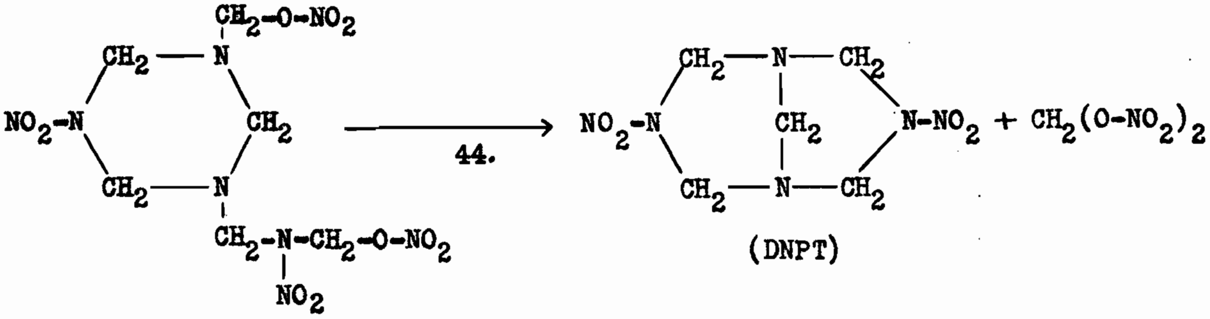
----- 40.

If the main course of the reaction is represented by equation 39, the nitric acid was supposed to attack the ring containing the secondary amine group with the result that RDX would be formed. (The individual steps are not defined). If esterification and stabilization of the methylol group takes place (equation 40), as would be the case if nitrogen pentoxide were added to the system, the reaction would proceed to give the compounds ATX and 106. In the following equations, the two steps of nitrolysis and esterification are represented as one step (see equations 28 and 29). The formation of ATX was postulated as follows:

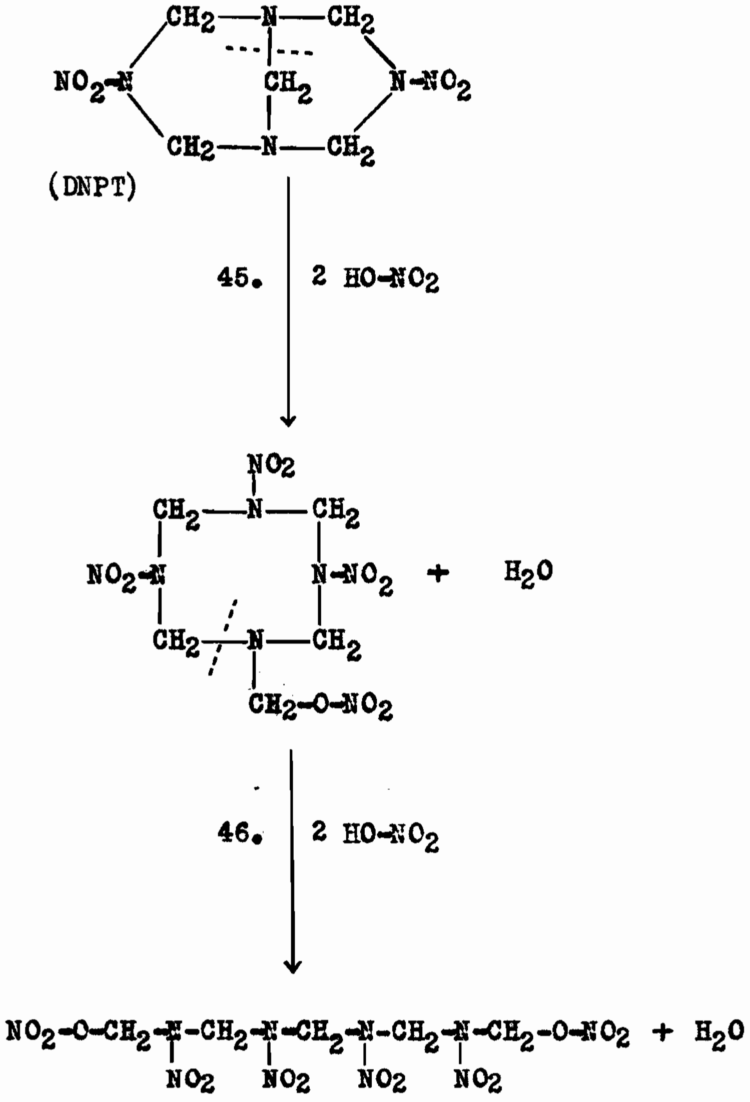


(ATX)

ATX has not been isolated in the nitrolysis reaction even in the presence of nitrogen pentoxide. The compound "106" is predicted, however, and has been isolated by Wright (21).



(DNPT)

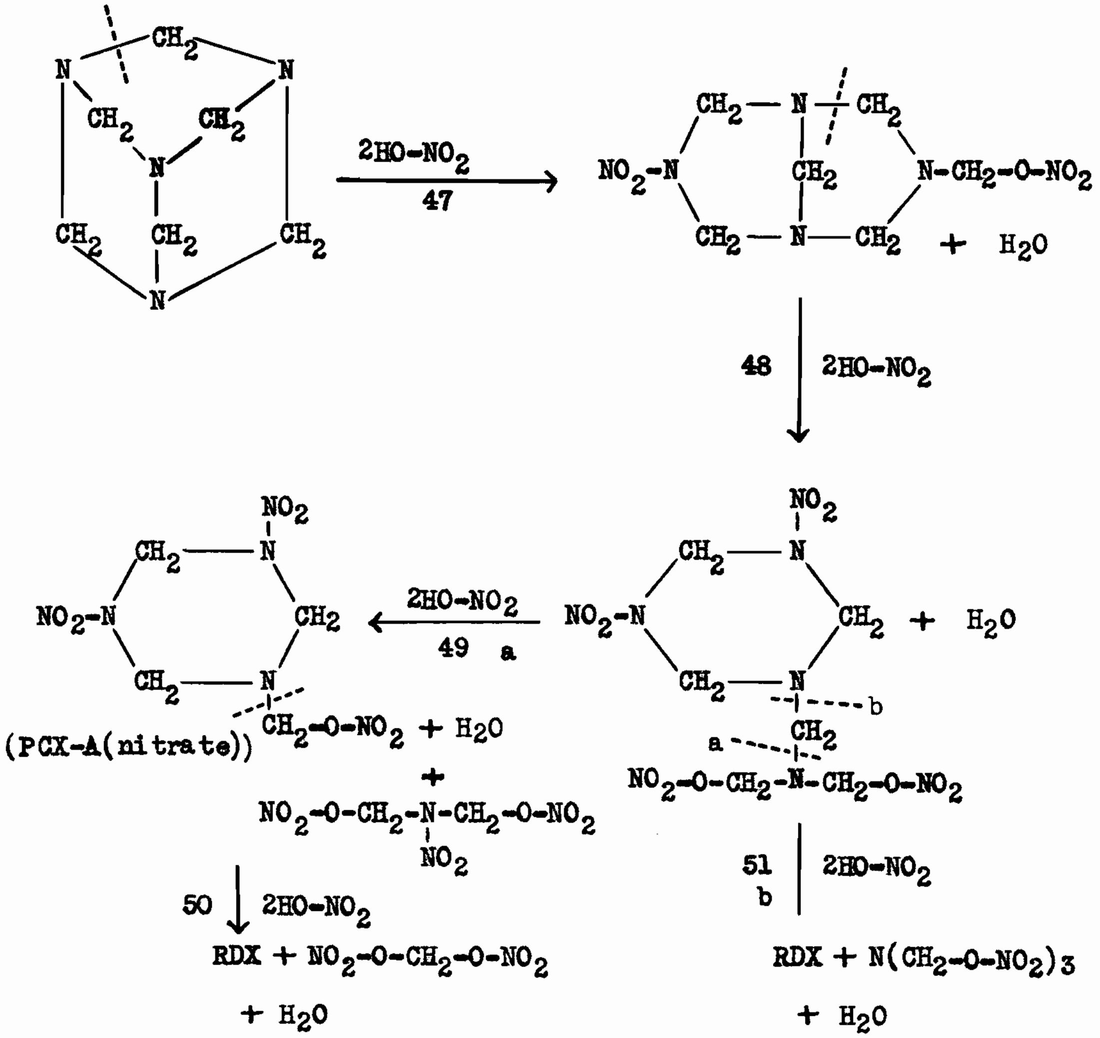


$$NO_2\text{-}O\text{-}CH_2\text{-}\underset{NO_2}{N}\text{-}CH_2\text{-}\underset{NO_2}{N}\text{-}CH_2\text{-}\underset{NO_2}{N}\text{-}CH_2\text{-}\underset{NO_2}{N}\text{-}CH_2\text{-}O\text{-}NO_2 + H_2O$$

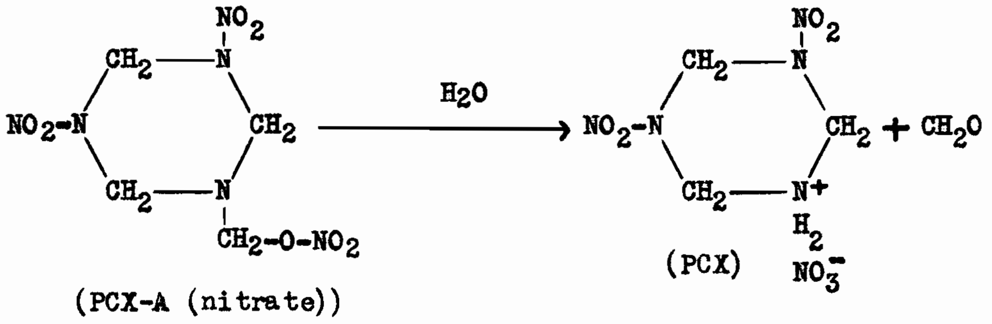
("106")

6. The Mechanism of Linstead II (1)

In his second monograph, Linstead reviewed his mechanism in the light of new developments. He postulated stabilization of the methylol group by esterification, but subsequent reaction with nitric acid to give RDX, not ATX and 106.



Linstead believes that PCX is a hydrolytic by-product of PCX-A (nitrate):



(PCX-A (nitrate)) (PCX) ----- 52.

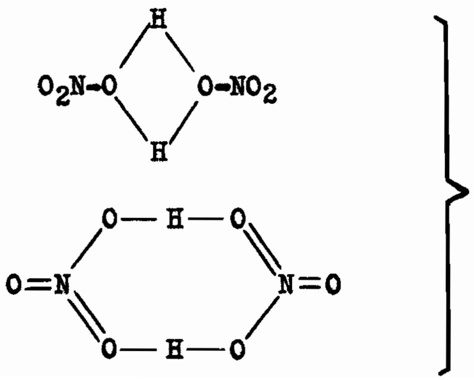
7. The Mechanism of Winkler. (22)

Winkler believes that PCX is a true intermediate in the nitrolysis reaction. He points out that the activation energy of the PCX - RDX conversion is the same as the rate-controlling step in the hexamine - RDX conversion. Further, a kinetic study of PCX decomposition shows that, like the predicted intermediate in the nitrolysis reaction, the decomposition of PCX is independent of the concentration of nitric acid.

Winkler has also obtained evidence that the nitrolysing agent in the nitrolysis reaction is the nitracidium ion rather than pseudo nitric acid or the undissociated bimolecular complex generally believed to be the main component of anhydrous nitric acid. (36)

$NO(OH)_2NO_3$ -- nitracidium nitrate

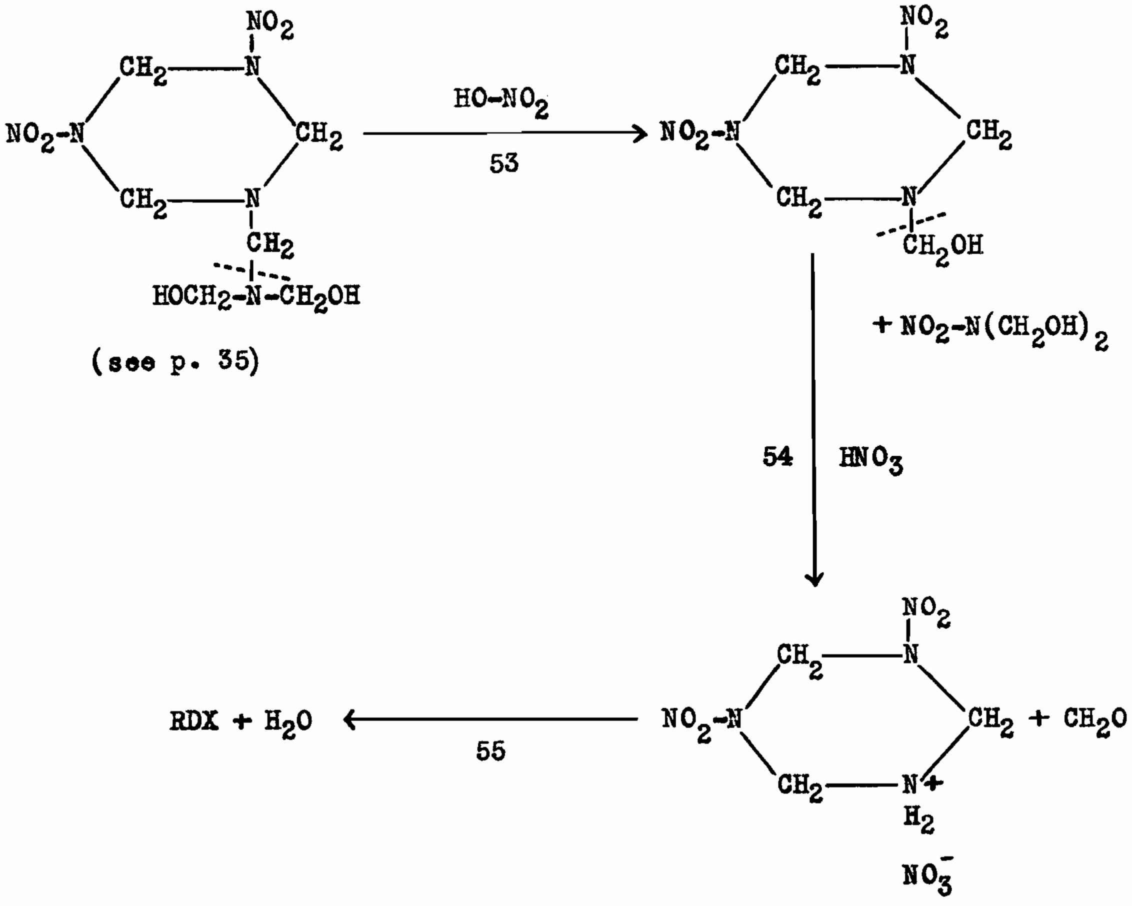
$HO{-}NO_2$ -- pseudo nitric acid



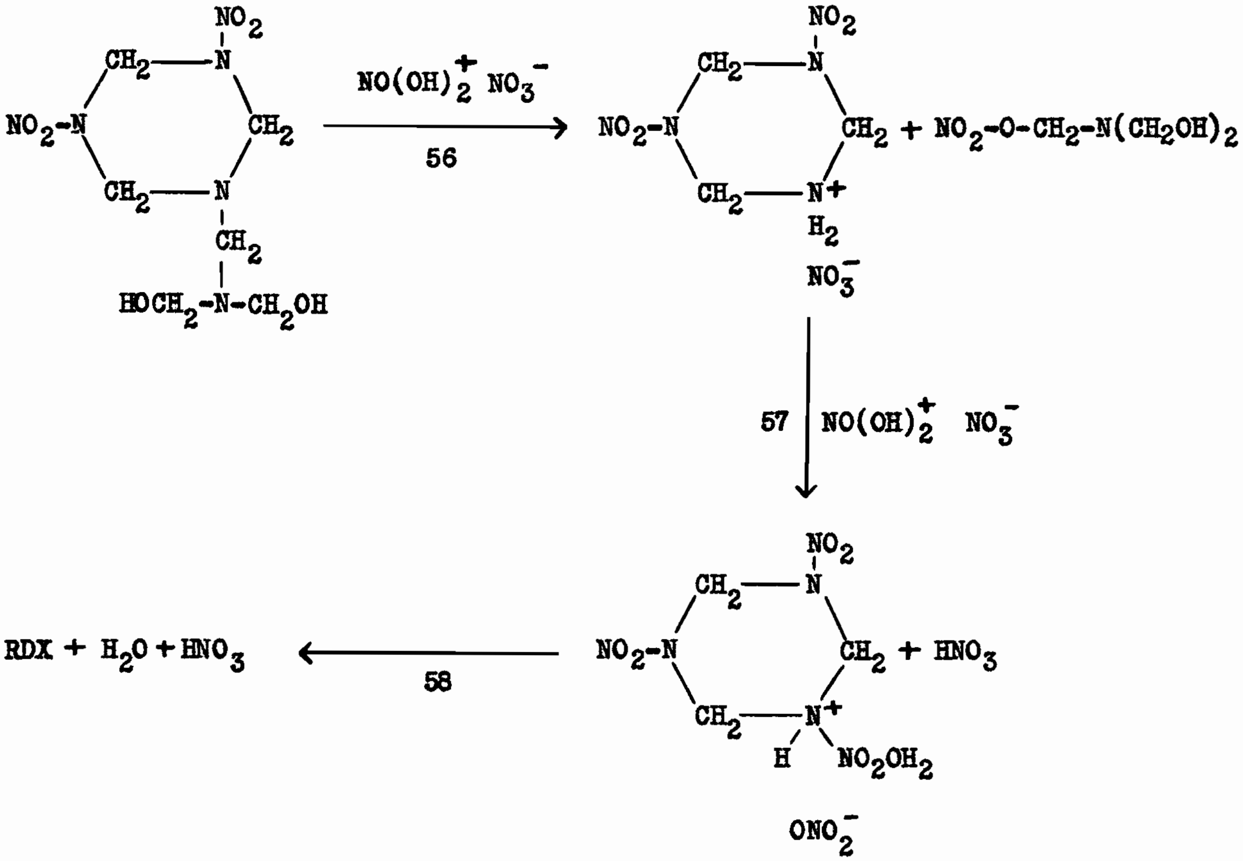
undissociated bimolecular complex.

He has shown that the initial rate of RDX formation is proportional to the nitracidium ion concentration. On the basis of this hypothesis, Winkler states that the large excesses of nitric acid in the nitrolysis reaction are necessary for the maintenance of a high nitracidium ion concentration.

Winkler formulates the later stages of the reaction as follows:



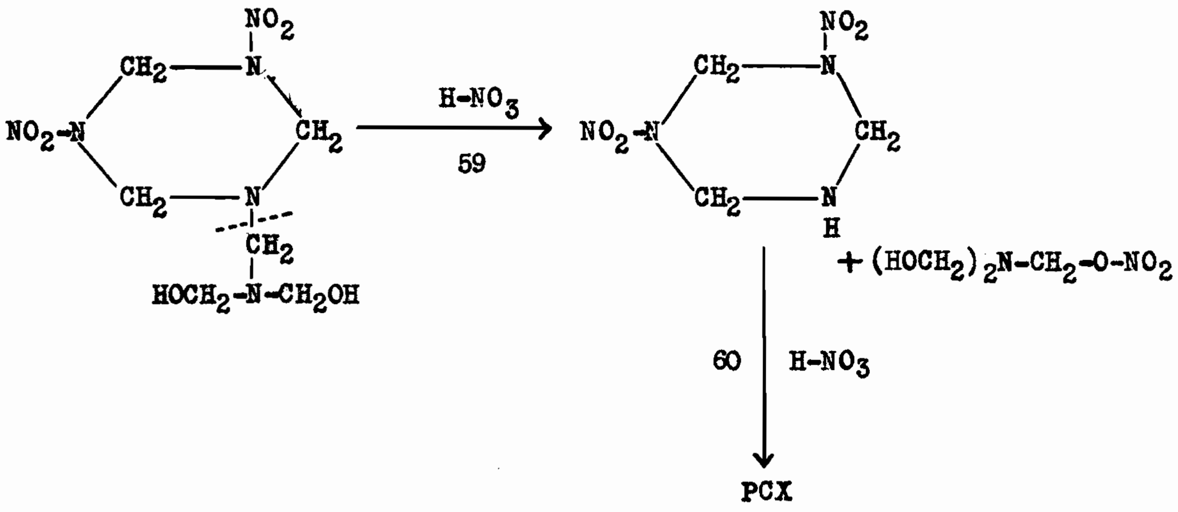
Or, alternately, using the concept of the nitracidium ion:



The English workers do not believe that PCX is a true intermediate. They base this belief on the fact that they could obtain no PCX when the nitrolysis reaction mixture was drowned with ether instead of water. They did obtain evidence, however, of a new compound, N-methylol PCX (PCX-A), which corresponds more closely to the predicted intermediate. Winkler believes PCX-A to be formed by the interaction of PCX and formaldehyde and to be a by-product.

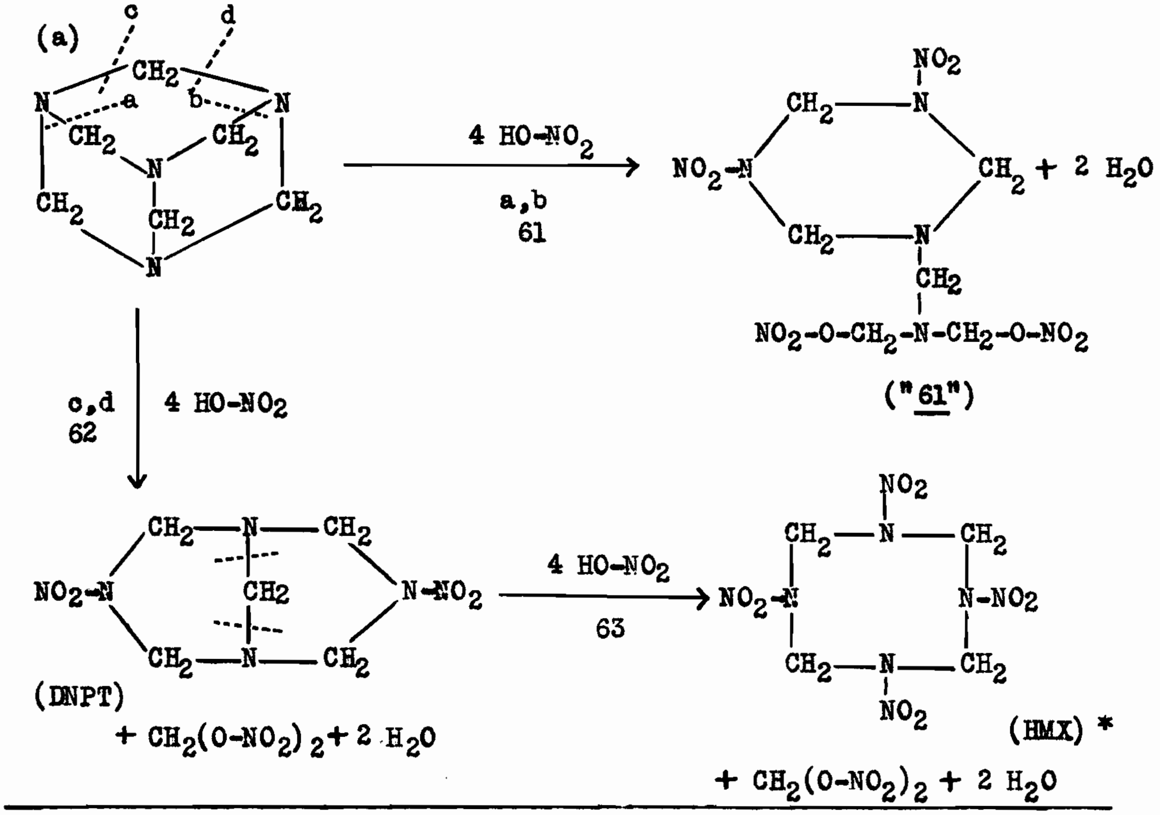
8. The Mechanism of Boyer (37)

Boyer has suggested that PCX is a by-product in the nitrolysis reaction due to the nitrating action of the nitric acid in more dilute solutions:



9. The Bristol Mechanism (38)

The Bristol mechanism is essentially the same as that of Linstead, but is much more extensive.



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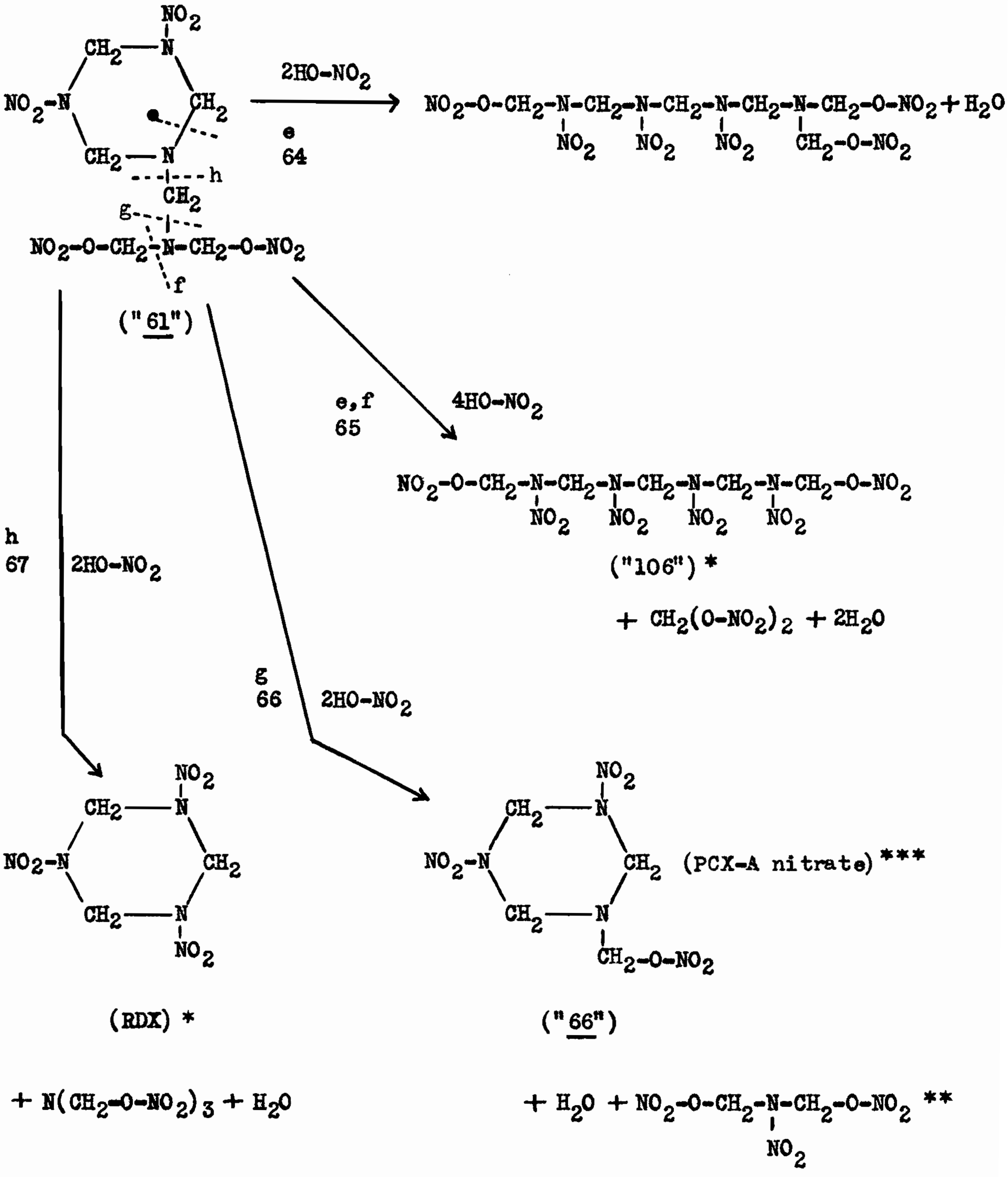
* Compounds thus marked may be isolated.

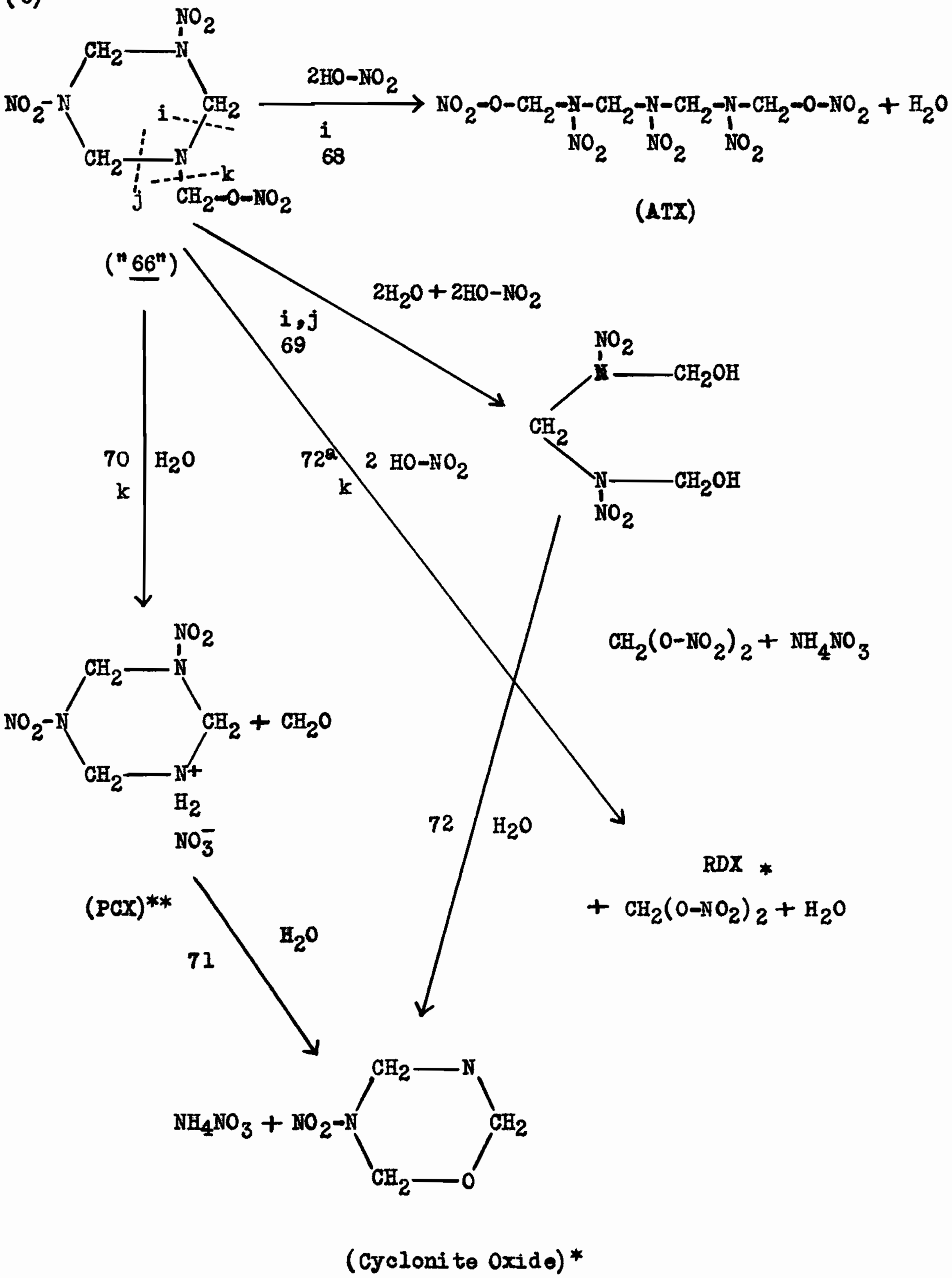
(b)



** Believed to be the precursor of DNPT.

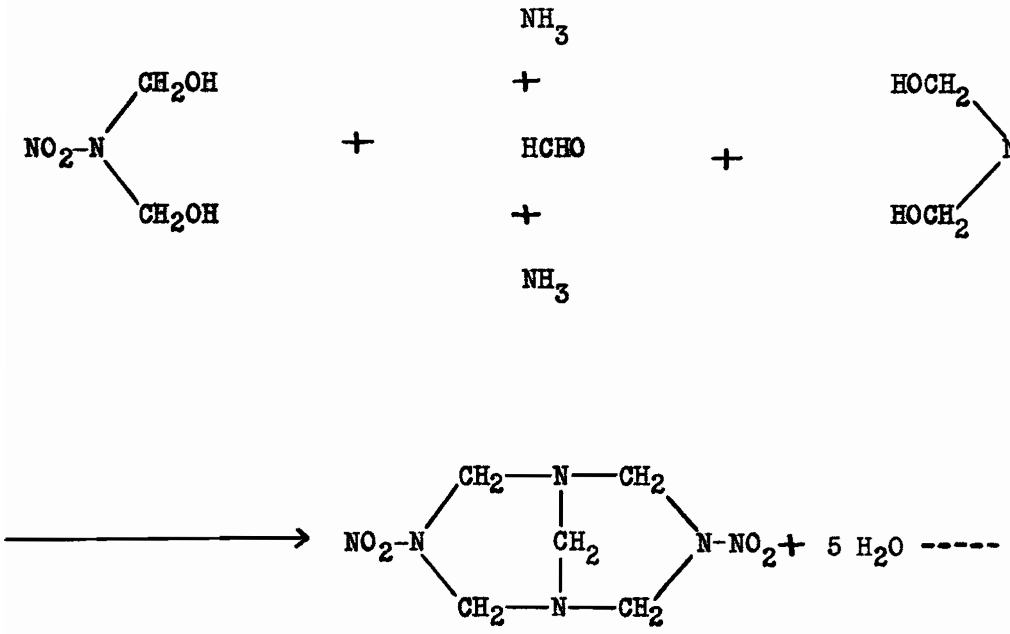
*** Believed to be the precursor of the alkoxy derivatives of PCX-A.

(c)



** Isolateable under special conditions.

Wright (39) has devoted considerable time and effort to the problem of the significance of DNPT in the diluted, neutralized mother liquors. His experiments indicate that DNPT rises through a synthetic reaction involving dimethylolnitramide, ammonia and formaldehyde:



73.

(DNPT)

Since the Bristol mechanism predicts the formation of dimethylolnitramide (as the dinitrate derivative), Wright states that the formation of DNPT in the diluted, neutralized mother liquors is evidence for this mechanism. It should be pointed out, however, that the estimated yields of dimethylolnitramide do not exclude other mechanisms.

The McGill Reaction

$$3(CH_2O)_n + 3nNH_4NO_3 + 6n(CH_3CO)_2O \longrightarrow n(CH_2)_3(N\text{-}NO_2)_3 + 12CH_3COOH \qquad \text{----- 5.}$$

There has been considerably less research carried out on the McGill Reaction than on either the direct nitrolysis or Bachmann reactions. In the opinion of the author, the following workers have made the most significant contributions: Ross and Boyer of McGill University (42), Johnson of Cornell University, Bachmann of the University of Michigan, Wright of the University of Toronto (21), Winkler of McGill University (43), and Linstead of the British Central Scientific Office. (1,5)

Experimental

1. Effect of Mode of Addition Of Reagents

Four methods have been developed which give RDX in quantity. The first method is due to Ross (13): ammonium nitrate, paraform and acetic anhydride are mixed in the cold and then heated; the yield is about 41 percent. The second method is due to Wright (21): paraform is added slowly to a heated mixture of ammonium nitrate and acetic anhydride; the yield in this case approximates 50 percent. The continuous addition of a mixture of paraform and ammonium nitrate to acetic anhydride gives a yield of about 50 percent (Ross and Winkler) (42). If the ammonium nitrate and paraform, in this procedure, are allowed to stand in contact for any length of time, or, if the ammonium nitrate and paraform are fused together before introduction into the acetic anhydride, the yield is lowered (42). The fourth procedure is that of Bachmann (44): a mixture of ammonium nitrate and paraform is added proportionately along with acetic anhydride to a small initial charge of acetic anhydride, the yield in this case being about 55 percent. It is noteworthy that no procedure calls for the pre-mixing of the paraform and the acetic anhydride. Any such procedure results in small yields (42).

2. Effect of Relative Concentrations of Reagents

For experiments in which the powdered paraform is added to a suspension of ammonium nitrate in acetic anhydride, it has been found that the optimum molar ratio of reagents is as follows:

$$CH_2O : NH_4NO_3 : (CH_3CO)_2O :: 1 : 2 : 2.5 \quad (45).$$

The yield in this case is about 50 percent based on the formaldehyde. When the paraform and ammonium nitrate are added proportionately along with the acetic anhydride to a small initial charge of acetic anhydride,* the optimum molar ratio is:

$$CH_2O : NH_4NO_3 : (CH_3CO)_2O :: 1 : 1 : 1.63 \quad (44).$$

Bachmann has reported that this procedure yields 56 percent RDX. The larger quantities of ammonium nitrate and acetic anhydride required by the first procedure are undoubtedly due to the decomposition of the ammonium nitrate by acetic anhydride. Ross has found that if the acetic anhydride concentration is increased beyond five moles per mole

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* A little nitric acid is used in this procedure to reduce the induction period.

of paraform, the yield of RDX falls off and the consumption of acetic anhydride increases (46).

3. Effect of Temperature

Various researchers have found different optimum temperatures: Ross recommends 68 - 70°C. (42), Wright, 70 - 72°C.(21), and Bachmann, 75 - 80°C.(44). Johnson found that there was little difference in yield for temperatures between 70 and 80°C.(45). When gaseous formaldehyde is used, the optimum temperature is 60°C. (45). The different results of different workers are due, in part, to the fact that slightly different procedures are used in each case and also to the fact that results are difficult to reproduce.

Winkler investigated the reaction at low temperatures and found it to be extremely slow. For example, after twenty hours, the yield of RDX at 25°C. was 0.27 percent, at 30°C., 9.8 percent, and at 35°C., 27 percent(43). At temperatures over 80°C., violent, uncontrollable decomposition takes place. This phenomenum is known as a kick-off (42).

4. Effect of Time

The McGill reaction is characterized by a long induction period. This may be reduced by use of catalysts and may be eliminated by allowing the ammonium nitrate and paraform to pre-react in acetic acid * (47). The reaction is extremely slow at low temperatures (43).

5. Effect of Type of Paraform

It was early realized that different commercial brands of paraform

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* Whether the pre-reaction of paraform and ammonium nitrate in acetic acid is actually a justifiable modification of the McGill reaction or not remains to be seen (see p. 49).

gave different yields. Johnson (45) was able to correlate the degree of polymerization (melting point) with the yield of RDX: the lower polymers of the polyoxymethylene type gave the best results. Acid and base precipitated paraforms (high polymers) were found to be unsatisfactory.

6. Effect of Substituting For the Standard Reagents

Paraform may be replaced by gaseous formaldehyde which gives yields corresponding to the best type of paraform (21). Paraform may not be replaced by trioxymethylene (21) or by glyoxylic acid (42).

The acetic anhydride may be replaced by propionic anhydride with little loss in yield (47). The acetic anhydride may not be replaced by maleic anhydride (42). The use of anhydrous glycerol, glacial acetic acid or toluene under reflux failed to give any RDX (13).

7. Catalysts and Diluents (1)

The McGill reaction has been extensively investigated with a view to finding catalysts or solvents which would be effective in improving yields or operating conditions.

The following salts have been found to be slightly catalytic: boron fluoride, antimony fluoride, cobalt nitrate, copper nitrate, nickel nitrate, zinc nitrate.

Mineral acids have been found to decrease the induction period. They do not, however, increase the yield, and are actually deleterious when used in quantity.

The following substances have been found to be ineffective when introduced into the McGill reaction in small amounts but to decrease the yield of RDX when introduced in quantity: magnesium acetate, manganese acetate, potassium acetate, sodium acetate, strontium acetate, uranium acetate, zinc acetate, potassium bromate, ammonium carbonate, ammonium fluoride, potassium iodate, bismuth nitrate, chromium nitrate, ferric nitrate, mercuric nitrate, stannic nitrate, zinc suphate, sodium sulphite, ferrous oxide, phosphorus pentoxide, iodine, methyl acetate, pyridine, triethylamine, and urea.

The following substances have been found to inhibit the formation of RDX in the McGill reaction: ammonium acetate, aluminium chloride, ferric chloride, zinc chloride, acetone, benzene, carbon tetrachloride and ethyl acetate.

Acetone, ethanol, ethyl acetate and methanol have been tested as solvents or diluents for the reaction mixture and were found to inhibit the formation of RDX in the McGill reaction. Glacial acetic and propionic acids may be used as solvents. Ninety percent acetic acid and nitromethane may also be used, but the yield of RDX is decreased.

8. Products, By-Products and Intermediates

The main product of the McGill reaction is RDX (B) * .

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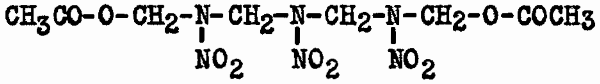
* It was proposed by the workers in England that the product of the direct nitrolysis reaction be called RDX, that the product of the Bachmann reaction be called RDX (B) and that the pure chemical substance, N-trinitrotrimethylenetriamine be called cyclonite (48). The product of the McGill reaction is often called RDX (B) as well. This terminology is applied somewhat loosely in this thesis.

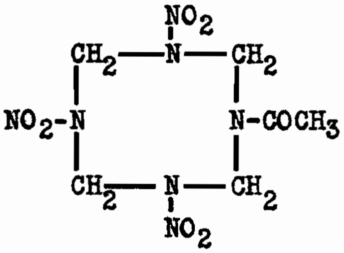
This is RDX contaminated with about five to fifteen percent by weight of HMX. The HMX and RDX can be separated only with difficulty and the mixture of the two is generally considered to be the product of the reaction.

Wright (21) has reported the presence of BSX, QDX, and TAX as by-products in the McGill reaction. These occur in small quantities and were isolated by Wright after neutralization of a diluted McGill reaction liquor. The structure of these compounds has been postulated as follows:

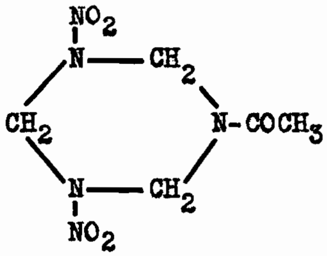


$$CH_3CO{-}O{-}CH_2{-}\underset{NO_2}{N}{-}CH_2{-}\underset{NO_2}{N}{-}CH_2{-}\underset{NO_2}{N}{-}CH_2{-}O{-}COCH_3$$

(BSX) (40,41)

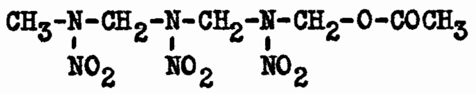


QDX (21)



TAX (21)

One other compound has been reported in a modified McGill reaction. Ross and Boyer (9) found that when paraform and ammonium nitrate are dissolved in acetic acid at 70°C. before being treated with acetic anhydride, MSX is formed as a reaction by-product. The accepted structure was proposed by Ross and Boyer and was confirmed by Connor.



$$CH_3-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-O-COCH_3$$ (MSX)

Whether this compound is a true by-product or not is open to question.

Winkler (47) has shown that when paraform and ammonium nitrate are allowed to react in glacial acetic acid at either 35 or 70°C., hexamine dinitrate is precipitated after several hours. This is in agreement with Whitmore's observation that paraform and ammonium acetate react in glacial acetic acid at 70°C. to yield hexamine (49). Winkler believes that hexamine dinitrate is an intermediate in the McGill reaction. In support of this view he cites the fact that the regular McGill reaction is characterized by a long induction period but that no induction period is observed if the paraform and ammonium nitrate are first dissolved in acetic acid.

Theoretical

1. The Mechanism of Ross (13)

The mechanism of Ross is based on the early R.D. mechanism for the formation of RDX in the direct nitrolysis reaction (see page 25). In fact, this mechanism actually lead to the discovery of the McGill reaction.

(a) $NH_4NO_3 + (CH_3CO)_2O \longrightarrow NH_2NO_2 + 2CH_3COOH$ ------74.

(b) $CH_2O + NH_2NO_2 \longrightarrow HOCH_2{-}NHNO_2$ ----- 75.

(c) $HOCH_2{-}NHNO_2 + (CH_3CO)_2O \longrightarrow CH_2{=}N{-}NO_2 + 2CH_3COOH$ ----- 76.

(d) $3CH_2{=}N{-}NO_2 \longrightarrow RDX$ ----- 77.

An alternate possibility for the cyclotrimerization was suggested:

(cd) $3HOCH_2{-}NHNO_2 + 3(CH_3CO)_2O \longrightarrow RDX + 6CH_3COOH$ ----- 78.

Later investigations showed that there is absolutely no experimental evidence for this mechanism. No dehydrating agents other than acetic anhydride and propionic anhydride were found to be effective (42). Fusion of the paraform and ammonium nitrate followed by acetic anhydride treatment gave little RDX (42). The dearrangement of nitrourea (which should give rise to nitramide) in the presence of formaldehyde gave no RDX (42). The use of nitramide in a simulated McGill reaction gave DNPT, but no RDX (21).

2. The Mechanism of Linstead I (5)

The first step in any postulated mechanism, according to Linstead, is the depolymerization of the paraform. This will be followed by condensation, dehydration, cyclization, and possibly by acetylation. There are several alternate possibilities as to which order these reactions assume. These possibilities are set forth below:

(a) Supposing the first step to be a condensation:

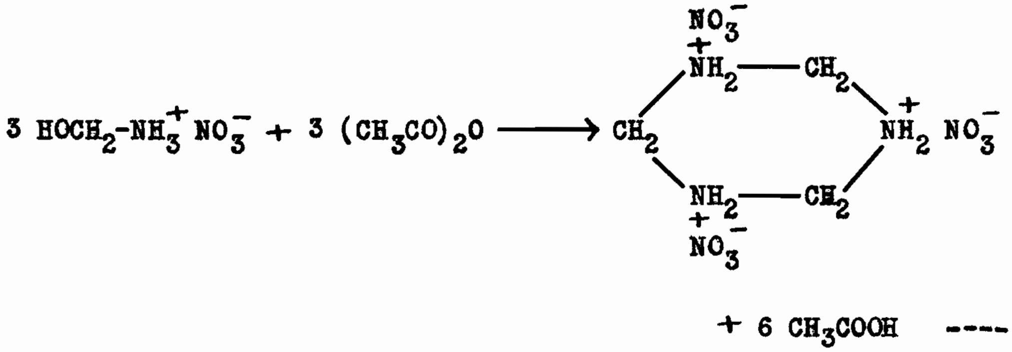
$CH_2O + NH_4NO_3 \longrightarrow HOCH_2{-}NH_3^+NO_3^-$ ----- 79.

The next stage may be a dehydration:

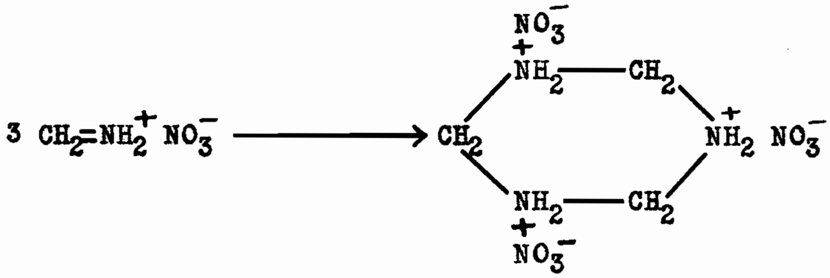
$$HOCH_2\text{-}NH_3^+NO_3^- + (CH_3CO)_2O \longrightarrow CH_2{=}NH_2^+NO_3^- + 2\ CH_3COOH$$ ---- 80.

$$HOCH_2\text{-}NH_3^+NO_3^- + 2\ (CH_3CO)_2O \longrightarrow CH_2{=}N\text{-}NO_2 + 4\ CH_3COOH$$ ---- 81.

Cyclization will follow:



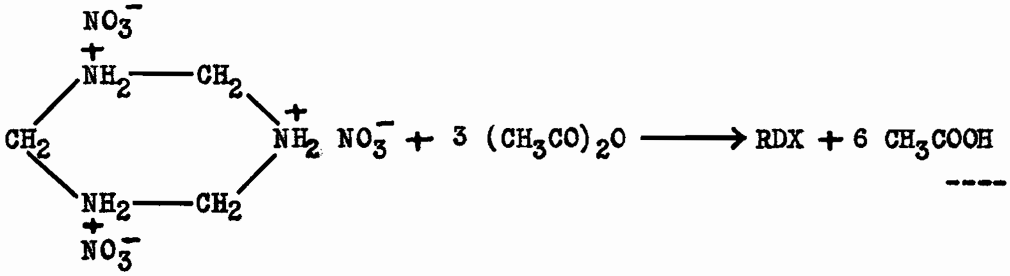
---- 82.



---- 83.

$$3\ CH_2{=}N\text{-}NO_2 \longrightarrow RDX$$ ---- 84.

In two of these three cases, further dehydration (nitration) is necessary:



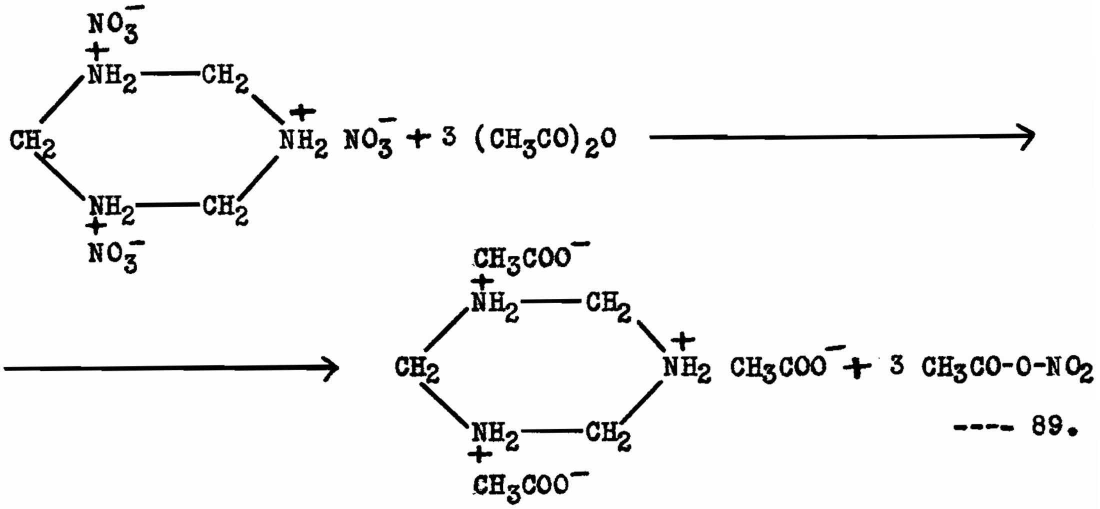
---- 85.

In the course of this series of reactions, there are several opportunities for the acetic anhydride to act as an acetylating agent rather than as a dehydrating agent:

$$HOCH_2\text{-}NH_3^+ NO_3^- + (CH_3CO)_2O \longrightarrow CH_3CO\text{-}O\text{-}CH_2\text{-}NH_3^+ NO_3^- + CH_3COOH \quad \text{---- 86.}$$

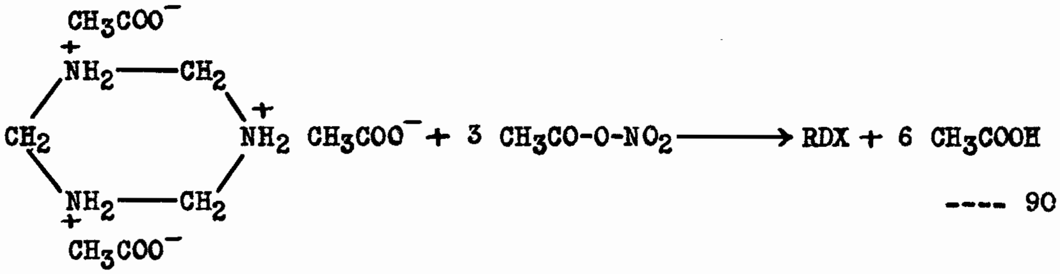
$$HOCH_2\text{-}NH_3^+ NO_3^- + (CH_3CO)_2O \longrightarrow HOCH_2\text{-}NH_3^+ CH_3COO^- + CH_3CO\text{-}O\text{-}NO_2 \quad \text{---- 87.}$$

$$CH_2{=}NH_2^+ NO_3^- + (CH_3CO)_2O \longrightarrow CH_2{=}NH_2^+ CH_3COO^- + CH_3CO\text{-}O\text{-}NO_2 \quad \text{---- 88.}$$



---- 89.

Even if the acetylation of intermediates in the McGill reaction does take place, it is likely that the nature of the individual steps would be essentially the same. The "dehydration" and "cyclization" steps could take place with the elimination of acetic acid rather than water and the nitration step could be represented as follows:



---- 90

The only advantage to picturing the reaction as involving the steps of N-acetylation and N-nitration lies in the consideration of the relative ease of dehydration and acetylation of primary and secondary amines.

Linstead preferred to consider the mechanism as involving equations 80, 81, 82, 84 and 85. As evidence for the validity of equation 80, Linstead cited the fact that formaldehyde condenses with ammonium chloride to give monomethylamine hydrochloride. He pointed out that this reaction probably involves the unsaturated intermediate

$$CH_2{=}NH_2^+\,Cl^-$$

Further, in support of equation 86, the dehydration of the cyclic trinitrate by acetic anhydride is precisely analogous to the conversion observed by Bamberger (50):

$$(CH_3)_2\overset{+}{N}H_2\,NO_3^- + (CH_3CO)_2O \longrightarrow (CH_3)_2N\text{-}NO_2 + 2\ CH_3COOH \quad \text{---- } 91$$

Linstead studied the action of nitric acid on the N-tribenzene sulphonyl derivative of trimethylenetriamine, but was unable to obtain any RDX. On the basis of these experiments, it is improbable that the N-triacetyl derivative is involved in the mechanism.

(b) Supposing the first step to be a dehydration:

$$NH_4NO_3 + (CH_3CO)_2O \longrightarrow NH_2NO_2 + 2\ CH_3COOH \qquad \text{---- } 74$$

This corresponds to the Ross mechanism.

(c) Supposing the first step to be an acetylation:

There are three possibilities in this connection:

$$NH_4NO_3 + (CH_3CO)_2O \longrightarrow NH_4^+\ CH_3COO^- + CH_3CO\text{-}O\text{-}NO_2 \qquad \text{---- } 92$$

$$NH_4NO_3 + (CH_3CO)_2O \longrightarrow CH_3CONH_2 + HNO_3 + CH_3COOH \qquad \text{---- } 93$$

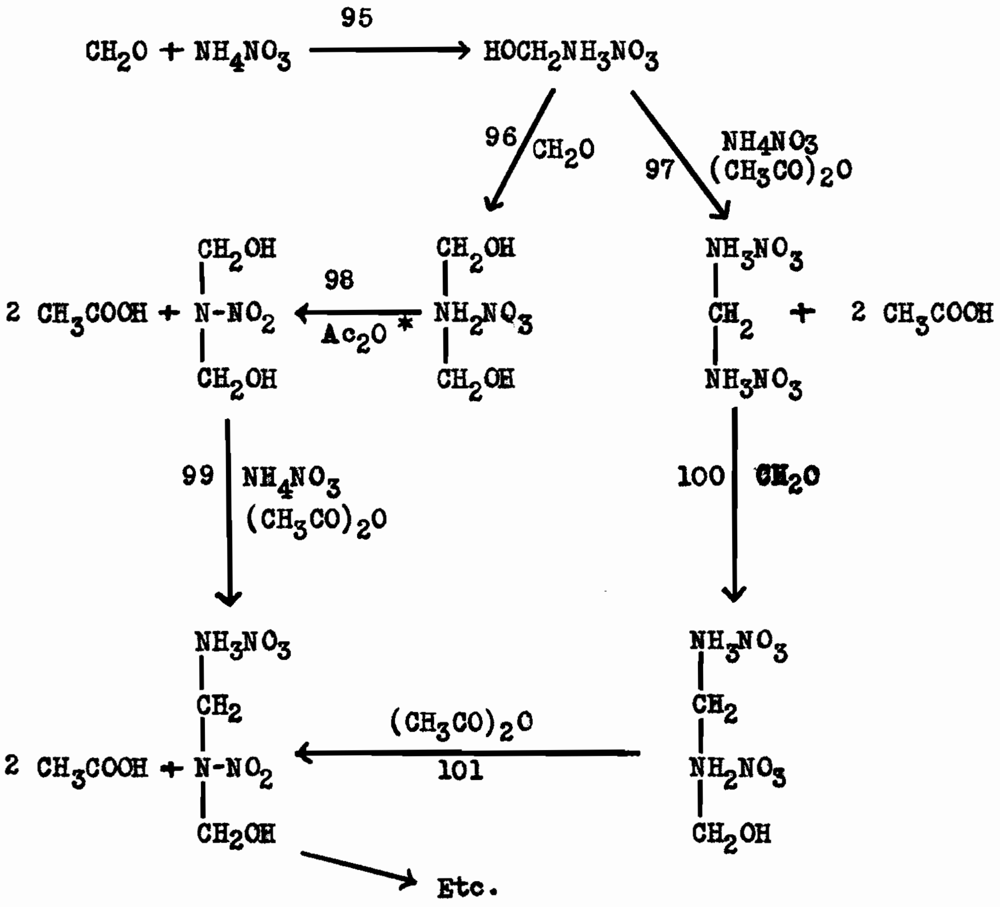
$$CH_2O + (CH_3CO)_2O \longrightarrow CH_2(O\text{-}COCH_3)_2 \qquad \text{---- } 94$$

Acetic anhydride and ammonium nitrate, however, do not seem to react to give acetyl nitrate (5). Furthermore, the latter two cases are ruled out by the fact that neither acetamide nor methylene bisacetate yield RDX when used in a simulated McGill reaction (42).

In his discussion of the McGill process, Linstead points out that only about 50 percent of the available formaldehyde is recovered as RDX(B). A further 12 percent may be recovered on prolonged distillation and about 23 percent may be converted to hexamine. Little formaldehyde is lost as carbon dioxide. In order to account for the methylene groups which do not appear in the RDX(B), Linstead has suggested a number of side reactions: the formation of hexamine and polymethyleneamines, the reaction between formaldehyde and ammonium nitrate to give methylammonium nitrate, the disproportionation of formaldehyde to give methanol and formic acid, the oxidation of formaldehyde by ammonium nitrate, the acetylation of formaldehyde and the presence of undepolymerized polyoxymethylenes.

3. The Mechanism of Ross and Boyer (42)

Ross and Boyer assume continued condensation of formaldehyde and ammonium nitrate followed eventually by ring closure. Secondary amine nitrates are dehydrated (nitrated) upon formation.



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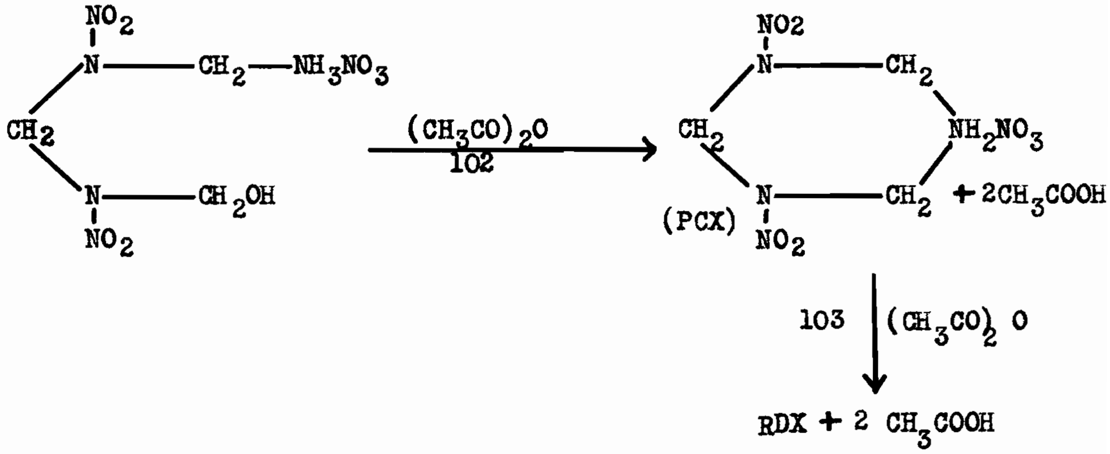
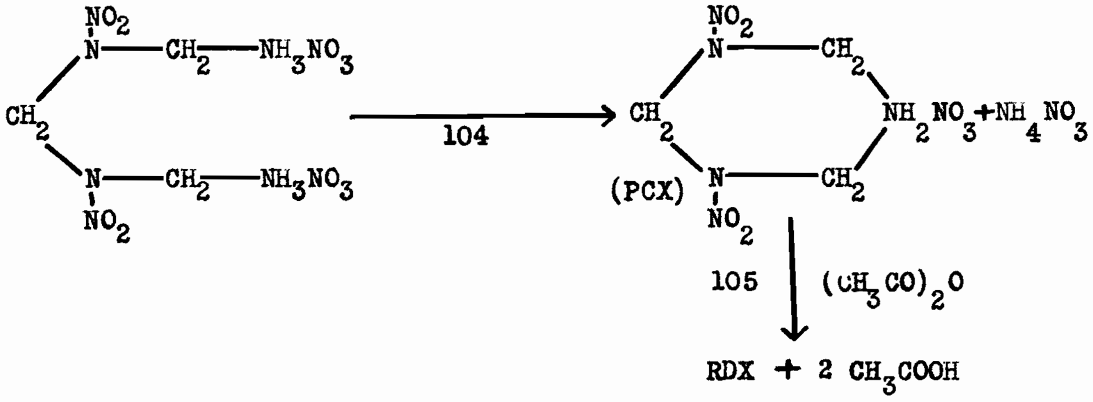
* $Ac_2O = (CH_3CO)_2O$; also $HOAc = CH_3COOH$.



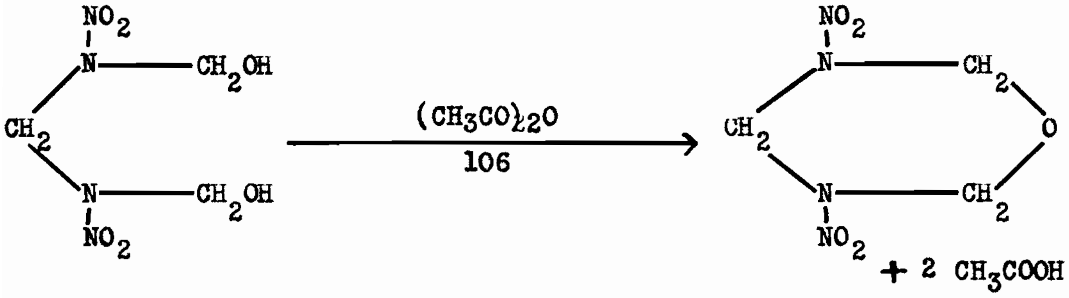
As evidence for the relative ease of dehydration of secondary amine nitrates as compared with primary amine nitrates,, Ross and Boyer cite the experiments of Bamberger and of Wright (51). Bamberger was able to obtain good yields of nitramines from dimethylammonium nitrate, piperidinium nitrate and several substituted aniline nitrates by the action of acetic anhydride. Wright, however was able to obtain only small yields of aliphatic primary nitramines by the same procedure.

An alternate method of ring closure is pictured as follows:

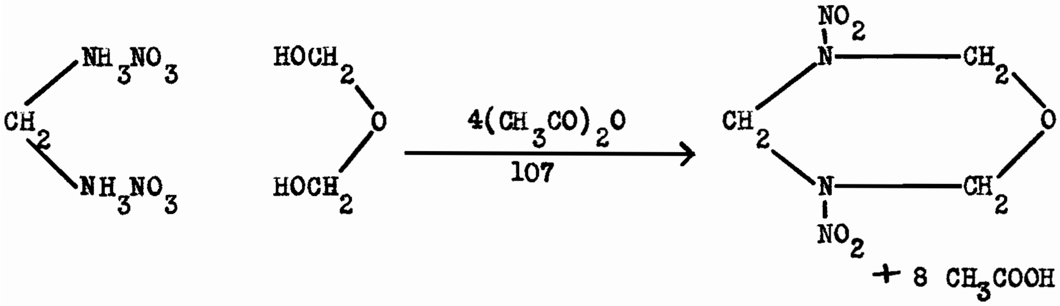


As evidence for this alternate method of ring closure, these authors have shown that methylenediamine dinitrate breaks down in acetic anhydride to give ammonium nitrate and RDX.

This mechanism predicts the extensive formation of oxygen-containing ring compounds:

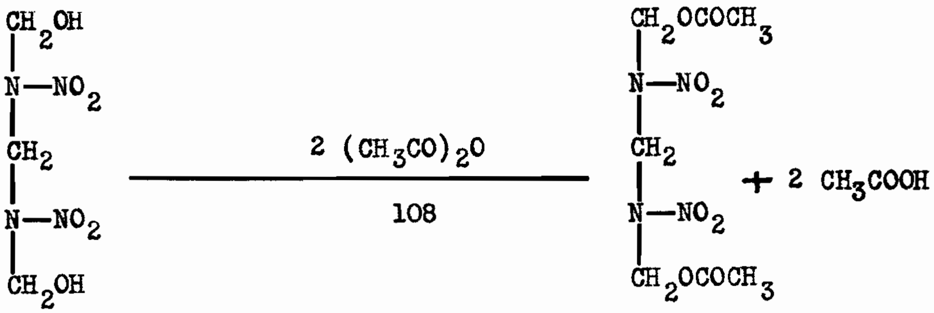


(cyclonite oxide)



These compounds would be water soluble and would be relatively resistant to hydrolysis. Their formation would be favored by the presence of an excess of formaldehyde. Ross and Boyer (42) have shown that an excess of paraform favors the formation of water-soluble products.

Ross and Boyer predict the isolation of BSX-TYPE compounds which could arise by the acetylation of the hypothetical intermediates:

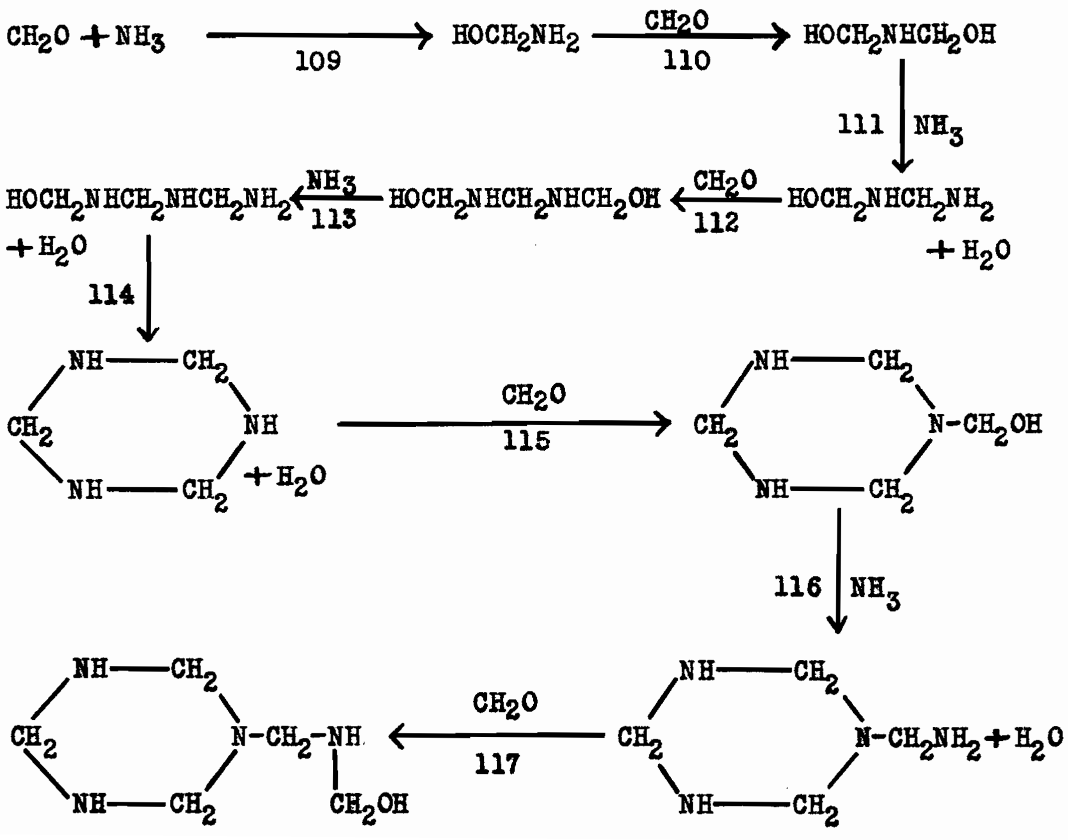


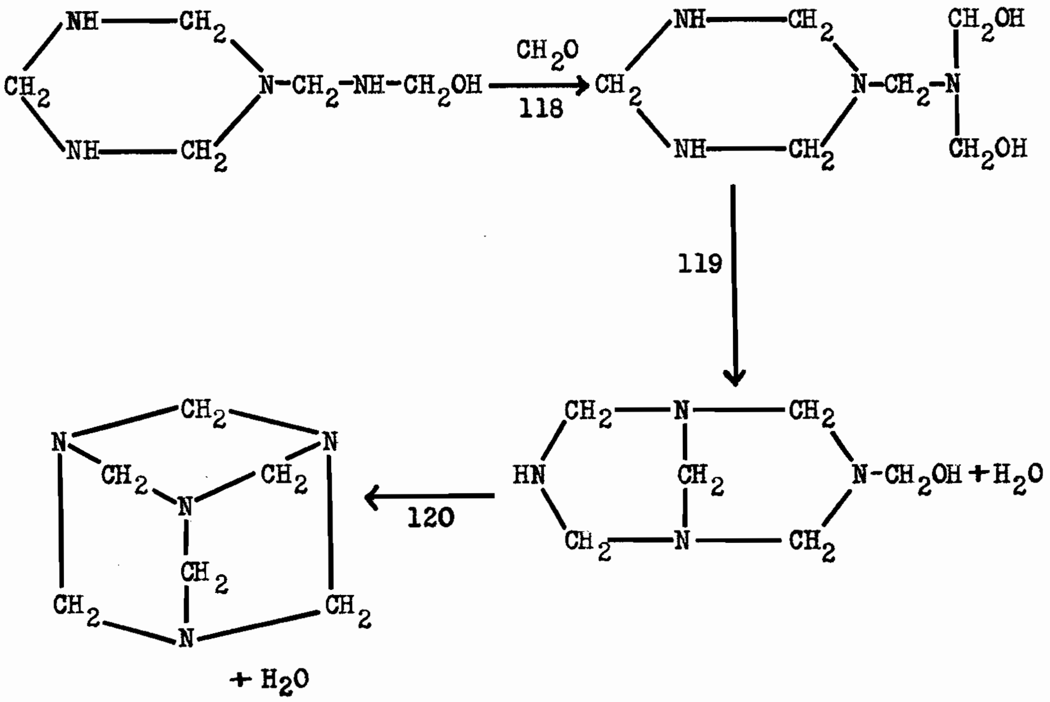
(TEX)

The recent isolation of BSX by Wright (21) from the filtrate of the McGill reaction adds weight to this mechanism.

4. The Mechanism of Linstead II (1)

This is the only mechanism which seriously considers the fact that Winkler (47) has isolated hexamine dinitrate by the reaction of paraform and ammonium nitrate in glacial acetic acid and which considers hexamine dinitrate as an intermediate in the McGill reaction. In it Linstead discusses the many ways in which hexamine can be synthesized (by stepwise reaction) from ammonia and formaldehyde. It is unnecessary to reproduce Linstead's complete analysis of the possibilities; the following formulation will illustrate his method:

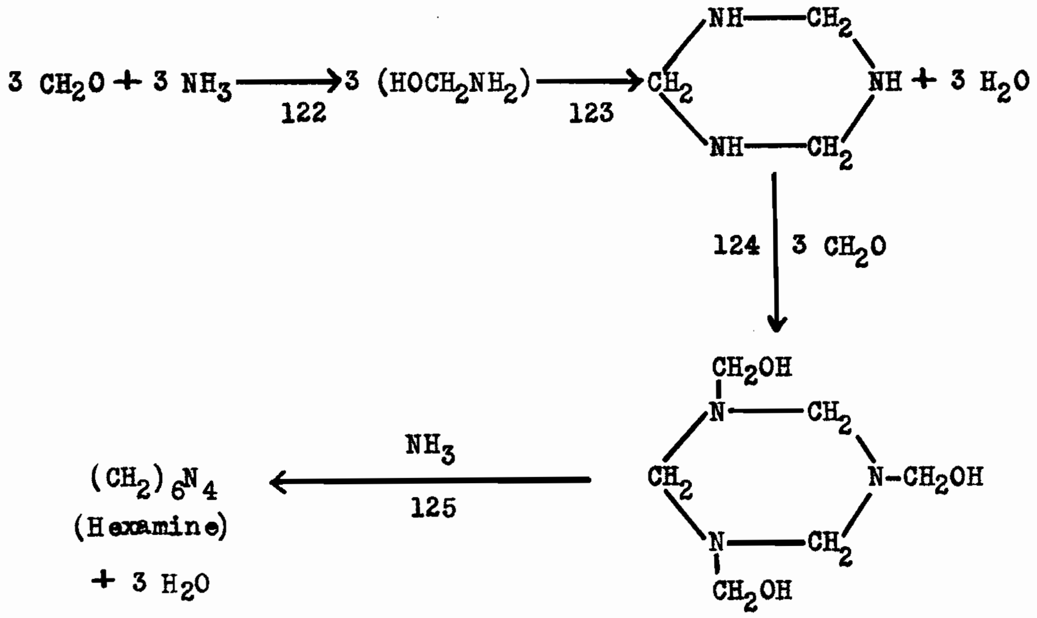




The mechanism of RDX formation from this point onwards is considered to be identical with the mechanism of the Bachmann reaction and will be considered in the next section.

Linstead has recognized the possibility that it might not be necessary for the complete synthesis of hexamine to take place in the McGill reaction. He points out that the synthesis illustrated above may proceed only to the point where the six-membered ring is formed.

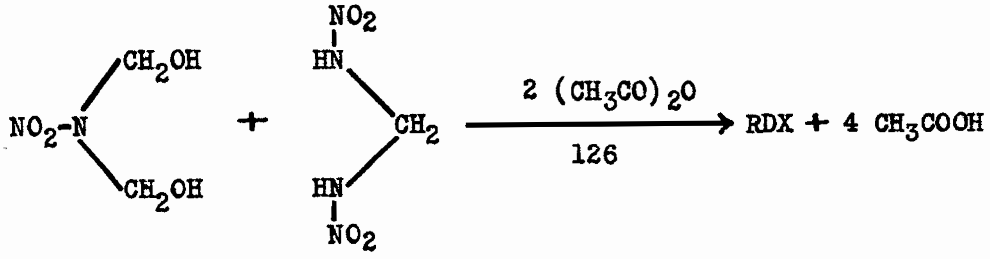
From his studies on the behaviour of formaldehyde-ammonia solutions in water, Wright (52) is lead to the conclusion that the mechanism of formation of hexamine may be represented as follows:



This alternative was also suggested by Linstead (1).

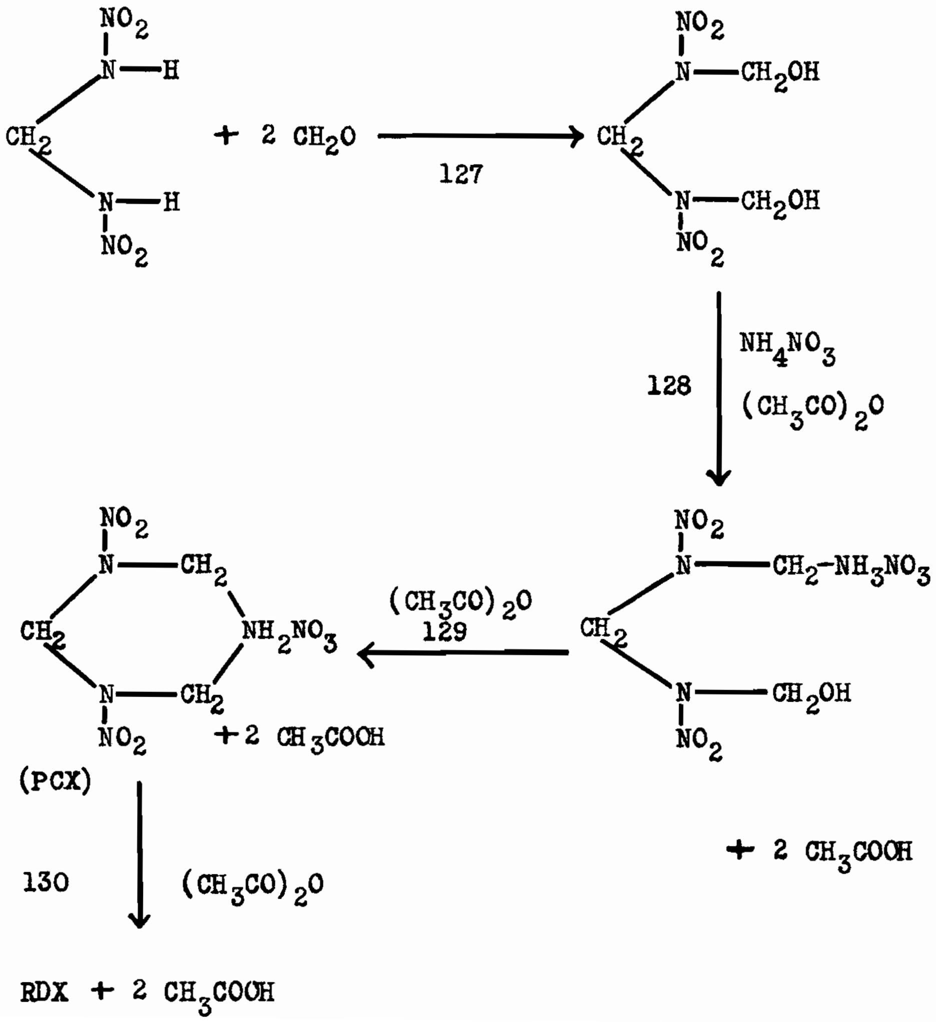
5. The Mechanism of Wright (21)

Wright has suggested that the formation of RDX in the McGill reaction involved the condensation of one mole of dimethylolnitramide and one mole of methylenedinitramine:



Many attempts have been made to condense these two substances, but without success. On this basis, Wright has abandonned the mechanism and now supports Winkler's view that hexamine dinitrate is an intermediate (53).

In the course of his series of experiments, Wright (21) found that methylenedinitramine enhanced the yield of RDX when added to an otherwise regular McGill reaction. Since he has shown that formaldehyde readily condenses with ethylenedinitramine, it is surprising that he did not modify his original theory as follows:



The Bachmann Reaction

$$(CH_2)_6N_4 + 4\ HNO_3 + 2\ NH_4NO_3 + 6\ (CH_3CO)_2O \longrightarrow$$

$$\longrightarrow 2\ (CH_2)_3\ (N\text{-}NO_2)_3 + 12\ \ CH_3COOH \qquad \text{----------}\ 3$$

Since the discovery of the Bachmann reaction in May, 1941, (6) many investigations of the reaction have been carried out. The result of these researches has been an improvement in the quality and yield of the product, the development of a continuous process and the achievement of some degree of understanding of the mechanism of formation of RDX and certain reaction by-products. The most important work on this reaction has been reported by Bachmann and his co-workers at the University of Michigan. Other researchers who have made significant contributions to the understanding of this reaction are Johnson at Cornell University, Whitmore at the Pennsylvania State College, Connor of the National Defense Research Committee, Carmack at the University of Pennsylvania, Wright (21) at the University of Toronto and Linstead of the British Central Scientific Office (1, 5).

Experimental.

1. Effect of Mode of Addition of Reagents

In his second monograph, Linstead (1) lists about thirty different modifications of the Bachmann reaction. Of these, however, many involve the use of solid hexamine or hexamine dinitrate. Since current practice is to use hexamine dissolved in acetic acid, the present discussion will be confined to procedures fulfilling this condition.

In one type of run, the acetic anhydride is placed in a flask either alone or along with part of the nitric acid and/or all of the ammonium nitrate. To this initial charge are added, slowly and proportionately from separate burettes, a solution of hexamine in acetic acid, and nitric acid, or, a solution of whatever ammonium nitrate and nitric acid as were not included in the initial charge (54). In a second type of run, all of the ammonium nitrate and part of the acetic anhydride constitute the initial charge and the hexamine - acetic acid solution, the nitric acid and the remainder of the acetic anhydride are added slowly and proportionately from separate burettes (45). A third general method for carrying out the Bachmann reaction consists in adding a solution of hexamine in acetic acid, a solution of ammonium nitrate in nitric acid, and a quantity of acetic anhydride to a simulated mother liquor. This simulated mother liquor consists of acetic acid, along with some acetic anhydride, nitric acid and ammonium nitrate (55). Since this general method closely resembles the continuous industrial process, it will be called the pseudo-continuous process and, unless otherwise specified, will be the one referred to in future discussion. The industrial process will not be described here (See Linstead (1), pp. 47 and 48).

In general, all of these methods of carrying out the reaction give good yields of RDX (8) provided that they do not imply the premixing of the acetic anhydride and nitric acid to any great extent, or, the introduction of hexamine into acetic anhydride and/or nitric acid in the absence of ammonium nitrate. If all of the Bachmann reagents are mixed at a low temperature (25°C.) and the reaction mixture is heated to the usual temperature, BSX rather than RDX is the principle reaction product (1).

A radically different method for carrying out the Bachmann reaction has been introduced by Roberts (56). Hexamine is mixed with a slight theoretical excess of a solution of two moles of nitric acid and one mole of ammonium nitrate at 25°C. This slurry is added slowly, with stirring and cooling, to a slight excess of acetic anhydride at 70°C. Good yields are obtained.

2. Effect of Concentrations* of Reagents

Operating with slightly different procedures, various researchers have found slightly different optimum molar ratios of reagents, but there is general agreement as to the effect of excesses or deficiencies of reagents relative to the optimum molar ratios. Most of the conclusions presented here are those of Bachmann who has made a very extensive study of the reaction variables. In determining optimum yields, he used the "pseudo-continuous process" described above. In his rate studies, the reaction was carried out in the presence of a large excess of acetic acid; this slowed down the reaction and made for homogeneity of the reaction mixture.

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* The term "concentration" is used rather loosely in this section. A more accurate designation would be "molar ratios". In each case the molar ratio is based on hexamine. See also: p. 44.

Acetic Anhydride (57) :- The theoretical requirement of acetic anhydride is 6.0 moles per mole of hexamine. If one takes into account the small amounts of water contaminating the other reagents, 6.5 moles of acetic anhydride will correspond more closely to the theoretical requirement. The practical optimum will vary somewhat depending on the molar ratio of the nitric acid. When 4.4 moles of nitric acid is added per mole of hexamine, the optimum molar ratio of acetic anhydride is about 7.0 moles per mole of hexamine. When larger quantities of nitric acid are used, the optimum acetic anhydride molar ratio is somewhat less than 7.0 moles, and vice versa. For a given nitric acid ratio, decreasing the amount of acetic anhydride below the critical minimum causes a rapid decrease in the yield of RDX (B). As the acetic anhydride molar ratio is increased beyond the critical minimum, the yield of RDX (B) remains fairly constant up to a point where the presence of excess acetic anhydride reduces the solubility of the ammonium nitrate; the yields of RDX (B) then decrease (58).

Ammonium Nitrate: - The theoretical requirement of ammonium nitrate is 2.0 moles per mole of hexamine. Improved yields of RDX are obtained, however, if an excess of ammonium nitrate is used. Wright believes that there are two optimums for the ammonium nitrate molar ratio, one occurring at about 2.5 moles and the other at about 2.9 moles of ammonium nitrate (59). Bachmann (60) and Winkler (58), on the other hand, present evidence that as the ammonium nitrate concentration is increased, the yield of RDX continues to increase until about 3.0 moles of ammonium nitrate are being added; beyond this point there is little advantage to be gained by increasing the amount of ammonium nitrate. Winkler places the maximum in the HMX - yield curve at 2.5 moles of ammonium nitrate. As the ammonium nitrate molar ratio is decreased from 3.0 moles, the yield of RDX decreases, the rate of RDX formation decreases, the yield of HMX increases (see above, however) and the rate of HMX formation decreases. As the quantity of ammonium nitrate is increased, the yield of RDX increases very slightly, the rate of RDX formation increases, the yield of HMX decreases and the rate of HMX formation is unaffected (58).

It is interesting to observe that, as the ammonium nitrate concentration is increased, the consumption of nitric acid decreases (61).

Nitric Acid: - The theoretical requirement of nitric acid is 4.0 moles per mole of hexamine. The actual optimal amount is about 4.25 moles when 7.1 moles of acetic anhydride and an excess of ammonium nitrate are used (57). When either greater or less amounts of nitric acid are used, the yields of both RDX and HMX fall off correspondingly (58). Thus the nitric acid molar ratio is critical. When smaller amounts of acetic anhydride or larger amounts of ammonium nitrate are used, or, when the reaction mixture is diluted with acetic acid, the critical optimum shifts upwards from 4.25 moles of nitric acid (58). The converse is also true. The rates of RDX and HMX formation are decreased for nitric acid in excess of or in deficeit of the optimum (58).

In the past considerable emphasis has been placed on the ratio of nitric acid to ammonium nitrate. In the opinion of this author, this emphasis is unjustified and has only served to complicate an already complex situation. All of the observed data can be explained by considering the ammonium nitrate and nitric acid as independent variables.

Bachmann observed that when the quantity of ammonium nitrate - nitric acid solution is increased, the consumption of acetic anhydride decreases and the consumption of nitric acid increases (62).

3. Effect of Relative Rates of Reagent Addition

Wright (59) conducted a series of experiments in which he varied the "leads" of the different reagents in the three-feed addition reaction. He found that if the hexamine solution was ahead of either the ammonium nitrate - nitric acid solution or the acetic anhydride or both, low yields of RDX and high yields of HMX were obtained. Bachmann (63) has developed a method of preparing HMX by reacting hexamine with a deficiency (in the early stages of the reaction) of ammonium nitrate, nitric acid and acetic anhydride.

Winkler (64) has found that a delay in the addition of ammonium nitrate to an otherwise normal, diluted run, decreases the yield of RDX to a level of one-third to two-thirds normal. When the ammonium nitrate is delayed, the rate of RDX formation is lowered but the rate of HMX formation is unaffected.

4. Effect of Dilution

As the reaction mixture is diluted with acetic acid, the yield and rate of RDX formation are decreased. Dilution, however, favors an increase in the relative yield of HMX (58).

5. Effect of Temperature

The Bachmann reaction has been variously reported to give optimum yields at different temperatures between 60°C. and 75°C. The most extensive investigation of the effect of temperature has been carried out at the University of Michigan (65,66); the optimum temperature was found to be 75°C. The yield of RDX falls off slowly above this temperature and falls off quite rapidly below a temperature of 60°C. It may be, however, that the decrease in yield at low temperatures is due to the slow rate of the reaction since it has been found that good yields of RDX may be obtained at as low a temperature as 45°C. if sufficient time is allowed (66). In a diluted run, Bachmann (67) observed that at 45°C., one-half of the product is formed in 15 minutes while at 65°C., one-half of the product is formed in 2 minutes. Further, the temperature coefficient of the rate of HMX formation is less than that of RDX formation so that at higher temperatures less HMX relative to RDX is formed (58). As the temperature of the reaction is increased, the consumption of acetic anhydride increases and the consumption of nitric acid decreases (65).

Whitmore (68) has studied the heat effects in the Bachmann reaction and found that there is a "primary heat effect" consisting of a rapid reaction when the reagents are first mixed and a "secondary heat effect", a slow reaction persisting over a period of some hours.

6. Effect of Time

It has been observed that the slow addition of hexamine to the reaction mixture or the use of solid hexamine dinitrate decreases the yield of HMX relative to RDX (67). An increase in the reaction time increases the yield of RDX at low temperatures and decreases the yield at high temperatures (62); an increase in the reaction time will also decrease the yield of HMX and will increase the acetic anhydride and decrease the nitric acid consumption (62).

7. Effect of Substituting for the Standard Reagents

If the acetic acid ordinarily used to dissolve the hexamine is replaced with propionic acid, the yield of RDX is reduced very slightly (69). If the acetic anhydride is replaced with propionic anhydride or butyric anhydride, the yield is slightly reduced (66).

Wright has replaced the nitric acid in the Bachmann reaction with diacetyl orthonitric acid and acetyl nitrate (59). In the first case he obtained a low-melting product (BSX ?), but in the second case a good yield of RDX (B) (high in HMX content) was obtained. Davy has been able to replace as much as 15 percent of the nitric acid with sulphuric acid (70). A number of workers have reported attempts to replace the ammonium nitrate of the

Bachmann reaction with other salts. Bachmann (71) found that the complete replacement of the ammonium nitrate with potassium nitrate gave no RDX. Ammonium acetate may replace the ammonium nitrate when an excess of nitric acid is used (72). Part of the ammonium nitrate may be replaced by ammonium sulphate without impairing the yields (70). Whitmore (69) has replaced the ammonium nitrate with various amine nitrates: methylammonium nitrate, dimethylammonium nitrate, trimethylammonium nitrate, tetramethylammonium nitrate, ethylammonium nitrate, diethylammonium nitrate, triethylammonium nitrate and pyridinium nitrate were used. Many gave rise to some RDX, but in no case did the yield approach the yield obtained in a regular Bachmann reaction. This work will be discussed further in the next section of this Thesis.

8. Catalysts and Diluents

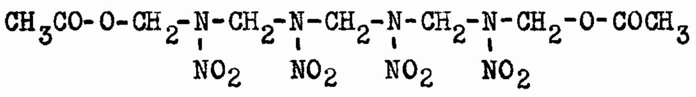
Benzoyl peroxide has no catalytic effect on the Bachmann reaction (73).

The effect of many nitrate salts has been investigated by Nicholls (74). The results of this investigation may be summarized as follows: mercuric nitrate gave a high yield of BSX and a low yield of RDX, nickel nitrate gave a low yield of BSX and a high yield of RDX, calcium nitrate appeared to decrease the RDX yield without increasing the BSX yield; barium nitrate gave a low yield of RDX without affecting the BSX yield; thorium nitrate appeared to double the yield of HMX and ferric nitrate gave only one-half of the usual amount of HMX.

9. Products, By-Products and Intermediates

The principle product of the Bachmann reaction is RDX (B), a mixture of RDX and HMX (See page 47). The proportion of HMX to RDX may vary considerably under different operating conditions but in the industrial product, it is about one to twenty parts by weight. The presence of HMX is very important since it exists in several polymorphic forms (75) and may cause the RDX (B) to be abnormally sensitive to shock. Much research has been carried out with a view to eliminating the HMX or reducing it to a low level: the most that can be said in this connection is that the formation of HMX is inhibited by an excess of reactants with respect to hexamine.

BSX (see page 48) is the principle by-product in the reaction. It is produced in yields of about 10 percent in a normal Bachmann run (21) and may be the chief product if insufficient ammonium nitrate is present or if the reaction is carried out at low temperatures (76). Other reaction by-products are AcAn (1,9 - diacetoxypentamethylene - 2,4,6,8 - tetramine), QDX and TAX (77,21). The structures for QDX and TAX are shown on page 48 while the structure of AcAn is given below:

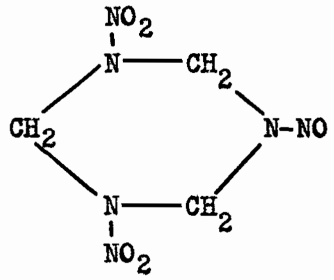


$$CH_3CO\text{-}O\text{-}CH_2\text{-}\underset{NO_2}{N}\text{-}CH_2\text{-}\underset{NO_2}{N}\text{-}CH_2\text{-}\underset{NO_2}{N}\text{-}CH_2\text{-}\underset{NO_2}{N}\text{-}CH_2\text{-}O\text{-}COCH_3$$

(AcAn) (21)

These last three compounds are isolated only in very small yields and they are unimportant except from a point of view of the reaction mechanism.

No intermediates have been isolated in the Bachmann reaction. Winkler (31) believes that hexamine mononitrate is an intermediate on the basis of his thermochemical studies, but this evidence is inconclusive. Ross and Boyer (78) have produced evidence that an intermediate does exist. When a diluted (homogeneous) Bachmann reaction is treated with acetyl chloride, hydrochloric acid or sodium nitrate, a fair yield of "nitroso PCX" is obtained:



These authors interpret this result as evidence for the existence of PCX as a reaction intermediate and as supporting the mechanism of Connor, Davy et al. (see below).

Theoretical

1. The Mechanism of Linstead (1)

The Bachmann reaction is also called the "Combination Process". This designation, first used by Bachmann (6), implied that it was a combination of the nitrolysis and McGill reactions:

$$\begin{array}{llr}
(CH_2)_6N_4 + 4\ HNO_3 \xrightarrow{\qquad\qquad\qquad} & (CH_2)_3(N\text{-}NO_2)_3 + 3\ CH_2O + NH_4NO_3 & \text{-- } 2 \\
3\ CH_2O + 3\ NH_4NO_3 + 6(CH_3CO)_2O \xrightarrow{\qquad\qquad} & (CH_2)_3(N\text{-}NO_2)_3 + 12\ CH_3COOH & \text{-- } 5 \\
\hline
(CH_2)_6N_4 + 4\ HNO_3 + 2\ NH_4NO_3 + 6(CH_3CO)_2O \xrightarrow{\qquad} & 2(CH_2)_3(N\text{-}NO_2)_3 + 12\ CH_3COOH & \text{-- } 3
\end{array}$$

While recognizing the great difference in reaction conditions, particularly with regard to the nitric acid concentration and the temperature, Linstead (5,1) has suggested that the first mole of RDX formed in the Bachmann reaction is formed by the stepwise degradation of the hexamine molecule as is supposed to be the case in the nitrolysis reaction; the second mole of RDX, it is suggested, is produced as a result of condensation reactions between the ammonium nitrate and the formaldehyde residues as is the (postulated) case in the McGill reaction (see page 50). Linstead's mechanism is given below at some length.

The nature of the attacking reagent:- Linstead points out that the reagents which are capable of converting methyleneamine linkages into nitramines are nitric acid, nitric acid plus acetic anhydride, nitric acid plus ammonium nitrate (plus acetic anhydride), and nitric acid plus nitrogen pentoxide. Linstead believes that in the direct nitrolysis process, the attacking reagent is either

$$HO{-\!\!-}NO_2$$

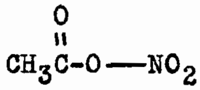
(pseudo nitric acid)

or

$$NO_3{-\!\!-}H_2NO_3$$

(nitracidium nitrate)

When nitric acid and acetic anhydride are used, the attacking reagent may be acetyl nitrate



$$CH_3\overset{\overset{O}{\|}}{C}\text{-}O\text{—}NO_2$$

or possibly nitrogen pentoxide

$$NO_2\text{-}O\text{—}NO_2$$

These reagents may be regarded as products of the following reactions:

$$(CH_3CO)_2O + HNO_3 \longrightarrow CH_3CO\text{-}O\text{-}NO_2 + CH_3COOH \qquad \text{----} \quad 131$$

and

$$2\ CH_3CO\text{-}O\text{-}NO_2 \longrightarrow (CH_3CO)_2O + N_2O_5 \qquad \text{----} \quad 132$$

When the reaction mixture contains nitric acid and ammonium nitrate, Linstead prefers to consider the attacking reagent as pseudo nitric acid and when it contains nitric acid, ammonium nitrate and acetic anhydride, as acetyl nitrate. When 106 percent nitric acid (nitric acid fortified with nitrogen pentoxide) is used, the attacking reagent is pictured as being nitrogen pentoxide.

In general, all* of these reagents may be represented as follows:

$$RO\text{—}NO_2$$

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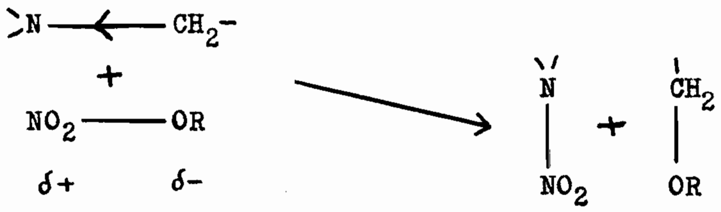
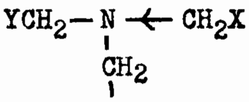
* In the case of nitracidium nitrate, consider the dehydrated form.

The Mode of Attack: - The mode of attack of a given reagent upon a methyleneamine linkage may be briefly pictured as follows:



The Position of Attack: - In the presence of large excesses of acidic reagents, it may be supposed that methyleneamines will give methyleneaminium salts. Linstead postulates that the salt will be in equilibrium with the free base and that salt formation will stabilize a given linkage. Thus the free-base, methyleneamine linkages will be most liable to attack.

In the case of a substituted polymethyleneamine linkage, it must be decided which of several linkages will undergo fission. If in the compound



$$YCH_2-\underset{\underset{|}{CH_2}}{\overset{}{N}}\leftarrow CH_2X$$

the group X can release electrons more readily on demand than can the group Y, then the $>N-CH_2X$ bond will break. On this basis it is possible to predict the order of ease of fission in a number of cases:

Ease of fission: $CH_3CO-\overset{|}{N}-CH_2 — N<$
(free base) $>N-CH_2 — N<$
$CH_3-O-CH_2 — N<$
$CH_3CO-O-CH_2 — N<$
$Cl-CH_2 — N<$
↓ $NO_2-\overset{|}{N}-CH_2 — N<$
Great Stability $^{+}-\underset{|}{\overset{|}{N}}-CH_2 — N<$

Further, in the case of amine salt formation, the greatest stability will be associated with the strongest base.

Linstead believes that another factor must be introduced in order that one may predict the sequence of bond fissions. He calls this the "side-chain factor": methylol acetate side-chains will be stable to acetic anhydride and acetyl nitrate while methylol nitrate side-chains will be stable to nitric acid. Linstead's reason for introducing the concept is obvious, but his justification is somewhat obscure.

The Function of the Ammonium Nitrate: - The function of the ammonium nitrate is one of the most important, unsolved questions in connection with the mechanism of the Bachmann reaction. If no ammonium nitrate is present, BSX is produced in quantity while, if it is present, RDX is the chief product. There is evidence to show that the reaction between hexamine and acetyl nitrate to give BSX is rapid and that this reaction is inhibited by the presence of ammonium nitrate. In connection with the function of the ammonium nitrate in the Bachmann reaction, Linstead states:

"If we set aside the idea that the ammonium nitrate acts by some rather nebulous buffer action, there are two possibilities.

"a" The ammonium nitrate itself acts with the intermediate compound and the compound so formed undergoes fission preferentially at a different part of the molecule from that of the original intermediate.

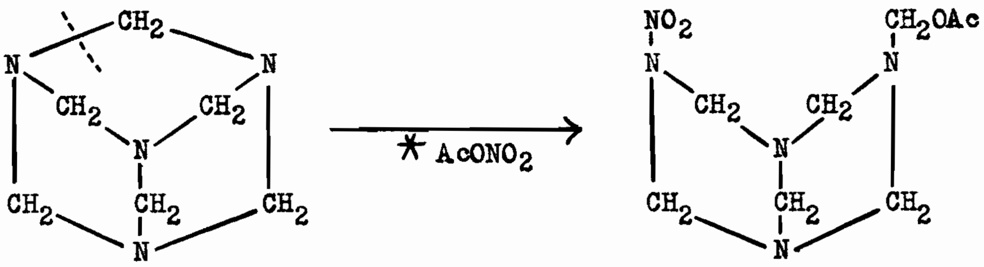
"b" The ammonium nitrate modifies the nature of the reagent, for example, by preventing the formation of the active agent which attacks the ring."

Linstead holds to the second explanation, principly because the ammonium nitrate slows down the degradation process and because there is no evidence for the reaction between the intermediates and ammonium nitrate. The modification in the nature of the reagent, if this be the function of the ammonium nitrate, would permit of preferential attack on "side-chains" and thus alter the course of the reaction.

The role of the ammonium nitrate in the synthesis process is recognized and is assumed to be the same as in the McGill reaction.

<u>The stepwise degradation of Hexamine:-</u> On the basis of the foregoing considerations, Linstead has suggested two alternate schemes for the production of RDX and BSX. HMX is supposed to arise through DNPT and PHX.

The initial fission is represented as follows:



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(Hexamine) (Precursor I)

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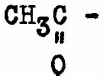
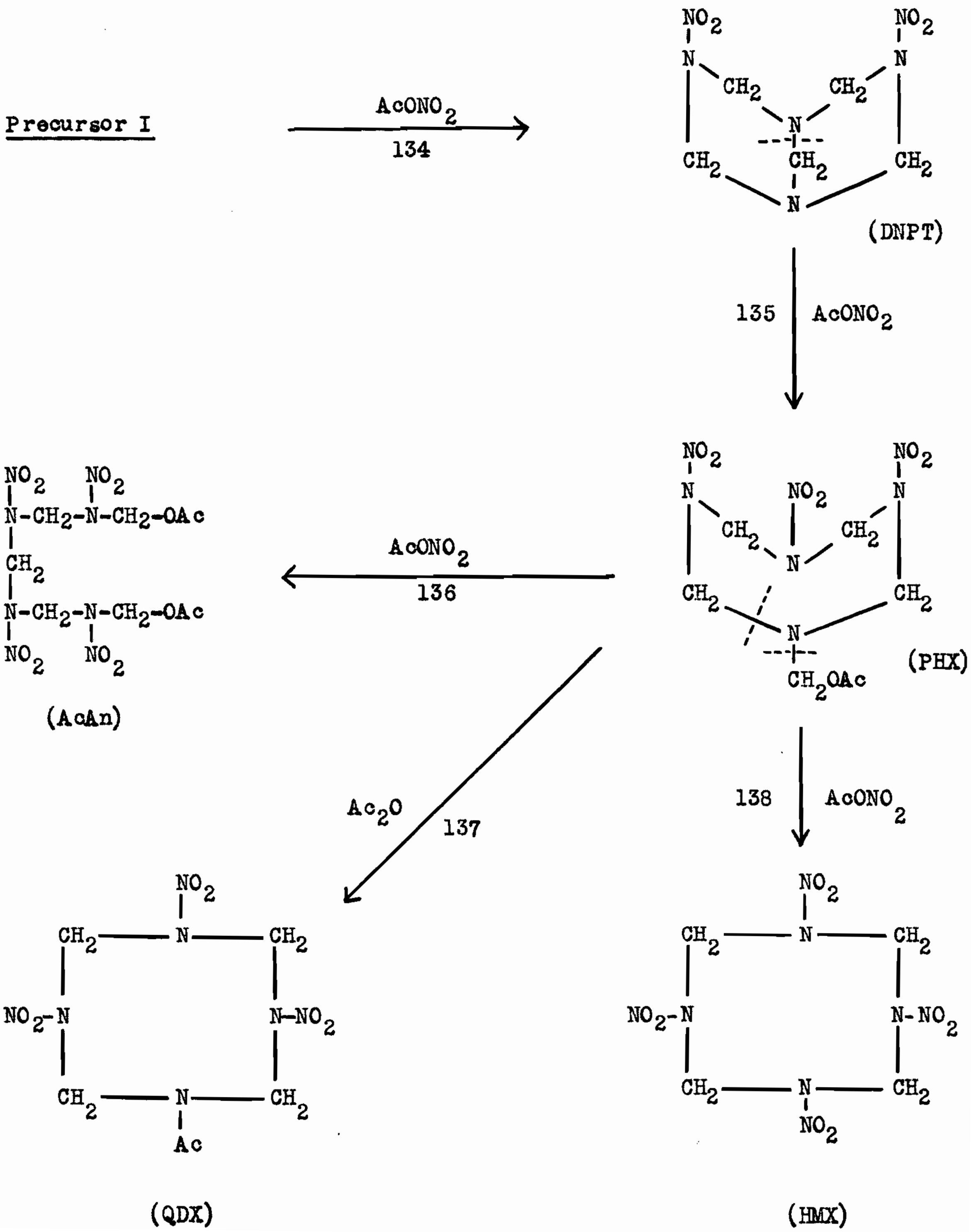
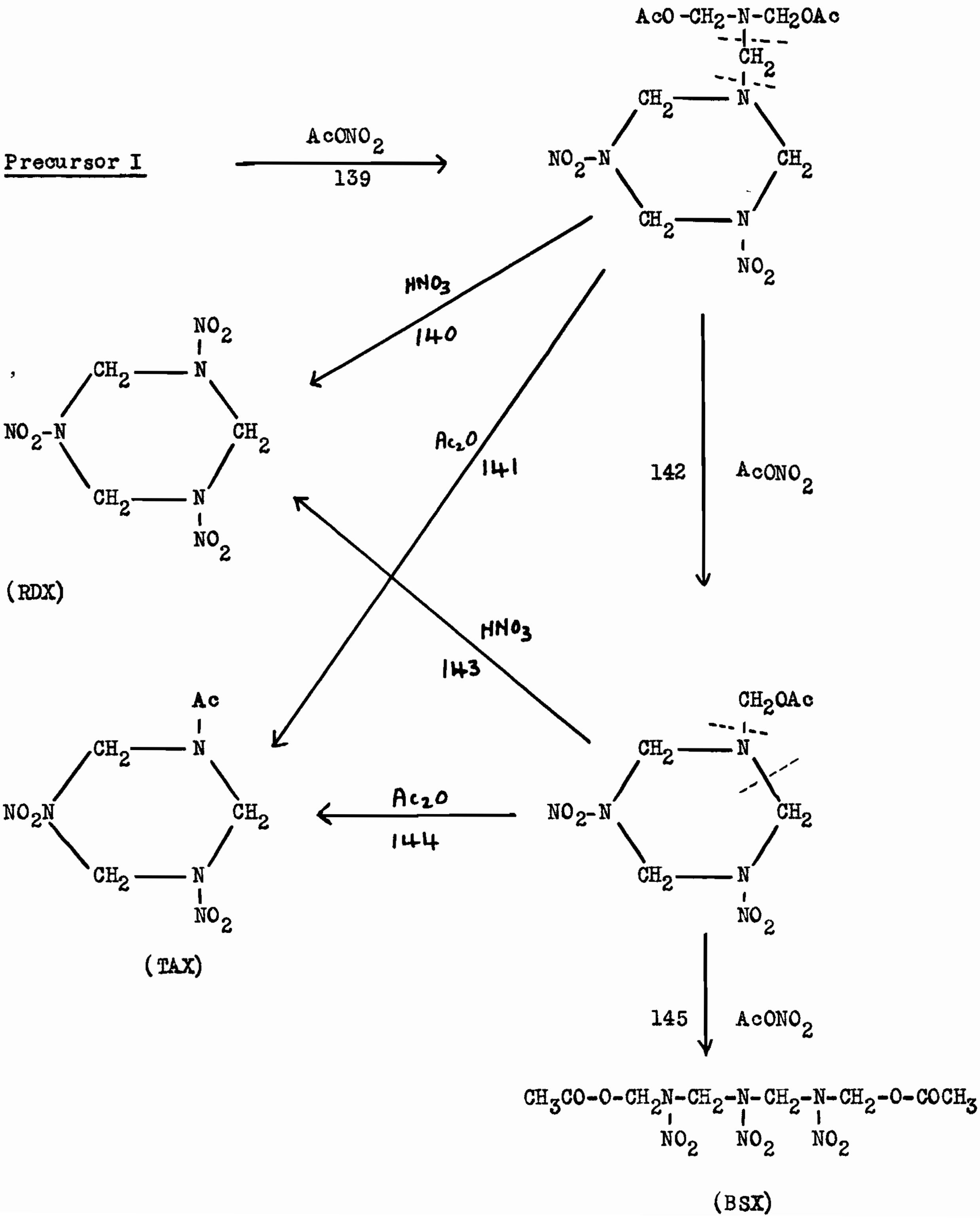
* Where Ac - = 
$CH_3\underset{\overset{\|}{O}}{C}-$

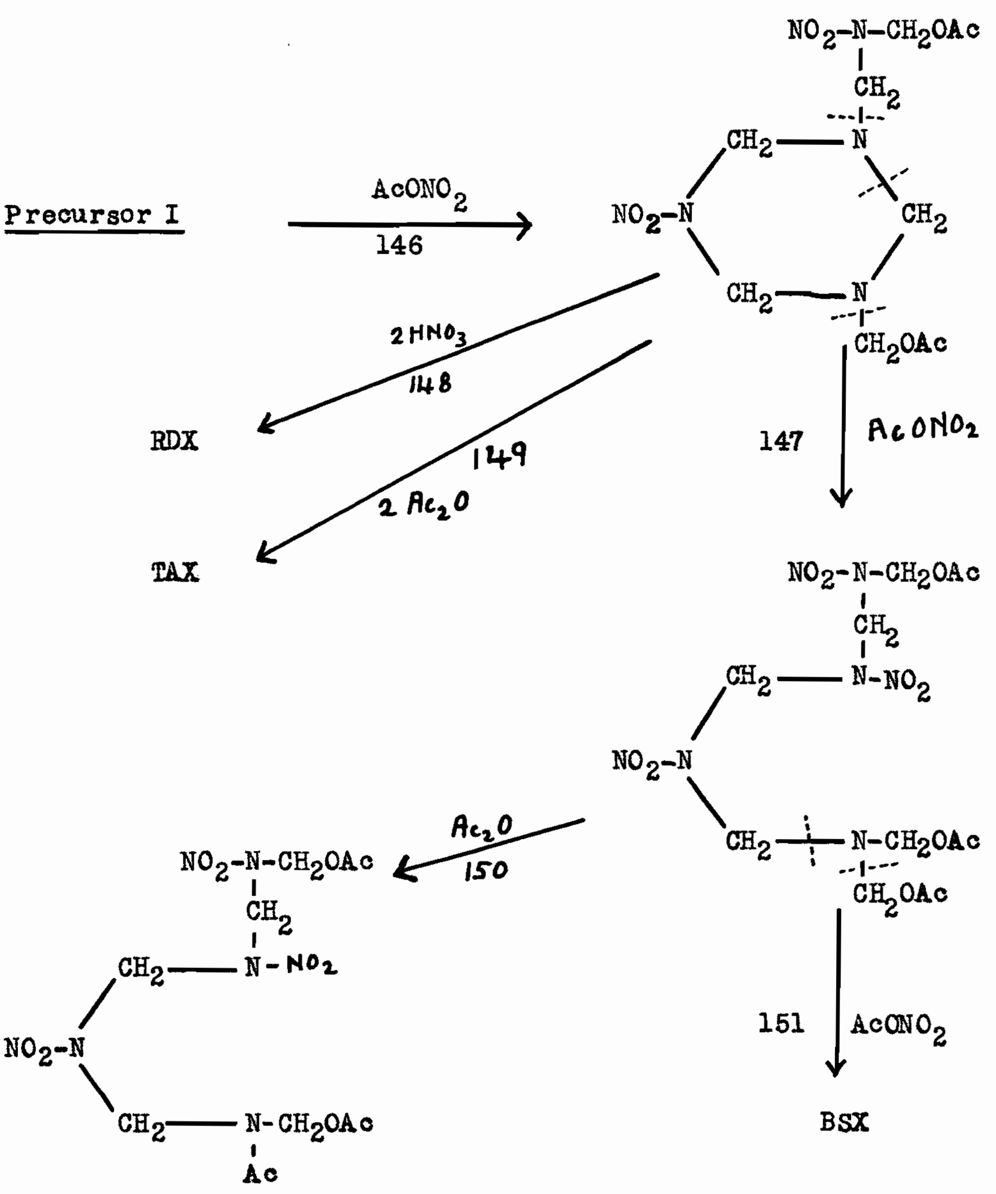
HMX, AcAn and QDX are then produced as follows:



RDX, BSX and TAX may result from the following series of reactions (Scheme A):



An alternate possibility is presented in Scheme B.



(H-16)

Linstead, in his discussion, points out that the mechanism of BSX formation as postulated by Connor (see below) is a perfectly acceptable alternative.

The synthetic aspect of the reaction:- Linstead regards the production of the second mole of RDX as being mechanistically similar to the McGill reaction (see page 5C). There is considerable uncertainty as to what chemical form the fragments from the hexamine degradation will assume, but there is no reason to assume that the process will be fundamentally different.

In support of his views, Linstead cites the clear-cut case of the conversion of DNPT through PHX to HMX and AcAn (79,71). In these comparatively simple conversions, all types of fissions postulated in this mechanism occur (See p. 77). The reaction of DNPT with acetyl nitrate to give PHX represents the fission of a C - N linkage in a polymethyleneamine. The conversion of PHX to HMX represents the elimination of a methylol acetate side chain in the presence of ammonium nitrate while the reaction of PHX to AcAn exemplifies ring fission in the absence of ammonium nitrate. In further support of his mechanism, Linstead points out that hexamine contains three six-membered rings and an eight-membered ring. HMX, a reaction product, contains an eight-membered ring; now eight-membered rings are rare in chemistry and are difficult to synthesize, therefore the simplest mechanism would be one involving the maintenance of the rings already present in hexamine.

2. The Theory of Connor, Davy, et al. (16).

The workers at the University of Pennsylvania have investigated the reaction of hexamine (and other compounds) with various molar equivalents of nitric acid in acetic anhydride. On the basis of their results they postulated a mechanism for the production of BSX from hexamine. These theoretical considerations were later combined with a mechanism of RDX formation which was originally developed by Davy of the Holston Ordnance Works (80). These postulated mechanisms constitute the so-called Connor-Davy theory of RDX formation. The experimental basis for this mechanism is contained chiefly in the following series of reactions:

i. Hexamine + 1 $HNO_3 + Ac_2O \longrightarrow$ H2

ii. Hexamine + 2 $HNO_3 + Ac_2O \longrightarrow$ DNPT

iii. Hexamine + 3 $HNO_3 + Ac_2O \longrightarrow$ H16

iv. Hexamine + 4 $HNO_3 + Ac_2O \longrightarrow$ BSX

v. H2 + 1 $HNO_3 + Ac_2O \longrightarrow$ DNPT

vi. H2 + 2 $HNO_3 + Ac_2O \longrightarrow$ H16

vii. H16 + $HNO_3 + Ac_2O \longrightarrow$ no reaction

viii. H16 + $HNO_3 \longrightarrow$ 106

ix. H2 + $HNO_3 \longrightarrow$ RDX

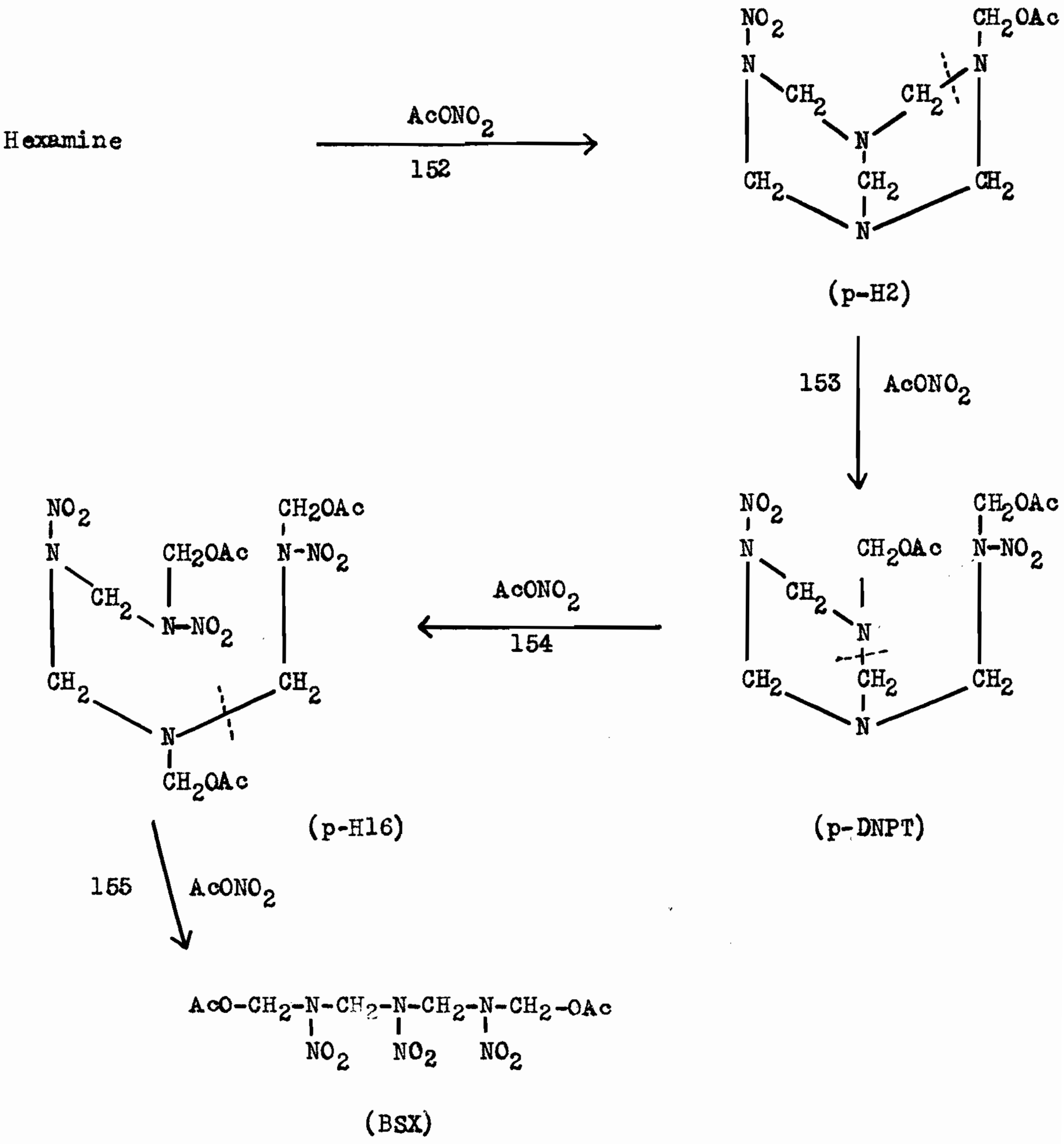
x. H2 + $HNO_3 + Ac_2O$ $NH_4NO_3 \longrightarrow$ RDX + HMX

xi. DNPT + $HNO_3 + Ac_2O$ $NH_4NO_3 \longrightarrow$ HMX + RDX

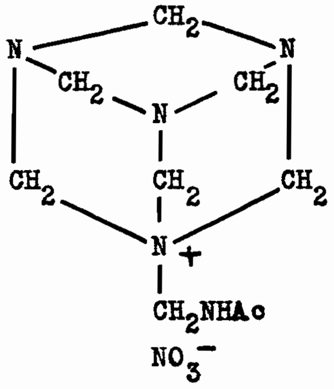
xii. DNPT + $HNO_3 + Ac_2O \longrightarrow$ AcAn

The various steps in the mechanism follow.

The formation of BSX:-

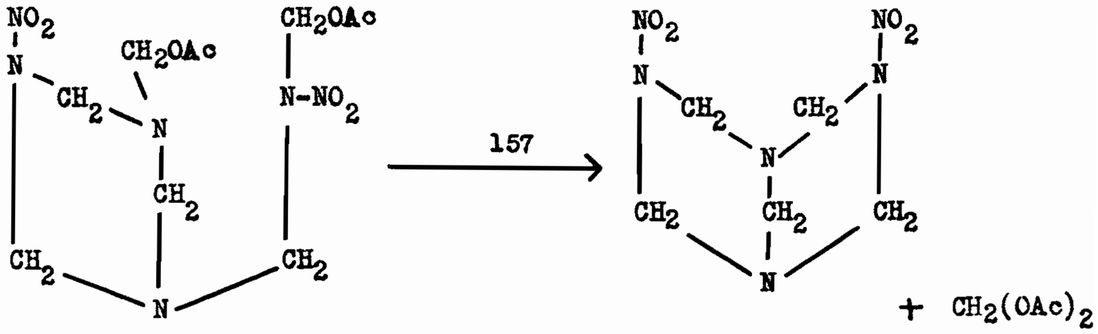


Actually, in this sequence of reactions, only BSX can be isolated but Connor believes that in the absence of excess nitric acid p-H2, p-DNPT and p-H16 will rearrange to H2, DNPT, and H16. At the time of writing, the structure of H2 was uncertain, but it now seems that H2 is not directly related to the proposed p-H2.



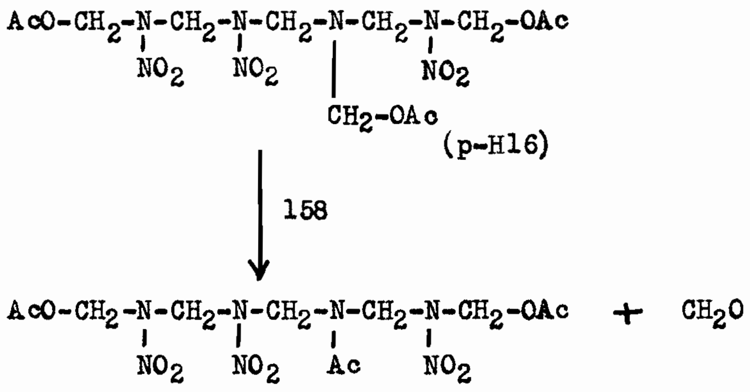
(H2)(81)

It seems rather that p-H2 is unstable and decomposes to give formaldehyde and acetamide which react with unchanged hexamine to give H2. Alternately, hexamine mononitrate may condense with acetamide and formaldehyde from decomposed hexamine. The formation of DNPT is pictured as follows:



(p-DNPT) (DNPT)

The conversion of p-H16 to H16 proceeds as follows:



$$AcO-CH_2-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-\underset{CH_2-OAc}{N}-CH_2-\underset{NO_2}{N}-CH_2-OAc$$

(p-H16)

$$\Big\downarrow 158$$

$$AcO-CH_2-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-\underset{Ac}{N}-CH_2-\underset{NO_2}{N}-CH_2-OAc \quad + \quad CH_2O$$

(H16)

It seems equally likely, however, that the methyleneamine linkage is split by the acetic anhydride to yield an acetamine and formaldehyde diacetate.

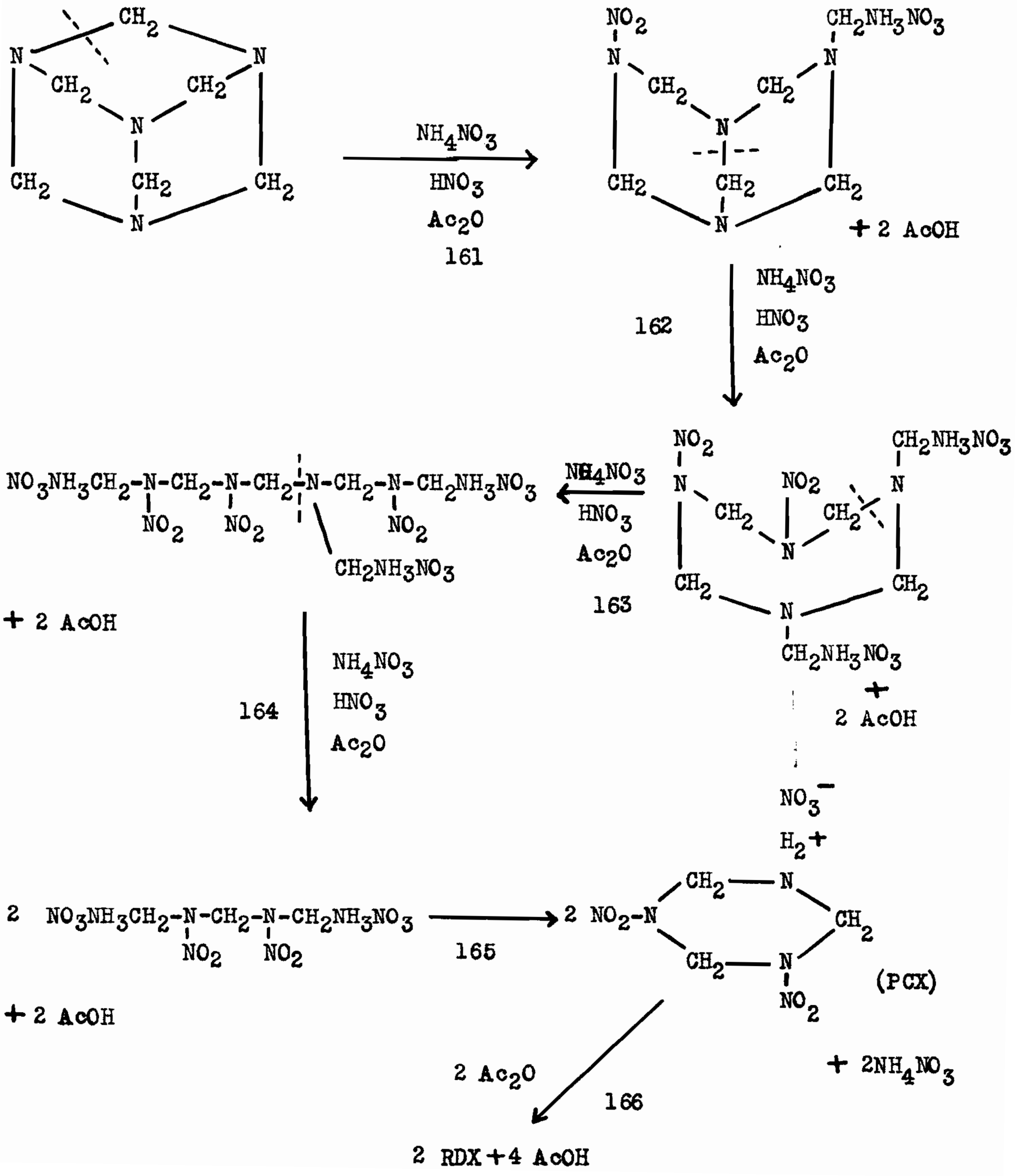
Connor also discusses the reaction of DNPT with acetyl nitrate to give PHX and AcAn. His conclusions are similar to those of Linstead (see p. 79).

The formation of RDX:- Davy postulated that the active agent in the Bachmann reaction is pseudo nitric acid and that the methylol groups resulting from the fission of methyleneamine linkages are stabilized by reaction with ammonium nitrate:

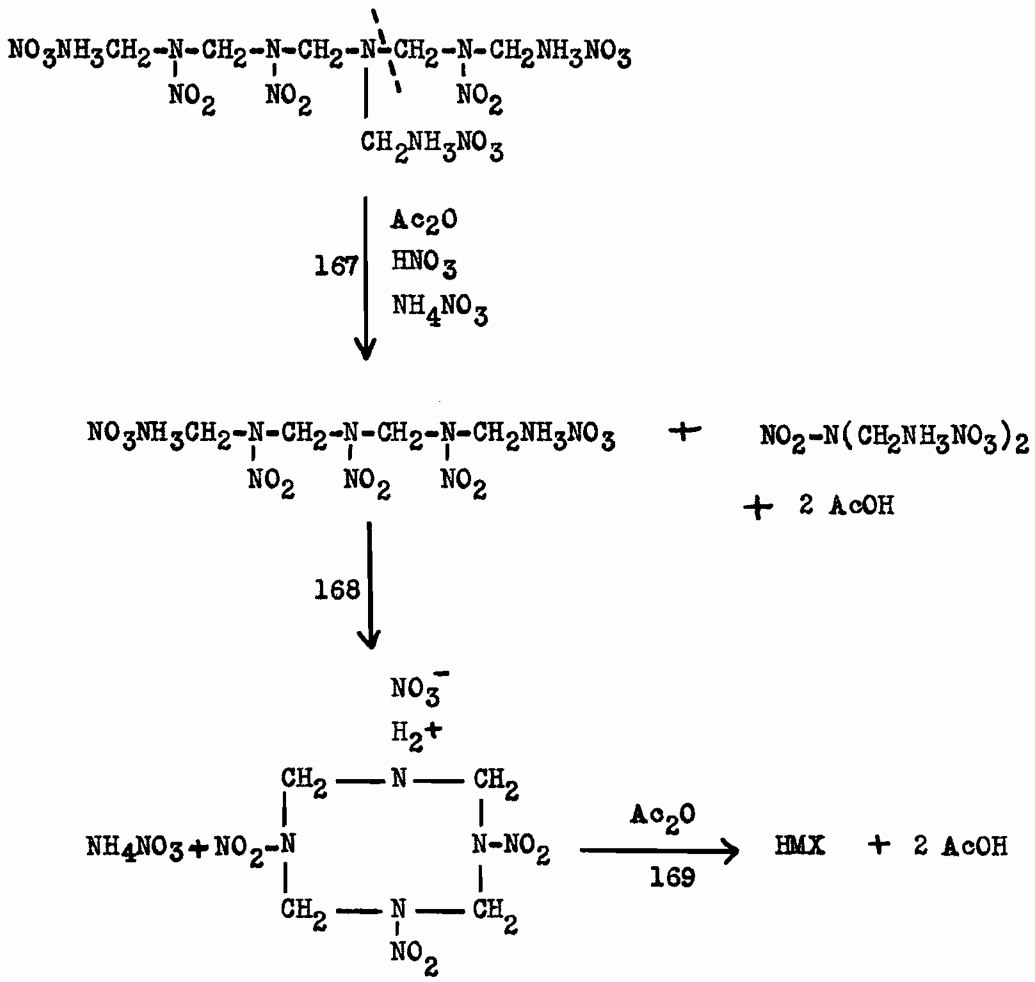
$$-CH_2-N\langle \; + \; HO-NO_2 \xrightarrow[159]{} -CH_2OH \; + \; NO_2-N\langle$$

$$-CH_2OH \; + \; NH_4NO_3 \xrightarrow[160]{Ac_2O} -CH_2NH_3NO_3 + 2\ CH_3COOH$$

The series of reactions leading to RDX may be pictured as follows:

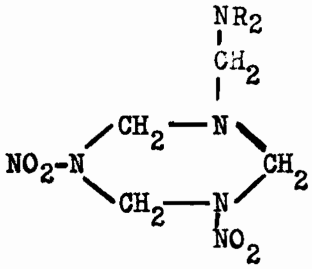


The formation of HMX is similar.



In this mechanism, the function of the acetic anhydride is to dehydrate secondary amine nitrates and to provide conditions for causing methylol groups to react with ammonium nitrate. There seems to be three pieces of evidence which support this mechanism. The first is that a pilot plant investigation at the Holston Ordnance Works showed that there is a molar equivalence between the RDX produced and the ammonium nitrate consumed. This indicates that both moles of RDX are produced in the same manner, a condition which is fulfilled in this mechanism. The second piece of evidence is that a run carried out with a deficiency of anhydride was divided in two; to one portion was added enough anhydride to make up the deficiency while the other was worked up as a control. The former portion gave 20 grams RDX while the latter gave only 6 grams. This increase in yield was interpreted as being evidence for the dehydration step (see equation 166) and of the existence of PCX in the reaction liquor. A third piece of evidence was reported by Boyer (78); to a diluted Bachmann run was added hydrochloric acid, acetyl bromide or sodium nitrite; good yields of nitroso PCX (see p.72) were obtained. This result may be interpreted as indicating the presence of PCX.

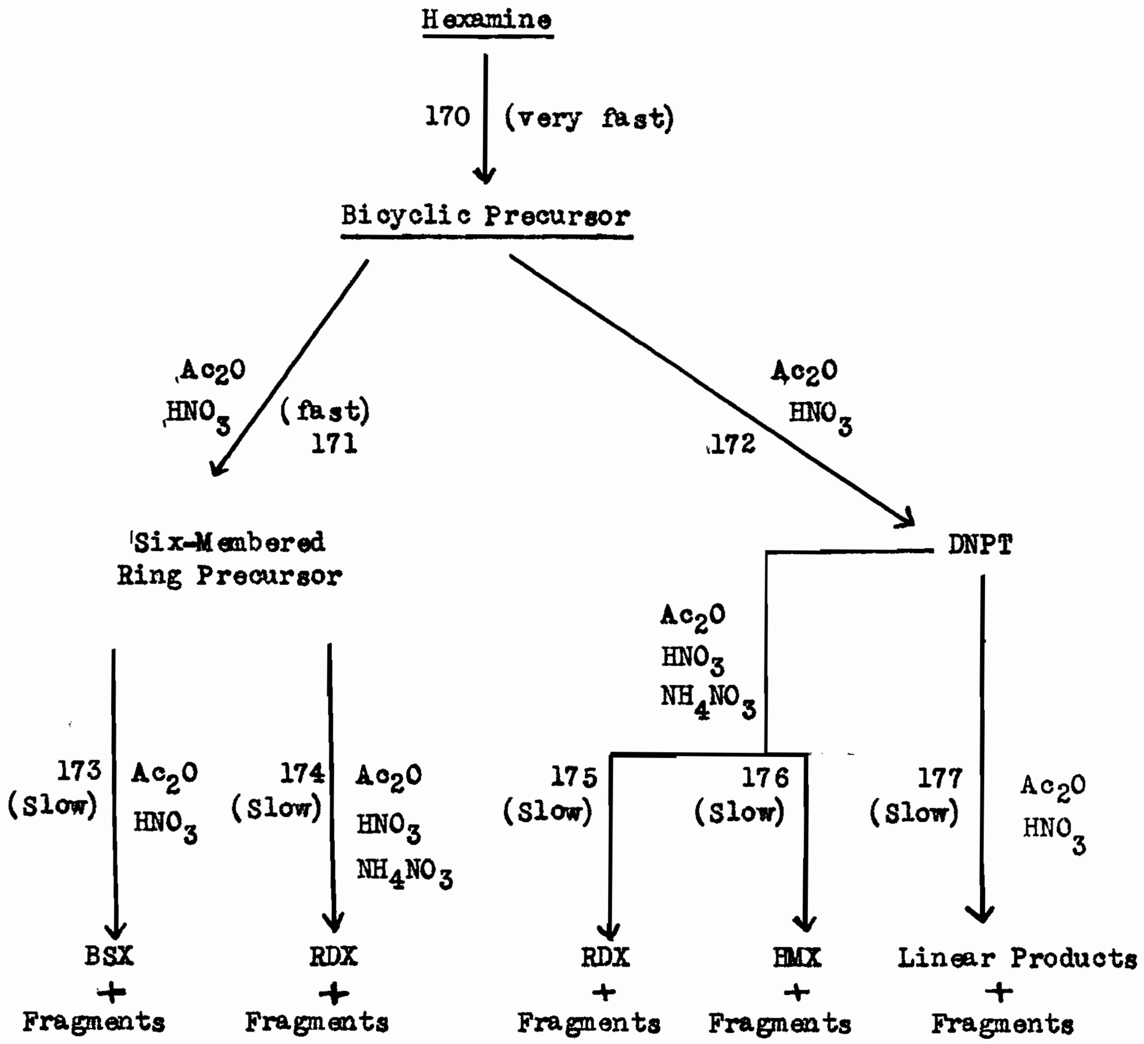
Linstead(1) points out that the equivalence of the molar RDX production and molar ammonium nitrate consumption does not necessarily prove the Connor-Davy mechanism and suggests that the same result would be expected on the basis of his theory. Again, no evidence has been produced to indicate that methylol side-chains will combine with ammonium salts in the fashion indicated in equation 160(1). The Connor-Davy theory does not use the simple case of the DNPT-PHX-AcAn-HMX conversion to as great advantage as does the Linstead mechanism, this case requiring separate treatment. The fact that straight-chain compounds such as BSX and AcAn have never been cyclized to RDX and HMX may be used as negative evidence for the ring-closure stage of the Connor-Davy mechanism. Linstead is in agreement with the author that the fact that RDX is obtained using amine nitrates does not support this concept. The evidence of Ross and Boyer (the isolation of nitroso-PCX) is capable of an alternate interpretation. It is well known that nitrous acid can exist in the pseudo form (HO-NO) much more easily than can nitric acid: for example, acidified sodium nitrite aqueous solution can react with hexamine to give trinitrosocyclotrimethylenetriamine. It may then be considered that nitrous acid, as used by Ross and Boyer, will attack compounds of the following type:



such as "139" (see p. 78), with the production of nitroso-PCX. Lastly, Winkler (58) has criticized the mechanism on the grounds that it does not explain the formation of RDX when the addition of ammonium nitrate is delayed.

3. The Mechanism of Winkler (58)

On the basis of his early work, Winkler (47) proposed a mechanism for the Bachmann reaction which was similar to that of Linstead. Later, however, he modified this view and postulated that at least two-thirds of the RDX is produced through the intermediate DNPT (58).



The synthesis step may be represented briefly as follows:

$$\text{Fragments} + Ac_2O + HNO_3 + NH_4NO_3 \longrightarrow \text{RDX} + \text{HMX} \quad \text{-- } 178$$

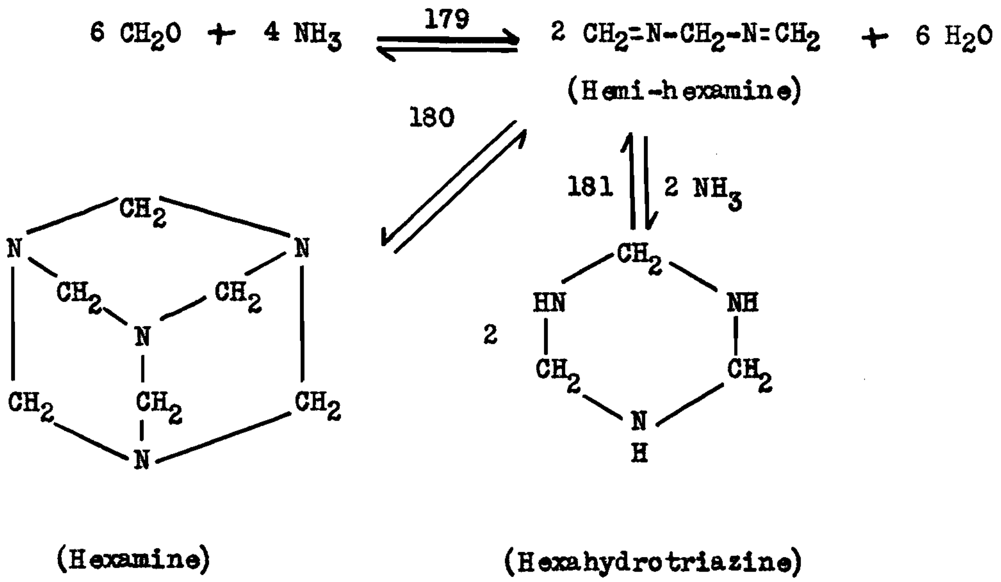
Winkler's evidence is that the reaction producing HMX is similar and closely associated with a reaction producing at least part of the RDX. Further, the delayed addition of ammonium nitrate indicates that hexamine is converted into at least two compounds, one producing RDX and the other producing RDX and HMX. The often-observed phenomenon of the complementary nature of the yields of HMX and RDX under certain circumstances also supports this view. Winkler believes that the precursor to the HMX and two-thirds of the RDX is DNPT. In support of this he points out a parallelism between the reaction of DNPT to give HMX and RDX and the reaction of hexamine to give RDX and HMX.

In connection with the question of the active agent in the Bachmann reaction, Winkler believes that the nitric acid is associated with the acetic anhydride rather than with the ammonium nitrate. The ammonium nitrate may, however, combine with excess nitric acid and thus act as a buffer. Since the belated addition of ammonium nitrate gives rise to RDX and HMX (from DNPT), the ammonium nitrate must have a function other than a buffer action and other than being a necessary component of the synthesis process.

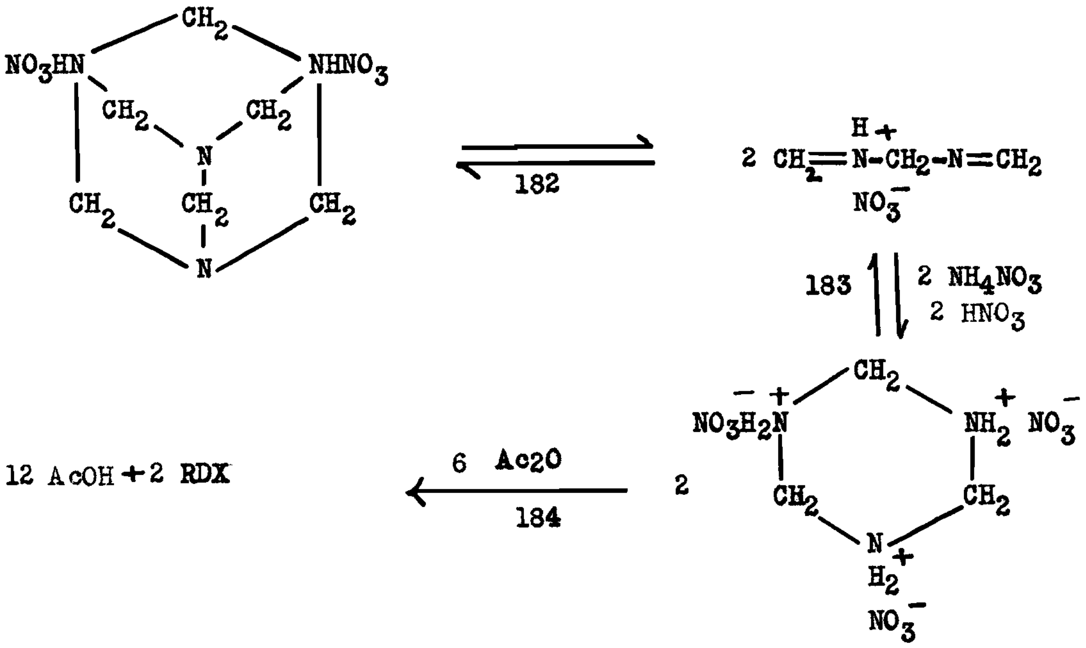
This mechanism is open to the important criticism that DNPT is known to give rise to large yields of HMX relative to RDX (21). All pieces of evidence are indirect and many are capable of alternate interpretations.

4. The Mechanism of Ross and Boyer (9)

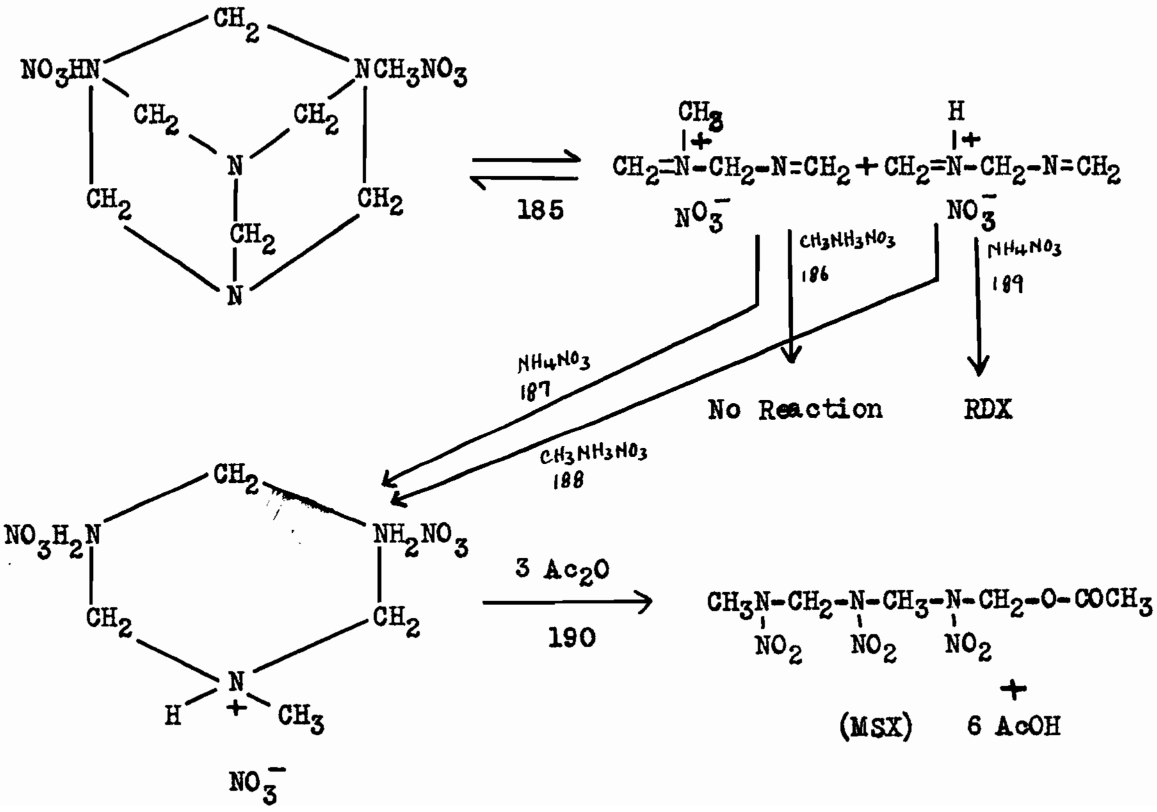
Ross and Boyer proposed a modification of the mechanism of Connor and Davy. It takes into account the long-suspected lability of hexamine in solution:



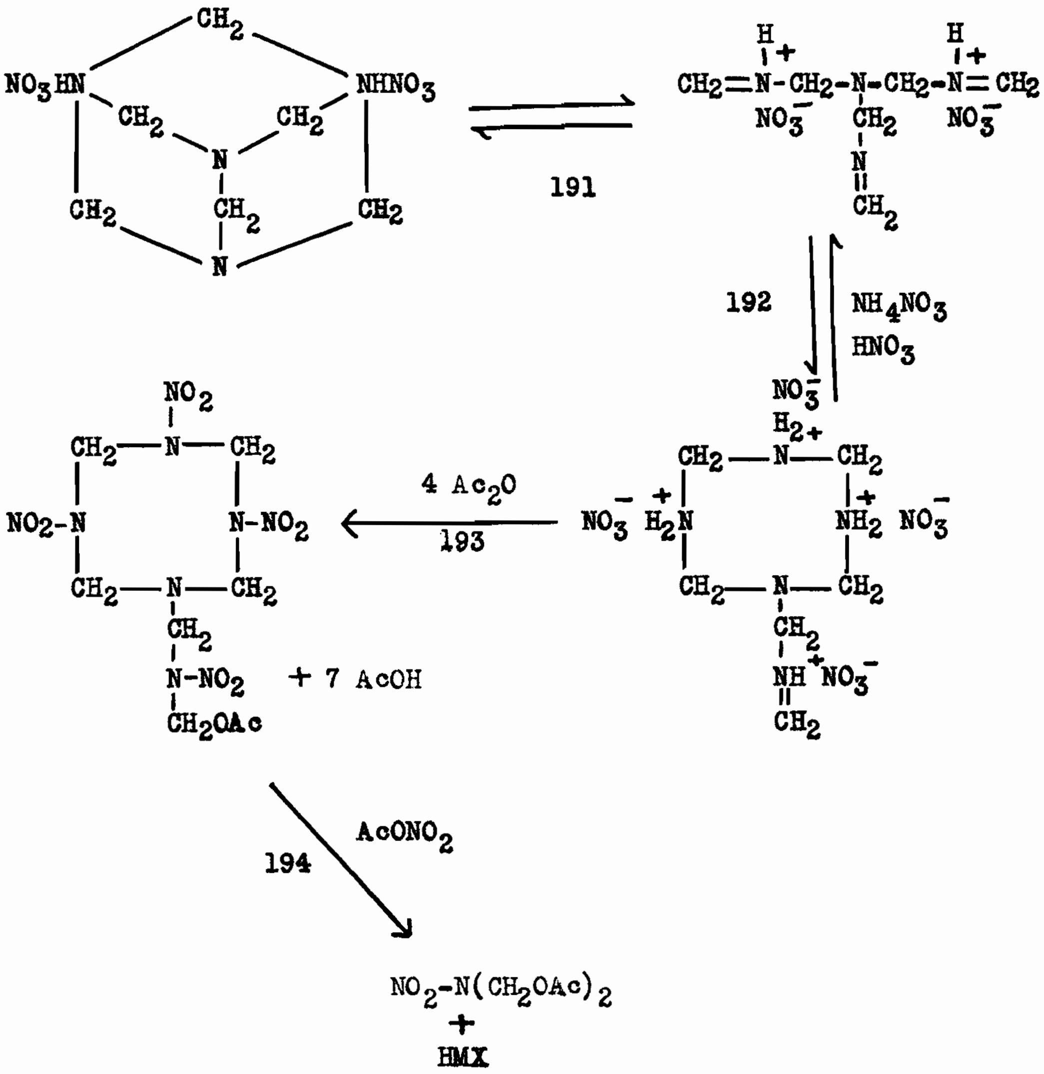
The hemi-hexamine fragments are postulated to undergo cyclization on reaction with ammonium nitrate to 1,3,5-hexahydrotriazine trinitrate, a compound which, theoretically, may be dehydrated to RDX.



In support of this view, Ross and Boyer point out that a solution of hexamine and ammonium nitrate in acetic acid gives an indifferent test for hexamine. Bachmann (67) found that the solubility of ammonium nitrate in acetic acid increased rapidly and in direct proportion to the amount of hexamine dissolved in the acetic acid; bases (other than hexamine) did not give this same effect. Furthermore, the recrystallization of H-18 (the monomethyl nitrate salt of hexamine) and ammonium nitrate from acetic acid gives hexamine. Some support for the above mechanism was obtained when H-18 was treated with nitric acid, acetic anhydride and either ammonium nitrate or methylammonium nitrate and the predicted yields of RDX and MSX were obtained:



In the Bachmann reaction the production of HMX is accounted for by using an alternate structure for hexamine (the Lösekann T structure) (82):



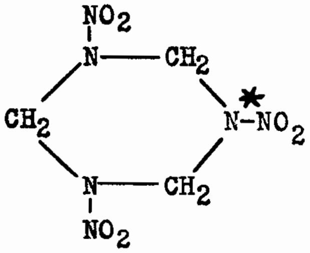
The proposed mechanism rests on somewhat the same evidence as does the Connor-Davy theory and is, in general, open to the same criticisms. The concept of hemi-hexamine has been strongly criticized by Linstead (1). Winkler (58) has criticized the theory on the basis of the fact that it does not explain the production of RDX upon belated addition of ammonium nitrate.

EXPERIMENTAL AND THEORETICAL

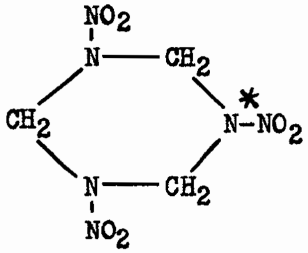
I. Attempts to Differentiate the Two Moles of RDX Formed in the Bachmann Reaction **

While several mechanisms have been postulated for the Bachmann reaction, they may be classified in two groups: those in which the two moles of RDX arise by means of identical or similar processes and those in which the two moles of RDX arise by different processes. If a mechanism of the first group (e.g., the Connor-Davy theory) represent the course of the reaction, the two moles of RDX will be indistinguishable from one another with respect to the history of their amino nitrogen atoms, whereas, if a mechanism of the second group (e.g., the theory of Linstead) represent the course of the reaction, the two moles of RDX will differ from one another in this respect. (See pp. 11 and 12 of this thesis.) The two cases may be represented as follows:

Case I:-



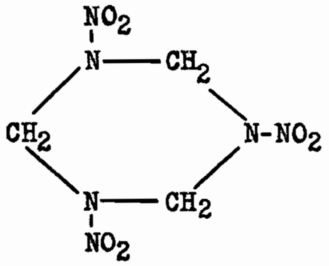
Type III RDX
(one mole)



Type III RDX
(one mole)

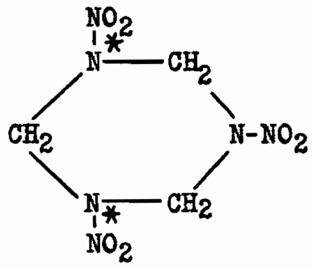
** This discussion is included here, not because the results obtained in this laboratory are either extensive or significant, but because the attempt to differentiate the two moles of RDX formed in the Bachmann reaction constituted the first experimental approach of this researcher to the problem of the mechanism (see p. 13). Bachmann's Tracer Experiments are considered at some length because of their direct bearing on the problem.

Case II:-



TYPE I RDX

(one mole)



TYPE IV RDX**

(one mole)

where N^{*} represents an amino nitrogen atom which originated in the ammonium nitrate rather than in the hexamine. The two moles of RDX are (in either case) physically and chemically identical, differing only with respect to the history of their amino nitrogen atoms. If, however, the amino nitrogens of either the ammonium nitrate or the hexamine can be tangibly "marked" with respect to the other, it should be possible to distinguish between the two moles of RDX formed.

The most direct approach to this problem lies in the use of an isotope of nitrogen. If the ammonium nitrate, for instance, contains

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** It should be emphasized, at this point, that Case II holds rigidly only in theory. In practice, TYPE IV RDX may well contain a random collection of amino nitrogen atoms. In the extreme case, the fourth amino nitrogen atom of the hexamine may in fact not appear in the product at all. Yields of RDX+HMX as high as 92 percent have been reported but these yields are based on the formaldehyde content of the hexamine and ammonium nitrate is always used in excess; thus it is not a necessary condition that the fourth nitrogen of the hexamine appear in the product.

heavy amino nitrogen (N15) one of the molecules of RDX (in Case II) will have two N15 nitrogen atoms while the other will have none. Obviously, there is little chance that the different "types" of RDX will be separable by simple physical or chemical means and, if in Case II the two moles of RDX are formed to about the same extent, even the mass spectrograph will be unable to distinguish between the two cases. Nevertheless, this approach was investigated by Bachmann (83) and, while not conclusive, a mathematical analysis of the results by G. T. Young of the British Central Scientific Office (84) suggests that Case II is indicative of the reaction mechanism.

A second approach to the problem of "marking" one type of amino nitrogen atoms, and the one used by this investigator, lies in the use of phosphonium nitrate in place of ammonium nitrate in the Bachmann reaction. Phosphorus, being in the same group of the periodic table as nitrogen, is able to form analogous compounds in many cases. Since nitrophosphines are unknown, it was considered that there was only a slight possibility that phosphorus analogs of TYPE III and TYPE IV RDX could be isolated and characterized, but it was considered that if any RDX (less than one mole per mole of hexamine) were isolated, it would constitute evidence for Case II. All attempts to prepare phosphonium nitrate either by the interaction of phosphonium iodide and silver or lead nitrates or by the interaction of phosphine and nitric acid were unsuccessful. Thus the desired replacement of ammonium nitrate was not achieved.

Experimental

1. The Use of Tracer Ammonium Nitrate (Bachmann)

Three experiments were carried out by Bachmann (83): (a) hexamine and tracer ammonium nitrate were heated together in acetic acid in order to determine the extent of nitrogen interchange, (b) a small-scale Bachmann reaction was carried out using the regular molar ratios of reagents, and (c) a small-scale Bachmann reaction was carried out using an unusually high molar ratio of nitric acid. These runs are described below.

"PROCEDURE #1 -(N^{15}-03)

> One-half gram of tracer ammonium nitrate was dissolved in 20 cc. of glacial acetic acid, 1 cc. of a glacial acetic acid solution containing 0.44 g. of hexamine was added, and the clear solution was warmed for 15 min. at 65°. After cooling, 0.3 cc. of 98% nitric acid was added. The precipitate of hexamine dinitrate and ammonium nitrate was filtered out and extracted with 10 cc. of cold 10% nitric acid to remove the ammonium nitrate. The hexamine dinitrate was titrated to a rough phenolphthalien end point with 50 cc. of 0.11 N NaOH. After evaporation to dryness at room temperature, the freed hexamine was extracted out with $CHCl_3$. Most of the $CHCl_3$ was blown off at room temperature and the hexamine was crystallized from absolute ethyl alcohol.

"PROCEDURE #2 -(N^{15}-04; N^{15}-08; and N^{15}-09)

> This identical procedure, using ordinary ammonium nitrate instead of tracer ammonium nitrate, was used to prepare samples N^{15}-06 and N^{15}-07.
>
> To a 100 cc. Soxhlet flask containing one-half gram of tracer ammonium nitrate, 3 cc. of Ac_2O, and 7 cc. of glacial acetic acid was added continuously, simultaneously, and equivalently 7.5 cc. of a glacial acetic acid solution containing 3.30 g. of hexamine, 15 cc. of acetic anhydride, and 7.45 cc. (0.2 cc. ahead and 7.25 cc. during addition) of a solution containing 4.91 g. of tracer ammonium nitrate and 4.48 cc. of 98% nitric acid. The mixture was efficiently stirred and kept between 70-75° throughout the 12½ min. addition period and subsequent 3 min. aging.

The reaction mixture was drowned in 200 cc. of H_2O, simmered $3\frac{1}{2}$ hrs., cooled, filtered, washed and dried. Yield of RDX (B) was 8.43 g. or 81%.

The filtrate was blown down to dryness on a steam bath, extracted with H_2O, and a small quantity of H_2O insoluble material filtered off. The H_2O solution was blown down to dryness again to yield 1.58 g. of crude recovered ammonium nitrate. Part of this was crystallized from glacial acetic acid (5 cc. to 1 g.), then recrystallized from a more dilute solution (25 cc. to 1 g.). Final purified ammonium nitrate (<u>N^{15}-04</u>) melted at $168\frac{1}{2}$-$169\frac{1}{2}$°, corr.

The RDX (B) product was dissolved in 50 cc. of warm nitromethane, 100 cc. of H_2O was added, and the nitromethane was slowly distilled off over a period of about $2\frac{1}{2}$ hrs. The resultant crystals, presumably a mixture of RDX and β-HMX only, were separated by repeated fractional centrifigations using a trimethylene bromide-fine mineral oil solution of 1.81 g/cc density.

RDX - 8.11 g. (192°) 197-200° (uncorr.)
HMX - .34 g. (267°) 268-269° (uncorr.)

The RDX was recrystallized twice from acetone to give the final purified sample (<u>N^{15}-08</u>) M.p. - 204-205°, corr.

The HMX was recrystallized twice from acetone to give the final purified sample (<u>N^{15}-09</u>) M.p. - 282-283°, corr.

"<u>PROCEDURE #3</u> -(<u>N^{15}-05</u> and <u>N^{15}-10</u>)

The procedure followed for this preparation of RDX (B) was identical to Procedure #2 except that 10.75 cc. (.75 cc. ahead and 10 cc. during addition) of a solution containing 5.77 g. of tracer ammonium nitrate in 7.75 cc. of 98% nitric acid was used. This was slightly more tracer ammonium nitrate and much more 98% nitric acid than before. The reaction mixture was filtered hot and anhydrous (Crop #1), the filtrate was diluted with H_2O, simmered, cooled, and filtered to yield Crop #2. Yield of RDX (B) Crop #1 = 2.36 g.; Crop #2 = 2.60 g.; Total = 4.96 g. or 47%.

The recovered ammonium nitrate was obtained from the crop #2 filtrate as before. (See Procedure #2) Wt. of crude ammonium nitrate = 4.77 g. Final purified ammonium nitrate (<u>N^{15}-05</u>) melted at $168\frac{1}{2}$-$169\frac{1}{2}$, corr.

Part of the RDX (B) crop #1 product was simmered for 15 min. in 70% nitric acid, water was added to incipient precipitation, and the solution was allowed to cool slowly. The long, white needles that crystallized out were recrystallized from acetone to give the purified RDX sample - <u>N^{15}-10</u> M.p.- 204-205°, corr."

A number of samples were analysed for total nitrogen by Wright (University of Toronto) and the nitrogen gas thus obtained was analysed for its N^{15} content by Keevil (University of Toronto). The results of this investigation are contained in Table I.

2. The Attempted Use of Phosphonium Nitrate

Preparation of Phosphonium Iodide:- Phosphonium iodide was prepared according to the method of A. W. Hofmann (85) which is described in Mellor's Treatise on Inorganic and Theoretical Chemistry (Vol. VIII, p. 825). The product was white and crystalline. It smelled strongly of phosphine and was slightly deliquescent. Phosphonium iodide may be stored, but glass-stoppered bottles should be used since the product attacks cork, rubber and paper. Yield: 70 g. While the reaction is not clear-cut, it may be represented by the following equation (85).

$$5\ I_2 + 18\ P + 32\ H_2O \longrightarrow 10\ PH_4I + 8\ H_3PO_4 \quad \text{---- } 195.$$

Attempted preparation of Phosphonium Nitrate:- Many attempts were made to carry out a reaction between phosphonium iodide and silver nitrate or lead nitrate:

$$PH_4I + AgNO_3 \longrightarrow PH_4NO_3 + AgI \quad \text{---- } 196.$$

The main difficulty encountered was the problem of finding a co-solvent. Water and alcohols reacted with the phosphonium iodide giving free phosphine. Oxygenated organic solvents appeared to be reduced by phosphonium iodide while halogenated solvents were unsatisfactory from a point of view of the silver nitrate. Hydrocarbons

TABLE I

BACHMANN REACTION:-USE OF TRACER AMMONIUM NITRATE. DISTRIBUTION OF ORIGINAL AMMONIUM NITROGEN (BACHMANN)

SAMPLE NUMBER	DESCRIPTION	PROCEDURE NUMBER	ATOM % N^{15} OF TOTAL NITROGEN	ATOM % N^{15} OF AMMONIUM OR AMINO NITROGEN	ATOM % OF AMINO OR AMMONIUM NITROGEN COMING FROM ORIGINAL AMMONIUM NITRATE
N^{15}-01	TRACER AMMONIUM NITRATE		7·5	14·6	100·0
N^{15}-02	HEXAMINE (BLANK)		0·40	0·40	0·0
N^{15}-03	HEXAMINE (TREATED WITH TRACER)	1	1·15	1·15	5·3
N^{15}-04	RECOVERED AMMONIUM NITRATE	2	3·95	7·50	50·0
N^{15}-05	RECOVERED AMMONIUM NITRATE	3	4·93	9·46	64·0
N^{15}-06	RDX (BLANK)		0·41	0·42	0·1
N^{15}-07	HMX (BLANK)		0·445	0·49	0·6
N^{15}-08	RDX	2	3·03	5·66	37·0
N^{15}-09	HMX	2	1·49	2·58	15·0
N^{15}-10	RDX	3	1·82	3·24	20·0

would not dissolve silver nitrate. Nitromethane appeared to be reduced by the phosphonium iodide. Liquid sulphur dioxide was reduced by the action of phosphonium iodide. Liquid ammonia dissolved the phosphonium iodide but rendered the silver nitrate inactive through complex formation. The introduction of phosphonium iodide into 97 percent nitric acid resulted in combustion. When solid phosphonium iodide and solid silver nitrate were ground together, a reaction took place but the product liberated no phospine when treated with dilute alkali.

An alternate method of synthesis would seem to lie in the reaction of phosphine with nitric acid.

$$PH_3 + HNO_3 \longrightarrow PH_4NO_3 \qquad \text{---- 197.}$$

Free phosphine was generated by reacting phosphonium iodide with dilute alkali.

$$PH_4I + NaOH \longrightarrow PH_3 + NaI + H_2O \qquad \text{---- 198.}$$

When this product was introduced into concentrated nitric acid or into a dilute solution of nitric acid and chloroform it burned vigorously.

The preparation of phosphonium metaphosphate, PH_4PO_3, as a phosphorus analog of ammonium nitrate, NH_4NO_3, was projected but never attempted.

Discussion

1. The Use of Tracer Ammonium Nitrate (Young)

An extended mathematical analysis of Bachmann's results was carried out by Young (84) of the British Central Schientific Office, Washington. This paper is discussed at some length below.

On the basis of run N^{15}-03, Young assumes that the rate of exchange of amino nitrogen atoms between hexamine and ammonium nitrate is small as compared with the rate of RDX formation and may be neglected.

If Case II is indicative of the course of the reaction, a simplified mechanism for the reaction is as follows:

$$(CH_2)_6N_4 + 4\ HNO_3 \longrightarrow (CH_2)_3(N\text{-}NO_2)_3 + 3\ CH_2O + \underline{NH_4NO_3}$$

---- 2.

$$3\ CH_2O + 3\ NH_4NO_3 + 6\ (CH_3CO)_2O \longrightarrow (CH_2)_3(N\text{-}NO_2)_3 + 12\ CH_3COOH$$

---- 5.

$$(CH_2)_6N_4 + 4\ HNO_3 + 2\ NH_4NO_3 + 6(CH_3CO)_2O \longrightarrow 2\ (CH_2)_3(N\text{-}NO_2)_3 + 12\ CH_3COOH$$

---- 3.

Since the formation of the first mole of RDX results in the production of one mole of ammonium nitrate, the tracer (N^{15}) ammonium nitrate will be diluted with unmarked (N^{14}) ammonium nitrate before the second mole of RDX is formed. Young then assumes that marked and unmarked will be incorporated indiscriminately into the second mole of RDX and the proportion (or strength) of marked ammonium nitrate in this mole will be directly proportional to the concentration of marked ammonium nitrate in the diluted mixture.

If Case I is indicative of the course of the reaction, it can be shown that at no stage of the reaction can unmarked ammonium nitrate dilute the marked ammonium nitrate and that the ammonium nitrate incorporated into the RDX will all be marked.

Now, consider procedure 2 of Bachmann (see above) and suppose that Case II represents the reaction mechanism. The yield of RDX in this run was 77.5 percent. Young assumes that under the optimum conditions prevailing in this reaction, the first mole of RDX is formed in 77.5 percent yield (based on the hexamine introduced) and that the second mole is formed in 100 percent yield (based on the formaldehyde liberated in equation 2).* In procedure 2, the following quantities were reported:

Hexamine added, 3.30 g. = 0.0236 g. moles containing 0.0944 g. atoms of amino N

Tracer ammonium nitrate, 5.41 g. = 0.0676 g. moles containing 0.0676 g. atoms of amino N

HMX formed, 0.34 g. = 0.0011 g. moles containing 0.0044 g. atoms of amino N

RDX formed, 8.09 g. = 0.0364 g. moles containing 0.1092 g. atoms of amino N

Since the yield of RDX is 77.5 percent, the hexamine actually yielding RDX will contain 0.0732 g. atoms of amino N. One-quarter of this will exchange freely with 0.0676 g. atoms of amino nitrogen from the tracer ammonium nitrate (100 percent strength) and the resulting average

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* This condition is not unlikely in view of the equivalence between the molar production of RDX and the molar consumption of ammonium nitrate holding under optimum conditions.

strength will be

$$\frac{0.0676 \text{ x } 100}{0.0676 \text{ x } 0.0183} = 78.7\%$$

Thus, in the final product, three amino nitrogens will have come from the hexamine (0 percent strength of tracer amino nitrogen) and three amino nitrogens will have come from the "diluted" ammonium nitrate (78.7 percent strength of tracer amino nitrogen) and the average atom percent of amino nitrogen coming from the original ammonium nitrate should be 39.4. Young calculates that the recovered ammonium nitrate (now further diluted through exchange with unreacted hexamine) will have a strength of 46.7 percent.

Still considering procedure 2, but supposing that Case I represents the reaction mechanism, it may be shown that the expected average atom percent of amino nitrogen coming from the original ammonium nitrate will be 33.0 percent in the case of the RDX and 59.4 percent in the case of the recovered ammonium nitrate.

In actual experiment (see Table I.), the atom percent of amino or ammonium nitrogen coming from the original ammonium nitrate is 37.0 percent in the case of RDX (N^{15}-08) and 50.0 percent in the case of the recovered ammonium nitrate (N^{15}-04). While these figures are not conclusive, they favour Case II. The argument in favour of Case II is strengthened if one considers that appreciable nitrogen interchange takes place between the hexamine and the ammonium nitrate or if one considers the possibility that some of the hexamine which is not converted to RDX can "dilute" the tracer ammonium nitrate before the second mole of RDX is formed. Further, if the original assumption that the yield of the process giving rise to the second mole of RDX is 100 percent is not entirely valid and the yield is somewhat less, the evidence in favour of Case II is strengthened once again.

Concerning the formation of HMX in procedure 2, Young shows that if this product arises directly from hexamine without the incorporation of ammonium nitrate (e.g. through DNPT), the strength of the tracer ammonium nitrate in HMX should be zero, while, if one mole of ammonium nitrate is incorporated into the HMX ring structure (as is the case in both the Connor-Davy mechanism and the Ross-Boyer mechanism), the strength of the tracer ammonium nitrate in the product should be 25.0 percent. Since the experimental result is 15.0 percent (N^{15}-09), Young states that it is probable that the tracer ammonium nitrate is "diluted" with ammonium nitrate from the hexamine (see equation 2) before it is incorporated into the HMX. It should be pointed out, however, that the postulation of two mechanisms for HMX formation (e.g., one mechanism giving HMX directly from hexamine and the other involving the use of ammonium nitrate) will explain the experimental result equally well. Thus, with regard to the mechanism of HMX formation, the experiments are inconclusive.

Now consider procedure 3 of Bachmann (see above) and suppose that Case II represents the reaction mechanism. The yield of RDX in this case is only 47.0 percent. If it is assumed that the first mole of RDX is formed in a yield of 47.0 percent and the second mole in 100 percent yield (based on the formaldehyde liberated in the first process), it may be shown that the expected strength of amino or ammonium nitrogen coming from the original ammonium nitrate would be 43.8 atom percent in the RDX and 46.4 atom percent in the recovered ammonium nitrate. If it is supposed that Case I represents the reaction mechanism, the expected strength would be 33.3 atom percent for the RDX and 53.0 atom percent for the recovered ammonium nitrate. The figures actually obtained by Bachmann were 20.0 atom percent and 64.0 atom percent respectively. These agree with neither Case I nor Case II. On this basis one is forced to the conclusion that the initial assumption was invalid and that the yields of RDX in the two processes (Case II) were not 47 percent and 100 percent.

The most important difference between the two experiments of Bachmann (procedure 2 and procedure 3) is the use of a large excess of nitric acid in procedure 3. Young assumes that this excess of nitric acid will not affect the efficiency of the process forming the first mole of RDX but will decrease* the efficiency of the process forming the second mole. It may be shown that, if the process making the first mole of RDX is 74.0 percent efficient (with respect to the hexamine introduced) and the process making the second mole of RDX

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* This is not without experimental basis since nitric acid is known to decrease the yield of the McGill reaction. See however Table XVI and section III H.

is 27.0 percent efficient (with respect to the formaldehyde produced in the first reaction), the final yield of RDX will be 47.0 percent and the expected strength of the amino nitrogen atoms in the RDX coming from the original ammonium nitrate would be 20.0 atom percent (experimental value 20.0) and the expected strength of original nitrogen atoms in the recovered ammonium nitrate would be 61.3 atom percent (experimental value 64.0).

While Young's treatment of Bachmann's experiments indicates the probability that Case II is indicative of the reaction mechanism, the evidence is by no means conclusive. The uncertainty as to the fate of the hexamine which is not converted to RDX or HMX is particularly disturbing (particularly in procedure 3). Furthermore, there is some doubt as to whether the amino nitrogen from the hexamine which does not appear in the first mole of RDX will act as another ammonium nitrogen from the ammonium nitrate: it is possible that it will be in a condition which will make for its preferential incorporation into the second mole of RDX, or vice versa.

A simpler, and perhaps equally convincing, analysis of Bachmann's results is contained in the following statement: since, under different reaction conditions different amounts of tracer ammonium nitrate appear in the RDX, any theory which requires that both moles of RDX incorporate the same number of amino nitrogens from the ammonium nitrate is invalid.

In summary, the use of tracer ammonium nitrate in the Bachmann reaction indicates that the two moles of RDX are formed by different processes.

2. The Attempted Use of Phosphonium Nitrate

Since the phosphonium ion is a strong reducing agent and the nitrate ion a strong oxidizing agent it is possible that phosphonium nitrate can have no real existence. If it does exist it would undoubtedly be too unstable to survive the conditions of the Bachmann reaction.

II. The Effect of Replacing Ammonium Nitrate with Amine Nitrates and the Effect of Belated Addition of Ammonium and Amine Nitrates

It has already been pointed out (p. 94) that the various postulated mechanisms for RDX formation in the Bachmann reaction may be classified in two groups depending on whether the two moles of RDX produced in the reaction arise through identical (similar) or different processes. If the two moles are formed by the same mechanism, the product obtained may be represented (in the case of the theoretical equation) by Case I (p. 94). In this event, both moles of RDX are identical with respect to the history of their amino nitrogen atoms and both moles contain one amino nitrogen which originated in the ammonium nitrate. Otherwise stated: the ammonium nitrate contributes directly to the actual synthesis of the triazine ring of both moles of RDX and is <u>synthetic</u> in its function with respect to both moles of RDX. If these two moles are formed by dissimilar processes, however, it is highly probable that the product obtained may be represented (in the case of the theoretical equation) by Case II (see p. 95). In this event, the two moles of RDX are unlike with respect to the history of their amino nitrogen atoms and one mole (TYPE I) will contain no amino nitrogen atoms which originated in the ammonium nitrate, while the other mole (TYPE IV) will have, on an average, two amino nitrogen atoms which originated in the ammonium nitrate and only one which originated in the hexamine. Since the ammonium nitrate does not, in this case, contribute directly to the actual synthesis of the first mole of RDX, it cannot be synthetic in its function, but since no RDX is formed in the Bachmann reaction when the ammonium nitrate is absent, it must be catalytic in function with respect to this mole of RDX. Ammonium nitrate does contribute directly to the synthesis of the triazine ring of the second mole of RDX, in Case II, and its function here is synthetic.

On the basis of this discussion, if Case II is indicative of the reaction mechanism, the first process producing RDX may be considered as "catalysed nitrolysis" of hexamine while the second may be regarded as a "synthesis" process involving the fragments resulting from the first. The overall mechanism, then, may be called the "catalysed nitrolysis - synthesis" mechanism.

If Case II is indicative of the reaction mechanism, it is possible that some substance other than ammonium nitrate may be found which is incapable of duplicating the synthetic function of the ammonium nitrate but which can function as a catalyst in the formation of the first mole of RDX. Thus, if a substance be found which gives rise to some RDX when used in place of the ammonium nitrate in the Bachmann reaction, and if it is unlikely that this substance can duplicate the synthetic function of the ammonium nitrate, then this fact will constitute strong evidence in favour of Case II.

The first approach to this phase of the problem lay in the replacement of the ammonium nitrate with other ammonium salts. Whitmore (69) found that ammonium acetate could replace ammonium nitrate in the Bachmann reaction provided that an excess of nitric acid was used. The author investigated the use of ammonium acetate and ammonium metaphosphate (NH_4PO_3) and obtained small yields of RDX. It soon became apparent, however, that the use of ammonium salts would not be significant from the point of view of the reaction mechanism since ammonium nitrate itself could be prepared from these salts by simple double-decomposition reactions:

$$NH_4A + HNO_3 \longrightarrow NH_4NO_3 + HA \qquad \text{---- 199.}$$

The proposed use of phosphonium nitrate and phosphonium metaphosphate (previously described) may be regarded as an attempt to catalyse the formation of one mole of RDX. Bachmann (71) used potassium nitrate in place of the ammonium nitrate but obtained no RDX.

A more fruitful approach proved to be the replacement of ammonium nitrate with amine nitrates. Researchers at the Pennsylvania State College (86) and the author* investigated this field. Of the eleven

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* Although the experiments described here were independently conceived and executed, the prior claim belongs to the workers at the Pennsylvania State College since they reported preliminary results (87) on the effect of monomethylammonium nitrate while the investigation of the effects of the mono-, di-, tri- and tetramethylammonium nitrates was in progress in this laboratory.

amine nitrates studied, all but three gave rise to some RDX and two gave yields of RDX approaching, but not exceeding, one mole per mole of hexamine. Since it is considered unlikely that all, if any, of these amine nitrates could either duplicate the synthetic function of the ammonium nitrate or give rise to ammonium nitrate itself through chemical reaction, the results of these investigations constitute strong evidence in favour of Case II.

Since it was felt that the use of amine nitrates in the Bachmann reaction constituted evidence for and gave rise to the first mole of RDX (independently of the second), a method was sought that would demonstrate the validity of the concept of and give rise to the proposed second mole of RDX (independently of the first). This technique was found in the experiments of Winkler (64) who, in his kinetic studies, discovered that if hexamine, acetic acid, acetic anhydride and nitric acid are mixed (BSX being produced), and if ammonium nitrate is added to this reaction mixture (even after several hours), considerable quantities of RDX are produced. Later, Winkler (90) was able to show that the formation of this RDX was not due to the presence of unchanged hexamine. This phenomenon was re-investigated by the author under a variety of circumstances and it was concluded that, when ammonium nitrate is added belatedly to a modified Bachmann reaction, the RDX is formed by essentially the same mechanism as is the second mole of RDX in the Bachmann reaction. While the results of this investigation do not defy alternate interpretation (see p.141), they constitute evidence in favour of Case II.

If the postulate that the formation of the first mole of RDX (in Case II) is inhibited by the belated addition of ammonium nitrate is combined with the postulate that the formation of the second mole of RDX is inhibited by the use of an amine nitrate in place of ammonium nitrate, it may be deduced that the belated addition of amine nitrates will inhibit the formation of both moles of RDX. Experimental results, while they do not defy alternate interpretation, generally uphold the validity of the above deduction. This is regarded as additional evidence for Case II.

Since it is considered that the use of amine nitrates in place of ammonium nitrate gives rise to the first mole of RDX (in Case II) and that the belated addition of ammonium nitrate gives rise to the second mole of RDX, it was thought that an experiment in which ammonium nitrate was added to the reaction mixture of a Bachmann run carried out in the presence of an amine nitrate might show that the two moles could be formed independently, one after the other. This experiment, however, was based on an ill-conceived and over-literal interpretation of the term "catalysis" as applied to the function of the ammonium and amine nitrates. Very little increase in yield resulted when the ammonium nitrate was added. While this result is without significance as regards the main problem of deciding in favour of Case I or Case II, it is valuable (when used in conjunction with other data) from the point of view of defining more explicitly the function of the ammonium nitrate in the Bachmann reaction.

Hitherto, all the discussion in this section of the thesis has been devoted to the study of the Bachmann reaction itself. Several of the techniques described in this connection, however, were applied to a study of the well-known conversion of DNPT (dinitropentamethylenetetramine) to HMX and RDX on one hand and to AcAn (1,9 - diacetoxypentamethylene - 2,4,6,8 - tetranitramine) on the other (see p. 77). This reaction is important from two points of view. First, the production of HMX, the most important by-product in the Bachmann reaction, may proceed through DNPT. Secondly, the close parallel between the conversion of hexamine to RDX, HMX and BSX makes the former reaction important from the viewpoint of a study of the mechanism of the Bachmann reaction, particularly in view of its comparative simplicity.

In Case II (p. 95) the first mole of RDX is supposed to arise directly from the hexamine without the incorporation of any ammonium nitrate. In other words, under the "catalytic" influence of ammonium nitrate, *three* methylene groups and one amino nitrogen are split off of the hexamine molecule leaving a six-membered methylenenitramine ring (RDX). If *one* methylene group is split off of the DNPT molecule under the "catalytic" influence of the ammonium nitrate, an eight-membered methylenenitramine ring (HMX) may result. In both reactions methylene groups are split off. In the Bachmann reaction mechanism (Case II) it is supposed that these methylene groups react with ammonium nitrate to synthesize the second mole of RDX. Thus, if Case II is indicative of the mechanism, it is safe to assume that the methylene group split off in the DNPT reaction will react with ammonium nitrate to synthesize

RDX (one-third of a mole).

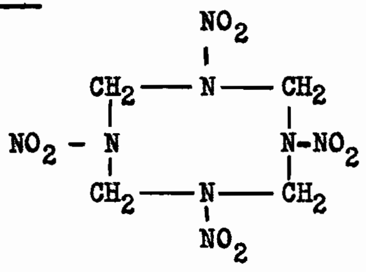
If the above analogy is correct, the theoretical equation for the DNPT reaction may be formulated as follows:

$$3\ (CH_2)_5(N\text{-}NO_2)_2N_2 + 6\ HNO_3 + 3\ NH_4NO_3 + 9\ (CH_3CO)_2O \longrightarrow$$

$$\longrightarrow\ 3\ \underset{(HMX)}{(CH_2)_4(N\text{-}NO_2)_4} + \underset{(RDX)}{(CH_2)_3(N\text{-}NO_2)_3} + 18\ CH_3COOH \qquad \text{--- } 200$$

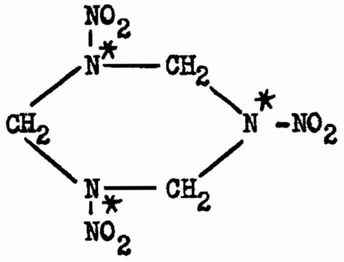
In terms of the symbolism previously employed, the product of this reaction may be represented by Case A (analogous to Case II):

Case A



HMX

(one mole)



TYPE II RDX

(1/3 mole)

where N^{*} represents an amino nitrogen atom which originated in the ammonium nitrate rather than in the hexamine. It is noteworthy that Case I in the Bachmann reaction has no analogy in the DNPT reaction. There is, however, another possible case which has been suggested by Wright (1) and supported by Winkler (58); depending on which bond is first broken in the DNPT molecule, an eight-membered or a six-membered ring results which is converted to either HMX or RDX. Thus, on this basis, if one mole of RDX is formed, the formation of one mole of HMX is inhibited. This case is obviously complicated by the possibility of synthesis of further RDX from the methylene fragments, but it may be said that the mechanism is now represented in part by the following two equations:

$$3\ (CH_2)_5(N\text{-}NO_2)_2N_2 + 6\ HNO_3 + 3\ NH_4NO_3 + 9\ (CH_3CO)_2O \longrightarrow$$

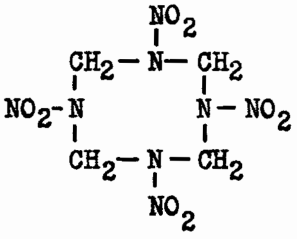
$$\longrightarrow\ 3\ \underset{(HMX)}{(CH_2)_4(N\text{-}NO_2)_4} + \underset{(RDX)}{(CH_2)_3(N\text{-}NO_2)_3} + 18\ CH_3COOH \qquad ----\ 200$$

$$3\ (CH_2)_5(N\text{-}NO_2)_2N_2 + 6\ HNO_3 + 3\ NH_4NO_3 + 9\ (CH_3CO)_2O \longrightarrow$$

$$\longrightarrow\ 5\ (CH_2)_3(N\text{-}NO_2)_3 + 18\ CH_3COOH \qquad ----\ 201$$

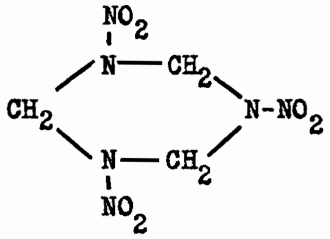
The product may then be represented by TYPE II and TYPE IV RDX (see pp. 11, 12) and by the following:

Case B



HMX

(1-x moles)



TYPE I RDX

(x moles)

Since amine nitrates appear to be able to duplicate the "catalytic" function of the ammonium nitrate in the Bachmann reaction, they should be able to "catalyse" the formation of HMX in the DNPT conversion; likewise, amine nitrates do not appear to be able to duplicate the "synthetic" function of the ammonium nitrate in the Bachmann reaction and they would not be expected to give rise to any RDX in the DNPT reaction (in Case A). Experimental evidence clearly confirms the validity of this reasoning. When amine nitrates are substituted for ammonium nitrate in the DNPT reaction, HMX only is obtained. The success of this application of the experimental technique provides strong confirmation of the whole hypothesis of the "catalytic" and "synthetic" functions of the ammonium nitrate in the Bachmann reaction and, correspondingly, supports Case II and Case A.

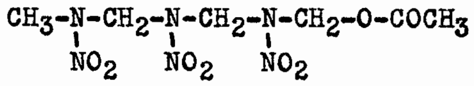
The experiments involving the belated addition of ammonium and amine nitrates as applied to the DNPT conversion were unsuccessful and without significance from a theoretical standpoint. Belated addition of ammonium and amine nitrates gave essentially the same result as did the more conventional-type run. This was later found to be due to the slow rate of conversion of DNPT to AcAn under the prevailing nitric acid concentrations as compared with the rate of conversion of hexamine to BSX.

In this introductory discussion, attention has been focused on the mechanism of RDX formation (particularly with regard to deciding between two important alternatives, Case I and Case II) and, to a lesser extent, on the mechanism of HMX formation. Little attention has been devoted to the significance of the presence of BS^{X} (in the Bachmann reaction) and AcAn (in the DNPT reaction). It is well-known that these compounds are formed in yield when the Bachmann or DNPT reactions are carried out in the absence of ammonium nitrate. They are important by-products in the normal reactions as well. It is generally accepted that BSX and AcAn are formed by the stepwise degradation of hexamine and DNPT. If this is true, then the production of one mole of BSX in the Bachmann reaction will inhibit the formation of two moles of

RDX (in Case I) or of one and one-third moles (in Case II). Similarly, the production of one mole of AcAn will inhibit the formation of one mole of HMX and one-third of a mole of RDX (in Case A). (Case B is so complex as to defy exact prediction.)

On the basis of this reasoning, it may be possible to test the validity of Case I by experiment. If Case I is indicative of the reaction mechanism, the sum of the molar yields of BSX and HMX plus one-half of the molar yield of RDX cannot exceed one mole per mole of hexamine; if Case II is indicative of the reaction mechanism, however, this sum may exceed one mole per mole of hexamine. Due to the complexity of Case B and due to the different nature of the alternatives, no such rule can be made in the case of the DNPT reaction. Experimental evidence, once again, supported Case II in that, in one run where a high proportion of the hexamine was converted to solid products, the above sum exceeded one mole per mole of hexamine. It thus seems that the formation of BSX is in direct competition with the production of the first mole of RDX and that, on the basis of analogy, the formation of AcAn is in direct competition with the formation of both HMX and RDX.

One last topic remains to be considered before passing on to a presentation of experimental results: the significance of MSX. This compound is produced in yield, along with RDX, in a Bachmann run in which monomethylammonium nitrate is substituted for the ammonium nitrate (87). The probable structure of MSX is as follows:



$$CH_3-\underset{NO_2}{\underset{|}{N}}-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-O-COCH_3$$

(MSX)

MSX seems to be quite closely related to both RDX and BSX in structure and in mode of formation. It does not seem to fit readily into mechanisms of either Case I or Case II, however. A more extensive consideration of the mechanism of its formation will be presented later. All that will be said now is that, in view of the large yields of RDX and MSX obtained, it is impossible to suppose that they both arise directly from hexamine without considering that one mole of methylammonium nitrate finds its way into the triazine ring of the RDX. Since this is in direct contradiction to all other evidence, it must be considered that MSX arises through a synthesis reaction. This is not very satisfactory, however, since the belated addition of monomethylammonium nitrate does not appear to give any MSX.

The question of the significance of MSX is not regarded as solved since its formation cannot be readily explained in terms of either Case I or Case II without the introduction of new concepts. This fact is a very serious one from the point of view of the concept of the "catalytic-synthetic" dual function of the ammonium nitrate in the Bachmann reaction postulated herein, since the monomethylammonium nitrate runs would otherwise be its strongest supporting evidence. Experiments are presently under way in this laboratory which are designed to measure accurately the relative quantities of RDX, HMX, BSX and MSX formed under a variety of conditions.

Experimental

1. A Study of the Bachmann Reaction

The preparation of Amine Nitrates:- The monomethyl-, dimethyl-, and trimethylammonium nitrates were prepared from aqueous solutions of the corresponding amines* (Commercial Solvents) and nitric acid by the following procedure. Thirty percent reagent nitric acid was added slowly and with cooling to 500 ml. of an approximately 30 percent amine solution until complete neutralization was indicated by an end point with methyl red. The neutral solution was then evaporated on a steam cone until crystallization took place on cooling. Successive crops were removed by filtration, washed with acetone and dried under vacuum. The monomethyl- and trimethylammonium nitrates were white, crystalline and not very hygroscopic. They were obtained in almost theoretical yield. The dimethylammonium nitrate was yellowish, crystalline and very hygroscopic. It was obtained in smaller yield. It was found advantageous to prepare the dimethylammonium nitrate salt on cold winter days when the relative humidity of the laboratory was low.

Tetramethylammonium nitrate was prepared by the interaction of methyl nitrate and trimethylamine in ether. The methyl nitrate was synthesized according to the directions given in "Organic Syntheses" (Vol. 19, p.64 (1939)). The trimethylamine was prepared by slowly

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* The Commercial Solvents Corporation state that these products contain but small amounts of ammonia and other amines.

adding a 50 percent alkali solution to solid trimethylammonium chloride (itself prepared from aqueous trimethyl amine and hydrochloric acid) and condensing the liquid trimethylamine in a flask cooled with an ice-salt mixture. This amine was added slowly to a 20 percent etherous solution of methyl nitrate. The product precipitated immediately and was filtered off, washed with ether, dried and used without further purification. The yield was only about 40 percent of theoretical, possibly due to the fact that the trimethylamine was added too quickly causing the ether to boil over. The product was white, crystalline and not very hygroscopic.

Pyridinium nitrate, piperidinium nitrate, ethylenediammonium nitrate and aniline nitrate were all prepared by the slow addition (with cooling) of 30 percent nitric acid to the liquid amine. The aqueous solution of the amine nitrate was then concentrated and the product was filtered off, washed and dried. The pyridine used was Merck's "pure" reagent. The product was white, crystalline and not hygroscopic. Good yields were obtained. The piperidine used was Schering-Kahlbaum's "pure" reagent. The white, crystalline product was obtained in good yield and was found to be moderately hygroscopic. The ethylenediamine used was Eastman Kodak's "95-100%" reagent. The salt was obtained in good yield and was white, crystalline and hygroscopic. The aniline used was redistilled Merck "reagent" grade. When one batch of aniline nitrate was being concentrated on a steam cone it caught fire. Another caught fire during the neutralization. A third batch which was evaporated more carefully gave only a deep-red product which was not identified. A fourth batch was evaporated in the cold in a current of dry air. In this case a good yield of the white, crystalline salt was obtained. It was not hygroscopic.

Urea nitrate was prepared by adding 70 percent nitric acid to a cold saturated solution of stock "recrystallized" urea. The mononitrate precipitated out immediately and was filtered off. Good yields of a white, crystalline, non-hygroscopic product were obtained.

The Bachmann Reaction:- The Bachmann runs were carried out in a 500 ml., 5-necked, round-bottom flask. Through the centre neck was introduced an efficient, high-speed, glass stirrer; one neck held a 100°C. thermometer while the other three held short thistle-tubes by means of which the reagents were introduced. The 5-necked flask was surrounded by a water bath which served to control the reaction temperature. This water bath was provided with a thermometer, a stirrer, a steam inlet, a water inlet and a constant-level siphon water outlet. The reagents were introduced from three special, calibrated burettes. These were of such diameter as to permit of accurate reading and yet not of such small diameter as to necessitate continued rate adjustment to compensate for the changing liquid head.

To the flask was added the following initial charge: 5.0 ml. glacial acetic acid (Shawinigan Chemicals Co., analysing 99.3 percent), 1.0 ml. acetic anhydride (Shawinigan Chemicals Co., analysing 99.2 percent) and 0.5 ml. of a solution of dry ammonium nitrate (Merck reagent grade) in absolute nitric acid (D.I.L., analysing 98.2 percent) having a weight proportion of 11:14. To this initial charge, heated to 65°C., were added at equivalent rates over a period of 25 minutes the following solutions:

(1) 171 g. (1.68 moles) acetic anhydride

(2) 55 g. (0.690 moles) of ammonium nitrate dissolved in 70 g. (1.11 moles) nitric acid, and

(3) 33.6 g. (0.240 moles) hexamine (Cities Service) dissolved in 55 g. acetic acid (0.92 moles).

Throughout the addition, the hexamine-acetic acid solution was retarded an estimated 5 percent in relation to the other reagents. The temperature was maintained at 68 - 71°C. (reaction temperature) by means of the water bath which was held at about 45 - 50°C. At the conclusion of the addition of the reagents, the reaction mixture was held for an additional 10 mins. (holding time) at a temperature of 68 - 71°C. (holding temperature). The reaction mixture was then cooled to 20°C. and after 30 minutes was filtered.

The products were isolated as follows. The solid reaction product was filtered off before dilution at a temperature of 20°C. and was washed with 300 ml. of hot water, the wash water being saved. The solid so obtained was called Product I. The filtrate was then poured slowly into 1500 ml. of cold water. This mixture was allowed to stand for at least five hours and was then filtered and washed with 300 ml. of hot water to give Product II. The combined wash waters from Products I and II were cooled and filtered and the precipitate washed with 100 ml. of cold water to give Product III.

Modified Bachmann Procedures:- The standard procedure just described was modified in a number of ways. Chief among these modifications were the following: variation in reaction temperature, variation in holding temperature, variation in holding time, variation in the mode of addition of ammonium nitrate, substitution of an amine nitrate for all or part of the ammonium nitrate, and variation in mode of addition of this amine nitrate. While most of these modifications will be apparent from an examination of Table II, several are described in greater detail.

When ammonium nitrate was replaced by an amine nitrate, equal molar quantities were used. In a number of runs, no ammonium or amine nitrate was added to the reaction mixture. In others, the addition of the ammonium or amine nitrate was delayed until 10 minutes (60 minutes in one case) after the completion of the addition of the other reagents. The mode of addition is described as "Nitrate Added Initially" and "Nitrate Added Subsequently". In several runs, one-half of the ammonium or amine nitrate was added "initially" and the other half "subsequently". Since tetramethylammonium nitrate would not completely dissolve in the quantity of absolute nitric acid used, it was added as a slurry with nitric acid. Urea nitrate was found not to be very soluble in nitric acid and was added as a solid proportionately with the other reagents.

Analysis of the solid products:- The above procedure (i.e., the isolation of three solid products) was designed to afford a preliminary separation of the solid reaction product into three fractions based on the extent of formation of the various compounds present in the reaction liquor and on their relative solubility in the undiluted reaction liquor, diluted reaction liquor and water. This aided subsequent fractional crystallization.

The crude products were air dried and weighed. One-half of each product was "fumed off" with nitric acid in order to determine the quantity of RDX+HMX in the crude product. This "fume-off" is a well-recognized and widely-used procedure. It consists of adding 7 ml. of 70 percent nitric acid per gram of solid to the crude product. This mixture is heated to 100°C. and all methyleneamines and methylenenitramines other than RDX and HMX are destroyed. At the conclusion of this reaction (5 minutes), the nitric acid is diluted with five volumes of water and the resulting precipitate is filtered off after 24 hours standing. The yield of RDX(B) may be calculated from the weight of the air-dried product.

The percent of HMX present in the RDX(B) was estimated microscopically. This procedure has not been widely used and will be discussed at somewhat greater length than the previous one. Blonquist and co-workers at Cornell University have made an extensive study of the crystallography of RDX and HMX (75). It was found that all four polymorphic modifications of HMX exhibited one refractive index which was very different from any of the refractive indices of RDX (which are all approximately the same). This fact, used in conjunction with the other recognition characteristics, made it possible to recognize HMX in the presence of RDX. In the procedure used in this laboratory, RDX(B) was suspended in a small quantity of a solution of Canada balsam in Arochlor 1240 (having an index of refraction of 1.585) on a microscope slide. A rough estimation of the composition of the RDX(B) was made on the basis of crystal-counting, and estimation of the relative average crystal size of the RDX and HMX and, most important, by comparison with a series of standard slides prepared under similar conditions. The researchers at Cornell recommend their method only for qualitative work and so the HMX analyses in this section of the thesis should be accepted with reserve. At the time that the research described herein was carried out, no satisfactory method for the estimation of HMX was available and the crystallograpic method was considered to give more significant results than an estimation based on the melting point of the RDX(B) (88). An excellent method based on the alkaline hydrolysis of RDX in RDX(B) is described later (58).

It is believed that in normal Bachmann reactions and in Bachmann reactions modified only with respect to temperature or ammonium nitrate concentration the principle by-product (other than HMX)is BSX. If this is true, then BSX may be estimated from the difference in weight between the fumed-off product and the crude product. The identity of the by-product was checked in a number of cases by fractional recrystallization of the crude product from chloroform, ether-ethyl acetate, ether-acetone and aqueous acetone solvents. In every case except when monomethylammonium nitrate was used, the chief by-product was found to be BSX; in the exceptional case, the by-product was found to be MSX. Since no other by-products could be identified, the difference in weight between the fumed-off product and the crude product was considered to be BSX (or MSX) and was calculated as such.

It should be pointed out, however, that since the possibility of other products is not excluded, the yields of BSX and MSX given in the table should be regarded as a maximum.

Experimental results:- The results obtained in this investigation are presented in Table II and are further qualified by a series of "footnotes" or "remarks" in the following paragraphs. (The numbers below refer to the reference numbers in Table II.)

1. The crude product was yellowish in colour, gummy in consistency and smelled strongly of formaldehyde. If allowed to stand for 24 hours in contact with the diluted liquor, the yield of the product was decreased but the quality was improved.

2. An exothermic reaction set in while the reaction mixture was being heated from 40 - 70°C. and cooling was necessary to control the temperature. This exothermic reaction was first observed at 51°C.

3. An exothermic reaction was observed during the early part of the holding period.

4. No exothermic reaction was observed. Analysis of the crude product showed that BSX was present, but little or no MSX.

5. The reaction mixture was held for 60 minutes (instead of 10 minutes) at 35 - 40°C. before the ammonium nitrate was added.

6. The RDX(B) is calculated as RDX.

7. The non-RDX(B) solid fraction was calculated as BSX in spite of the fact that MSX was undoubtedly present.

8. An acetone-insoluble, water-insoluble by-product was

TABLE II

THE PREPARATION OF RDX:- THE EFFECT OF USING VARIOUS AMINE NITRATES IN MODIFIED BACHMANN REACTIONS

RUN NO.	NITRATE ADDED INITIALLY	REACTION TEMP.	NITRATE ADDED SUBSEQUENTLY	HOLDING TEMP.	HOLDING TIME	YIELD RDX-B	HMX IN RDX-B	SUBSTANCES OTHER THAN RDX-B	NOTES
		°C.		°C.	MINS.	(6) MOLES	%	(9) MOLES BSX	
1	NH_4NO_3	68-71	NONE	68-71	10	1·500	8·0	0·14	
2	NH_4NO_3	35-40	NONE	35-40	10	0·268	1·5	0·36	
3	NH_4NO_3	35-40	NONE	35-40	60	0·346	1·5	0·61	
4	NH_4NO_3	35-40	NONE	68-71	10	0·778	0·5	0·43	
5	NONE	68-71	NONE	68-71	10	0·042	TRACE	0·27	1
6	NONE	35-40	NONE	35-40	10	0·042	TRACE	0·48	1
7	NONE	35-40	NONE	68-71	10	0·044	TRACE	0·67	1
8	NONE	35-40	NH_4NO_3	68-71	10	0·508	0·5	0·68	1,2
9	NONE	35-40	NH_4NO_3	68-71	10	0·480	3·0	0·63	5
10	NONE	35-40	NH_4NO_3	35-40	10	0·086	0·5	0·41	1
11	NONE	35-40	NH_4NO_3	35-40	60	0·252	1·5	0·75	1,2
12	NONE	35-40	NH_4NO_3	68-71	120	0·534	3·0	0·84	3
13	$CH_3NH_3NO_3$	68-71	NONE	68-71	60	0·624	0·1	0·68 (MSX)	1,10
14	NONE	35-40	$CH_3NH_3NO_3$	68-71	60	0·166	TRACE	0·80	1,4
15	$(CH_3)_2NH_2NO_3$	68-71	NONE	68-71	60	0·482	15·0	0·41	1
16	NONE	35-40	$(CH_3)_2NH_2NO_3$	68-71	60	0·208	1·0	0·74	1
17	$(CH_3)_3NHNO_3$	68-71	NONE	68-71	60	0·078	6·0	0·47	1
18	NONE	35-40	$(CH_3)_3NHNO_3$	68-71	60	0·084	TRACE	0·78	1
19	$C_5H_5NHNO_3$	68-71	NONE	68-71	60	0·270	2·0	0·30	
20	NONE	35-40	$C_5H_5NHNO_3$	68-71	60	0·078	0·5	0·64	
21	$C_5H_{10}NH_2NO_3$	68-71	NONE	68-71	60	0·400	TRACE	—	
22	$(CH_2NH_3NO_3)_2$	68-71	NONE	68-71	10	0·420	TRACE	—	
23	NONE	35-40	$(CH_2NH_3NO_3)_2$	68-71	60	0·162	TRACE	—	
24	$NH_2CONH_3NO_3$	35-40	NONE	35-40	60	0·668	TRACE	—	10
25	NONE	35-40	$NH_2CONH_3NO_3$	35-40	60	0·064	TRACE	—	8
26	$\frac{1}{2}NH_4NO_3$	68-71	NONE	68-71	10	1·006	2·0	0·54	
27	$\frac{1}{2}NH_4NO_3$	68-71	$\frac{1}{2}NH_4NO_3$	68-71	10	1·160	3·0	0·29	
28	$\frac{1}{2}NH_4NO_3$	68-71	$\frac{1}{2}CH_3NH_3NO_3$	68-71	10	0·476	1·5	0·20	7
29	$\frac{1}{2}CH_3NH_3NO_3$	68-71	NONE	68-71	10	0·550	0·5	0·42	7
30	$\frac{1}{2}CH_3NH_3NO_3$	68-71	$\frac{1}{2}CH_3NH_3NO_3$	68-71	10	0·556	0·5	0·41	7
31	$\frac{1}{2}CH_3NH_3NO_3$	68-71	$\frac{1}{2}NH_4NO_3$	68-71	10	0·630	0·1	0·46	7

obtained which was thought to be a urea-formaldehyde polymer. This product yielded formaldehyde slowly on acid hydrolysis and compared favourably with a genuine sample of urea-formaldehyde resin as regards behaviour on heating and decomposition with dilute and concentrated nitric acids.

9. BSX (and MSX) is calculated by difference and the figure given thus represents a maximum.

10. This run has been checked.

A run was also carried out using tetramethylammonium nitrate. About 6.0 g. of solid material separated on dilution (the run was based on 0.12 moles hexamine rather than 0.24 moles) which appeared to be chiefly BSX. No RDX was isolated through recrystallization but it is possible that a fume-off would have shown its presence. When aniline nitrate was substituted for the ammonium nitrate, the reaction mixture was blood-red in colour and no RDX could be isolated from the gummy precipitate formed on dilution.

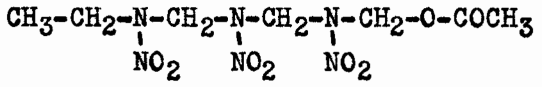
A summary of the results obtained by the workers at the Pennsylvania State College is presented in Table III. In their procedure, the initial charge in the reaction flask was 60 ml. of acetic anhydride and the overall quantity of acetic anhydride used was somewhat greater than in the runs described previously, but these and other minor differences in procedure are considered to be insignificant. BSX was found to be the chief by-product in all cases except when monomethyl- and monoethylammonium nitrates were used: in the former exception, MSX was found to be the chief by-product, and in the latter case, an ethyl

TABLE III

THE PREPARATION OF RDX:- USE OF AMINE NITRATES IN THE BACHMANN REACTION (WHITMORE)

RUN NO.	COMPARE TABLE II RUN NO.	NITRATE ADDED	REACTION TIME	YIELD RDX-B	IDENTITY BY-PRODUCT	YIELD BY-PRODUCT	NOTES
			MINS.	(6) MOLES		MOLES	
1	13	$CH_3NH_3NO_3$	19	0·621	MSX	0·358	7
2	15	$(CH_3)_2NH_2NO_3$	19	0·450	BSX	0·158	
3	17	$(CH_3)_3NHNO_3$	17	0·083	BSX	0·425	2
4		$(CH_3)_4NNO_3$	20	0·063	BSX	0·075	3, 4
5		$C_2H_5NH_3NO_3$	25	0·354	ETHYL-MSX	0·198	
6		$(C_2H_5)_2NH_2NO_3$	17	0·200	BSX	0·447	3
7		$(C_2H_5)_3NHNO_3$	7	0·000	BSX	0·058	1, 3
8	19	$C_5H_5NHNO_3$	15	0·225	BSX	0·142	1
9	28, 31	$\left\{ \begin{matrix} NH_4NO_3 + \\ CH_3NH_3NO_3 \end{matrix} \right\}$	25	0·934	MSX	0·396	5

homolog of MSX:



$$CH_3-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-O-COCH_3$$

(Ethyl - MSX)

Table III is qualified further by the following notes:

1. In these runs, 0.12 moles hexamine was used instead of 0.24 moles.
2. The crude product of this run appeared to decompose partially on drying.
3. The crude product was found to be gummy in consistency.
4. The yield of BSX was calculated after recrystallization.
5. The results of this run are not strictly comparable to those of Runs 28 and 31 (Table II) since, in these runs, the nitrate salt was added in two portions.
6. Calculated as RDX.
7. This run has been checked.

As was previously pointed out, the experiments in which the addition of the ammonium nitrate was delayed paralleled earlier experiments of Winkler. The results of these investigations, however, are not strictly comparable to those reported in this thesis since Winkler carried out his reactions in very dilute (homogeneous) systems and added the reagents in a different sequence and in vastly different mole ratios. In view of these facts, the results are not reproduced in this thesis, but free reference is made to them in discussion.

2. A Study of the DNPT Reaction

The preparation of DNPT (Dinitropentamethylenetetramine):-DNPT was prepared from hexamine in about 30 percent yield by the procedure recommended by Blonquist (89).

The DNPT Reaction:- The procedure adopted was a modification of that described by Bachmann (79). A three-neck flask, equipped with a thermometer, a short thistle tube and an efficient stirrer was surrounded by a water bath (previously described p.121). The flask was charged with 78.6 g. (0.240 moles) of DNPT and 260 g. (2.55 moles) of acetic anhydride. To this initial charge was added slowly over a period of 10 minutes a solution of 23.0 g. (0.288 moles) of dry ammonium nitrate in 33.8 g. (0.537 moles) of 98 percent nitric acid. The temperature was maintained at 68 - 71°C. during the reaction and during the subsequent 10 minute holding period. At the end of this time the reaction mixture was diluted with about 1500 ml. of cold water and the solid was filtered off after five hours and air dried.

Modified procedures:- The procedure described above was modified in several ways. The reaction temperature and/or the holding temperature were varied, the holding time was varied, the mode of addition of the ammonium nitrate was varied, amine nitrates were substituted for the ammonium nitrate and the mode of addition of the amine nitrate was varied. The variations in temperature are recorded in Table III and the mode of addition of the ammonium or amine nitrate is designated as "nitrate added initially" and "nitrate added subsequently".

in the cases where the addition of the nitrate was delayed, it was added as a solid 10 minutes after the addition of the nitric acid.

Analysis of the solid products:- The crude product was air-dried and weighed. One-half of the product was fumed off with 70 percent nitric acid in order to determine the quantity of HMX + RDX in the crude. At the conclusion of the fume-off (see p.124), the solution was diluted with five volumes of water and the precipitate was filtered off after standing for one day in an ice chest. The yield of HMX + RDX was calculated as moles HMX. No attempt was made to analyse the HMX - RDX mixture but melting point determinations gave a qualitative indication of its composition. Pure HMX melted in the range 271.5 - 272.5°C. under the conditions used in these determinations. Since the melting point falls rapidly and the melting point range increases greatly as HMX is contaminated with RDX, it may be stated that the HMX is relatively pure, contaminated with a little RDX or contaminated with a considerable quantity of RDX in a given case.

Aside from HMX and RDX, the crude product contains AcAn and possibly PHX and unchanged DNPT as well. No systematic attempt was made to analyse the reaction by-products, but in the run in which methylammonium nitrate replaced the ammonium nitrate AcAn could be identified by the fractional recrystallization procedure described in connection with the Bachmann reaction. The non-HMX-RDX fraction of the crude product was calculated as moles of AcAn.

Experimental results:- The results obtained in this investigation are presented in Table IV. The only qualifying remarks necessary are to point out that reference is made to analogous runs in Table II and that the melting points of the fumed-off products are recorded as softening points and melting point ranges.

Discussion

The general significance of the experimental results here presented has already been discussed in the introduction to this section of the thesis. It is the purpose of the following discussion to qualify this general evidence with reference to specific cases, to point out the deviation of the experimental results from the predicted results and to discuss the possible theoretical implications of these deviations. This purpose may be stated more formally by saying that the inductive and deductive reasoning hitherto presented will be subjected to the revealing process of critical analysis.

In view of the fact that much of the general evidence presented in this section of the thesis may be interpreted as supporting Case II (of the mechanism of the Bachmann reaction) and Case A (of the DNPT conversion), it will be assumed, for the purposes of discussion, that these cases are truly indicative of the reaction mechanisms. In other words, the experimental data here presented will be considered in terms of a "catalysed nitrolysis-synthesis" mechanism (see p.109).

The general evidence was discussed in the introduction in a logical order; in the following discussion it is presented in what this researcher

TABLE IV

THE PREPARATION OF HMX:- THE EFFECT OF USING VARIOUS AMINE NITRATES IN MODIFIED DNPT ⟶ HMX REACTIONS

RUN NO.	COMPARE TABLE I RUN NO.	NITRATE ADDED INITIALLY	REACTION TEMP.	NITRATE ADDED SUBSEQUENTLY	HOLDING TEMP.	HOLDING TIME	YIELD HMX-RDX	MELTING POINT HMX-RDX	SUBSTANCES OTHER THAN HMX-RDX
			°C.		°C.	MINS.	MOLES HMX	°C.	MOLES AcAn
1	1	NH_4NO_3	68-71	NONE	68-71	10	0·665	200, 248-66	0·180
2	2	NH_4NO_3	35-40	NONE	35-40	10	0·188	198, 219-20	0·080
3	3	NH_4NO_3	35-40	NONE	35-40	60	0·610	235, 253-54	0·466
4	4	NH_4NO_3	35-40	NONE	68-71	10	0·716	219, 248-51	0·153
5	5	NONE	68-71	NONE	68-71	10	0·014	268·0-269·0	0·340
6	6	NONE	35-40	NONE	35-40	10	0·010	270·0-270·5	0·149
7	7	NONE	35-40	NONE	68-71	10	0·011	266·0-267·0	0·282
8	8	NONE	35-40	NH_4NO_3	68-71	10	0·602	257·0-259·0	0·265
9	13	$CH_3NH_3NO_3$	68-71	NONE	68-71	60	0·331	269·0-269·5	0·573
10	13^a	$CH_3NH_3NO_3$	68-71	NONE	68-71	10	0·336	270·0-270·5	0·348
11	14	NONE	35-40	$CH_3NH_3NO_3$	68-71	60	0·320	271·0-271·5	0·466
12	17	$(CH_3)_2NHNO_3$	68-71	NONE	68-71	60	0·082	272·5-273·0	—

considers to be an order of descending significance. The references in brackets refer to a run in Tables II, III or IV (e.g. II-24 indicates Run 24 Table II).

1. When the ammonium nitrate of a standard Bachmann reaction is replaced by various amine nitrates, RDX may be produced in considerable quantity, but never in a quantity exceeding one mole per mole of hexamine.

Urea mononitrate (II-24), monomethylammonium nitrate (II-13, III-1), dimethylammonium nitrate (II-15, III-2), ethylenediammonium dinitrate (II-22), piperidinium nitrate (II-21), monoethylammonium nitrate (III-5), pyridinium nitrate (II-19, III-8) and diethylammonium nitrate (III-6) all gave rise to substantial quantities of RDX. Urea mononitrate gave the greatest yield, 0.67 moles per mole of hexamine; this result was achieved in spite of the fact that the run was carried out at a low temperature, 40°C.* (II-24). A comparable run using ammonium nitrate gave only 0.35 moles of RDX (II-3). Of these amine nitrates, diethylammonium nitrate produced the smallest yield, 0.20 moles (III-6). A comparable run using ammonium nitrate gave 1.50 moles (II-1).

Three of the amine nitrates reported gave rise to very little or no RDX. Trimethylammonium nitrate produced 0.08 moles per mole of hexamine (II-17, III-3), tetramethylammonium nitrate, 0.06 moles (III-4) and triethylammonium nitrate, none at all (III-7). The values

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* When urea nitrate was introduced into a 70°C. run, the reaction was violent and a large volume of gas was evolved.

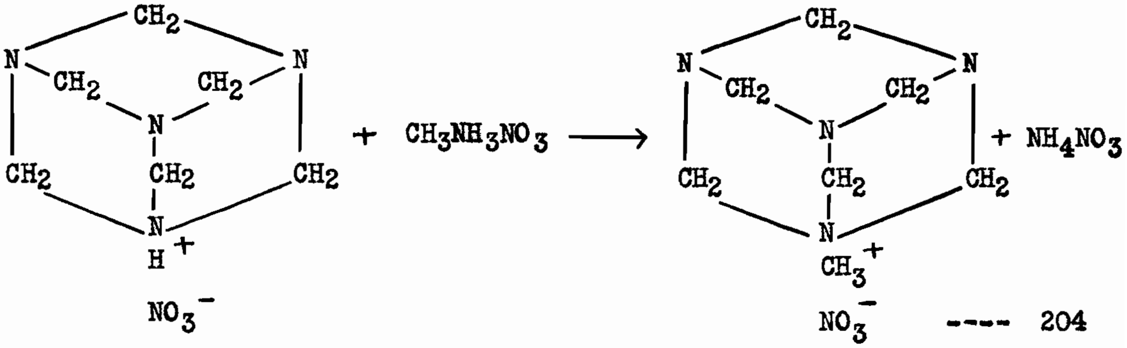
0.08 and 0.06 obtained in the two former cases are almost negligible from a theoretical standpoint, particularly when it is considered that Bachmann runs carried out in the absence of any ammonium nitrate or amine nitrate yielded 0.04 moles of RDX (II-5,6,7).

On the basis of the "catalysed nitrolysis-synthesis" hypothesis, the RDX produced in the former group of runs is considered to have arisen by a catalysed nitrolysis process. Theoretically, one mole of RDX should be obtained from one mole of hexamine; in actual practice the yields vary from 20 to 67 percent of one mole. It is believed that these differences are significant and that they may be indicative of the "catalytic" function of the amine nitrates in the Bachmann reaction. This function will be considered in some detail in the theoretical section of this part of the thesis. In those runs of the second group (i.e. those in which little or no RDX is produced), it is considered that the RDX does not arise by a catalysed nitrolysis step but rather by direct nitrolysis. The reason for this view is that when no ammonium or amine nitrates are introduced into the system, a small quantity of RDX is produced. In this connection, see (3) below.

The results in this series of experiments cannot be easily explained on any other basis than the "catalytic nitrolysis-synthesis" mechanism. The Connor-Davy theory cannot accommodate them and other explanations are equally unsatisfactory. One possible explanation is that the amine nitrates contain ammonium nitrate as an impurity or, alternately, generate this substance in the reaction mixture. It is possible that several of the amine nitrates were slightly contaminated with ammonium nitrate (dimethylamine gave a faint positive test for ammonia with Nessler's reagent) but it is extremely unlikely that the observed results are due to this impurity. Ammonium nitrate could have been generated by double decomposition

$$CH_3NH_3NO_3 + HNO_3 \longrightarrow NH_4NO_3 + CH_3NO_3 \quad \text{----} \quad 203$$

or by nitrogen interchange



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The former case is considered unlikely and the latter case is impossible when secondary or tertiary amine nitrates are used.

2. When the ammonium nitrate of a standard DNPT conversion is replaced with an amine nitrate, HMX may be produced in considerable quantity, but RDX is not produced as would otherwise be the case.

Monomethylammonium nitrate (IV-9,10) gives rise to 0.33 moles of HMX per mole of DNPT, but no RDX. Trimethylammonium nitrate (IV-12) yields only 0.08 moles HMX per mole of DNPT, but no RDX. (A comparable run using ammonium nitrate gave 0.67 moles HMX+RDX calculated as moles HMX (IV-1).

The HMX produced in these runs is regarded as the product of a process strictly analogous to the "catalysed nitrolysis" step of the Bachmann reaction. The differences in yield are believed to be significant as in the case of the modified Bachmann reaction previously described.

3. When a Bachmann reaction is carried out in the absence of ammonium nitrate (or amine nitrates), a very small yield of RDX is obtained. The magnitude of this yield is unaffected by changes in temperature. In this reaction large yields of BSX may be produced.

Three runs gave rise to 0.04 moles of RDX when carried out in the absence of ammonium nitrate (II-5,6,7). The yields of BSX varied somewhat with the reaction conditions but were always greater than in corresponding runs in which the ammonium nitrate was added in the usual manner (II-1,2,4). In one case the yield of BSX was 0.67 moles per mole of hexamine (II-7). The greatest BSX yield observed by Winkler in his homogeneous runs was of the order of 35 to 40 percent.

The RDX produced in these runs is regarded as being the product of an "uncatalysed nitrolysis" step and there is no reason for not believing that the mechanism involved is identical or very similar to that proposed by the Bristol group for the direct nitrolysis (Woolwich) reaction (see p. 39). There seemed to be a possibility that the RDX might have arisen by a synthesis process since the degradation of hexamine would undoubtedly result in the production of simple fragments containing methyleneamine or methylenenitramine linkages such as have been postulated in the Ross reaction. This possibility seems to be excluded by analogy: the degradation of DNPT in the absence of ammonium nitrate gives rise to HMX, not RDX. (See further below (4).) The BSX produced in these runs is regarded as being the product of an "uncatalysed nitrolysis" reaction modified, in this case, by intermediate acetylation. BSX is also produced in regular Bachmann runs, probably by the same mechanism.

4. When a DNPT conversion is carried out in the absence of any ammonium or amine nitrate, a very small yield of HMX (relatively free from RDX contamination) is obtained. The magnitude of the yield appears to be only slightly affected by temperature. In this reaction large yields of AcAn may be produced.

Three runs gave rise to 0.01 moles of HMX when carried out without ammonium nitrate (IV-5,6,7). This HMX does not seem to be contaminated with any appreciable quantity of RDX. The yields of AcAn varied somewhat with the reaction conditions but were always greater than in corresponding runs in which the ammonium nitrate was added in the usual manner (IV-1,2,4). In one case, the yield of AcAn was 0.34 moles per mole of hexamine.

The HMX produced in these runs is regarded as being the product of an "uncatalysed nitrolysis" process as was supposed to be the case in the analogous hexamine conversion. The possibility of the HMX being the product of a "synthesis" process is unlikely since this type of reaction appears to yield largely RDX rather than HMX. AcAn is regarded as being the product of an "uncatalysed nitrolysis" process modified by intermediate acetylation.

5. If ammonium nitrate is withheld from a Bachmann reaction until the other reagents have been added, considerable quantities of RDX may still be produced.

This phenomenum was investigated in a series of five runs. The amounts of RDX and BSX produced seemed to decrease but slightly for an increase in the length of time for which the addition was delayed (II-8,9). At high temperatures, the production of RDX was essentially complete in 10 minutes after the addition of the ammonium nitrate (II-8,12); at low temperatures the reaction is very slow being only half complete in one hour (II-10,11). The yield of BSX is increased by long holding times after the addition of the ammonium nitrate both at high temperatures(II-7,12) and at low (II-10,11) but the rate of BSX formation is relatively much more rapid at low temperatures than the rate of RDX formation (II-10,11). It may be seen that the rate and extent of BSX formation is relatively independent of the presence of ammonium nitrate in the later stages of the reaction (II-6,10; II-7,8).

In his experiments (carried out at 35°C. in the presence of large excesses of acetic acid and acetic anhydride), Winkler observed that the yields and rates of formation of RDX were the same when the addition of ammonium nitrate was delayed for 15 minutes to 5 hours and that the yields and rates were approximately half those of the reaction when ammonium nitrate was added initially. Winkler also points out that BSX formation is apparently independent of the presence of ammonium nitrate in the later stages of the reaction. In other words: "It appears that the fate of the hexamine molecule when no ammonium nitrate is present is determined in the first 15 minutes of the reaction at 35°C."

The RDX arising in this series of runs is supposed to be produced by a "synthesis" process. Winkler has shown that hexamine does not persist unchanged in the reaction liquor. This series of experiments shows that if ammonium nitrate is not present at the beginning of the reaction (or, better, during the reaction proper), a very large part of all the hexamine introduced will be converted to BSX sooner or later. During the production of BSX or its precursors, methylene groups, methyleneamine groups or methylenenitramine groups may be split off. These may be able to take part in a synthesis reaction along with ammonium nitrate giving RDX as in a Ross reaction. It must be admitted, however, that there is no positive evidence that the RDX produced in this series of runs arises through a synthesis process. It is quite conceivable, for instance, that the precursor lying between hexamine and BSX (since hexamine disappears very quickly and BSX is produced very slowly) may contain the triazine ring and may be convertable to RDX when ammonium nitrate is introduced into the reaction liquor. Against this possibility stands the fact that the production of RDX by the belated addition of ammonium nitrate does not seem to interfere with the extent of the BSX reaction. Alternately, it is quite conceivable that the portion of the hexamine which is not converted to BSX may be converted to some other compound (other than "fragments") which may yield RDX under suitable conditions. If either of these two alternatives are to represent the reaction mechanism when ammonium nitrate is added belatedly, each mole of RDX precursor in these runs must give rise to more than one mole per mole of hexamine. This necessary* condition almost eliminates the possibility of excluding "synthesis" as a mechanism altogether. The possibility is considered to be even less likely on the basis of one run (II-12) in which the sum of the BSX yield and one-half of the RDX yield exceeds one mole per mole of hexamine (see 9 below).

Winkler, in a discussion of his own experiments, offers several alternate explanations for the production of RDX when the addition of ammonium nitrate is delayed:

(a) Hexamine persists in the reaction mixture and gives RDX when ammonium nitrate is added.

(b) RDX is formed by a mechanism which is entirely different from that which produces RDX in the Bachmann reaction.

(c) The regular Bachmann reaction is really made up of two reactions, one of which requires ammonium nitrate at the start and whose absence results in BSX production, while the second consists of a synthesis reaction involving fragments of the hexamine and ammonium nitrate.

(d) Hexamine is rapidly converted to at least two compounds: one of these is converted to RDX if ammonium nitrate is present

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* It should be pointed out, once again, that the BSX yields reported in Table II are a maximum.

at the beginning of the reaction and to BSX if it is absent; the other is relatively stable in the absence of ammonium nitrate and is converted to RDX and HMX when ammonium nitrate is added.

The first of these proposed explanations is invalid since it has been shown that hexamine disappears very rapidly in the Bachmann reaction. It is quite possible, however, that some substance quite closely related to hexamine may persist in the reaction mixture. The second proposed explanation is unlikely since Winkler has shown that the two reactions are subject to the same changes in rates and yields under varying conditions of dilution and reagent concentrations. The author has also arrived at similar conclusions (see 6 below). In his early paper Winkler supported the concept of the synthesis reaction but on the basis of later experiments advanced the fourth alternate explanation. When stated in general terms, this concept, with its supporting evidence, is a valuable contribution to the mechanism of the Bachmann reaction but it seems regretable that this evidence was used to attempt to prove that DNPT is the compound which is the precursor of a large part of all the RDX produced. From the point of view of most researchers in this field, DNPT is quite unacceptable as a reaction intermediate. There are many reasons for this but the chief among these is the fact that DNPT is converted to HMX, RDX being only a by-product of this reaction. In the opinion of the author, there is no reason for not considering that the precursor of the RDX and HMX (in the sense suggested in d above) is the "fragments" themselves and regarding the subsequent reaction as a synthesis rather than as a degradation.

It must be admitted that there is no proof that the RDX produced on belated addition of ammonium nitrate is produced by the same mechanism as is proposed for the second mole of RDX (i.e. by a synthesis reaction). There is, however, no contrary evidence and it is significant that the results of these experiments cannot easily be explained on the basis of any other theory of RDX formation.

6. A Bachmann run carried out at 40°C. (but otherwise unmodified) gives a small yield of RDX and BSX. These yields increase slowly with increased holding time.

One run, carried out at 40°C., gave a yield of RDX of 0.27 moles and a yield of BSX of 0.36 moles per mole of hexamine (II-2). When the holding time was increased from 10 minutes to 60 minutes, the yield of RDX increased to 0.35 moles and the yield of BSX to 0.61 moles (II-3). There is no reason to believe that the yield of RDX will not increase still more on even longer holding times. A Bachmann run carried out at 40°C. and subsequently heated to 70°C. for 10 minutes gave a yield of 0.78 moles of RDX and 0.43 moles of BSX (II-4). The yield of RDX in this run is considered to be the maximum that could be obtained if the 40°C. run had been held at this temperature for an infinite time.

The RDX obtained in the short-time, 40°C. run is regarded as arising by means of a "catalysed nitrolysis" reaction. This process is inefficient at low temperatures. Any increase in the RDX yield resulting from increased holding time is considered to be the result of a "synthesis" process. This process is slow at low temperatures. The 40°C. run which was subsequently heated to 70°C. is regarded as being equivalent to a 40°C. run followed by an infinitely long holding time at 40°C., particularly with respect to the RDX yield. On the basis of these suppositions, the maximum yield of RDX attributable to the synthesis process may be calculated at 0.51 moles per mole of hexamine (II-2,4). This compares favourably with the yield (0.51 moles) of the postulated synthesis reaction in the case where ammonium nitrate was added belatedly (II-8). While the extent of these two reactions seems to be identical, the rates of RDX production seem to be different: in a regular (low temperature) Bachmann run, only 0.08 moles RDX per mole of hexamine were synthesized in 50 minutes (II-2,4,); in a modified Bachmann run involving delayed ammonium nitrate addition, 0.17 moles were synthesized in the same period (II-10,11). These two factors (extent and rate) seem to indicate that the two mechanisms involved are essentially but not entirely the same.

A study of the yields of BSX in this series, in the series where the addition of ammonium nitrate was delayed and in the series where the ammonium nitrate was omitted altogether seems to indicate the fact that the fate of the hexamine molecule is decided very early in the reaction. These considerations will form part of a separate piece of evidence (9 below) and all that will be said now is that the yield of BSX plus the yield of the RDX arising by catalysed nitrolysis (in the low temperature reactions) is of the same order of magnitude as the yield of BSX in comparable runs where the ammonium nitrate is omitted or delayed (II-2,6,10; II-31; II-4,7,9).

7. If ammonium nitrate is omitted from a Bachmann run, and if an amine nitrate is added after the complete addition of all the other reagents, little or no RDX is produced.

When dimethylammonium nitrate, monomethylammonium nitrate or ethylenediammonium dinitrate were added belatedly to modified Bachmann reactions, small amounts of RDX were produced; these yields were 0.21, 0.17 and 0.16 moles per mole of hexamine respectively (II-16, 14,23). When pyridinium nitrate, trimethylammonium nitrate and urea nitrate were used, essentially no* RDX was produced: the values were 0.08, 0.08 and 0.06 moles respectively (II-18,20,25). In a corresponding run where ammonium nitrate was used, 0.53 moles of RDX was produced (II-12).

It was predicted that runs in which an amine nitrate was added belatedly would give rise to no RDX. Two amine nitrates fulfilled this condition (i.e. urea nitrate and pyridinium nitrate -- trimethylammonium nitrate did not give rise to RDX even in a regular run).

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* Compare with Table II, Runs 5, 6, 7.

Three amine nitrates, however, gave rise to small yields of RDX. In view of the possibility that these yields may be significant, several explanations have been advanced to account for them. First, it may be that the amine nitrate used was contaminated with ammonium nitrate. The amines used in the preparation of the amine nitrates were the best commercial grades and were stated to contain but small quantities of ammonia but no actual analyses were carried out. It is significant that dimethylammonium nitrate gave a faint positive test with Nessler's reagent. It may be shown that the observed result in the case of the dimethylammonium nitrate (the worst offender) could have been caused by an ammonium nitrate contamination of 2 percent. It is also significant that urea nitrate which is relatively water insoluble and could easily be separated from ammonium nitrate merely by crystallization and washing gave no RDX when added belatedly to a modified Bachmann reaction. It thus seems that this "contamination" explanation is a likely one. At the same time it is unlikely that such contamination could account for the relatively large quantities of RDX produced when the amine nitrate is added in a more orthodox fashion. However, future experiments should take this into account. Alternate explanations are much less acceptable: the presence of unreacted hexamine or an unnitrated cyclic precursor in the reaction mixture, the interchange of nitrogen between methyleneamines and amine nitrates or the generation of ammonium nitrate from amine nitrate by some process such as the following:

$$CH_3NH_3NO_3 + HNO_3 \longrightarrow NH_4NO_3 + CH_3NO_3 \quad \text{-----} \quad 205$$

8. If less than the theoretical requirement of ammonium or amine nitrate is added to a Bachmann reaction in the usual manner, considerable RDX is produced; if the deficiency is made up by adding ammonium nitrate, the yield of RDX is increased; if, however, the deficiency is made up by adding amine nitrate, the yield of RDX is not increased.

In three runs, only one-half of the usual amount of ammonium nitrate was included in the initial stages of the Bachmann reaction. A control run gave 1.01 moles RDX (II-26). When the rest of the ammonium nitrate was added (after the addition of all the other reagents), the yield of RDX was increased to 1.16 moles (II-27). When an amount of methylammonium nitrate, equivalent to the one-half of the ammonium nitrate usually added, was introduced, the yield of RDX was not increased (0.98 moles) (II-28). Similarly, in three runs, only one-half of the amount of monomethylammonium nitrate generally used was added. A control run gave 0.55 moles RDX per mole hexamine (II-29). When the other half of the monomethylammonium nitrate was added, the yield of RDX was not increased (0.56 moles) (II-30), but when an equivalent amount of ammonium nitrate was added, the yield of RDX was increased to 0.63 moles (II-31).

The results of this series of experiments illustrate the fact that amine nitrates can only duplicate the function of the ammonium nitrate to a limited degree or, better, can only duplicate one of its functions. After the initial reaction (in the presence of one-half of the usual amount of amine nitrate), the fate of the hexamine molecule had been decided (giving RDX, BSX and MSX) and only the fragments remained. These underwent a synthesis reaction with the added ammonium nitrate to give additional RDX. Additional amine nitrate could not perform this function. The fact that larger amounts of RDX were not produced on the belated addition of ammonium nitrate (II-31) shows that the amine nitrate had combined with most of the fragments. This is significant in that it throws some light on the "catalytic" function of these compounds. It seems that in order to act as a catalyst in the nitrolysis step, the given substance must combine with methylol groups.

9. In a Bachmann run, the sum of the BSX yield and one-half of the RDX yield may exceed one mole per mole of hexamine.

In one run where the addition of the ammonium nitrate was delayed, the yields of RDX and BSX were 53 and 84 percent respectively (II-12). On the basis of the Connor-Davy theory (or similar mechanisms), this represents a conversion of 110 percent of the hexamine introduced. This is obviously unacceptable. These yields are easily explained on the basis of the "catalysed nitrolysis-synthesis" mechanism since all of the RDX is produced by means of the synthesis reaction.

10. In the DNPT conversion, the yield of RDX plus the yield of HMX plus the yield of AcAn may exceed one mole per mole of DNPT.

In one run, carried out at low temperature, 0.61 moles* of RDX

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* This is a minimum value since the fumed-off product is calculated as HMX.

plus HMX and 0.47 moles of AcAn were produced (IV-3). It is obvious that the three products could not have arisen from DNPT on a mole for mole basis. Hence it is necessary that the RDX be considered as arising by a synthesis process.

11. In Bachmann runs where the ammonium nitrate is omitted in the initial stages of the reaction, the yields of BSX are independent of the presence of ammonium or amine nitrates in the later stages of the reaction and they seem to depend on the temperature and time factors. These yields are comparable in magnitude to the yield of BSX plus the yield of RDX arising by catalysed nitration (see 6 above) in the case of (unmodified) low-temperature Bachmann runs.

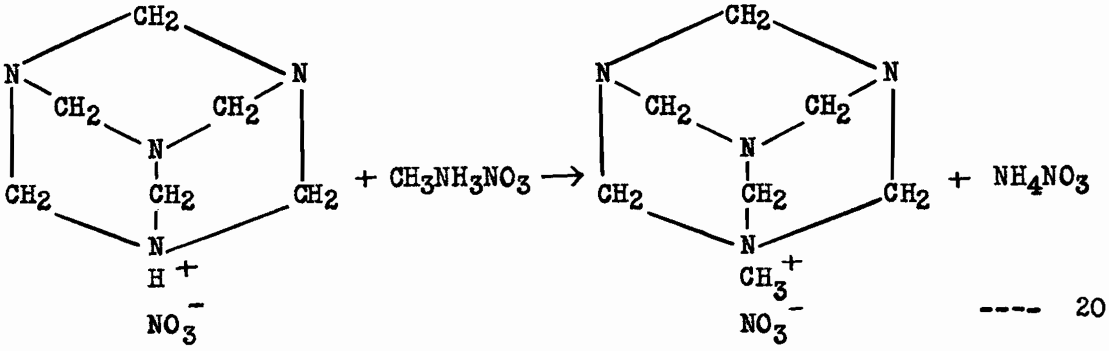
In one series of runs, nitric acid, acetic anhydride, hexamine and acetic acid were allowed to react at 40°C. for 10 minutes; at the end of this time ammonium nitrate or an amine nitrate (or neither) was added and the reaction mixture was heated to 70°C. for varying lengths of time. The yields of BSX obtained were as follows: ammonium nitrate for 120 minutes, 0.84 moles (II-12); ammonium nitrate for 10 minutes, 0.68 moles (II-8); monomethylammonium nitrate for 60 minutes, 0.80 moles (II-14); dimethylammonium nitrate for 60 minutes, 0.74 moles (II-16); trimethylammonium nitrate for 60 minutes, 0.78 moles (II-18); and pyridinium nitrate for 60 minutes, 0.64 moles (II-20). When no ammonium nitrate was added, 0.67 moles of BSX were formed after 10 minutes (II-7). These runs are to be compared with the regular, low-temperature Bachmann run; 0.27 moles of RDX was produced by the catalysed nitrolysis process and 0.43 moles of BSX was produced by uncatalysed nitrolysis -- total 0.70 moles after a 10 minute holding period (II-2,4).

In another series of runs, the reaction mixture was not heated to 70°C. but was maintained at 40°C. for a specified time. When ammonium nitrate was added during the later stages of the reaction the yields of BSX were 0.41 moles (after 10 minutes) and 0.75 moles (after 60 minutes) (II-10,11). When no ammonium nitrate was added, the yield of BSX was 0.48 moles at the end of 10 minutes (II-6). These results do not compare very favourably with those obtained in the regular, low-temperature Bachmann runs: here the yield of RDX is 0.27 moles and the yields of BSX are 0.36 and 0.61 moles after 10 minutes and 60 minutes respectively; the totals are then 0.63 and 0.88 moles (II-2,3,).

The significance of these observations is that it is apparent that the fate of the hexamine is decided very early in the reaction. Furthermore the production of additional RDX by heating or adding ammonium nitrate in the later stages of the reaction does not decrease the yield of BSX. And lastly they show that BSX production is only in competition with the formation of some of the RDX. All of these conclusions are in agreement with the properties of the "catalysed nitrolysis-synthesis" mechanism. Similar conclusions have been reached by Winkler.

During the course of this discussion, for one reason or another, several important results have not been mentioned.

The first of these is the fact that good yields of MSX are obtained when monomethylammonium nitrate is substituted for the ammonium nitrate. This phenomenum is very difficult to explain on the basis of the proposed "catalysed nitrolysis-synthesis" mechanism unless some new concept is invoked. One such concept is that MSX is formed by a synthesis reaction. This implies, ultimately, that methylammonium nitrate can condense with a methylol group in the presence of acetic anhydride with loss of methyl alcohol or, alternately, that the tertiary methyl nitrate salt of a methyleneamine-type compound can lose the elements of methyl alcohol to give a secondary nitramine. While these possibilities are not theoretically unacceptable, they introduce reactions which are more speculative than is desirable. Another concept is that nitrogen interchange can produce the compound H-18 and ammonium nitrate:



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H-18

The mechanism of this interchange is unknown and its existence is questionable, but it is known that H-18 and ammonium nitrate react under Bachmann conditions to give MSX and RDX. In this case it would be postulated (on the basis of the "catalysed nitrolysis-synthesis" mechanism) that MSX arose by catalytic nitrolysis and that RDX arose by synthesis. It should be noted that other theories (based on the symmetrical fission of the hexamine molecule) do not explain the production of MSX any more easily, excepting the theory of Ross and Boyer which makes provision for nitrogen interchange of the above type. For the purposes of future discussion it will be considered that MSX is produced by a synthesis process; this in spite of the fact that no MSX can be detected in runs where monomethylammonium nitrate is added belatedly.

A second important result which has not yet been considered is that when ammonium nitrate is replaced with monomethylammonium nitrate, very little HMX is produced. This result is not in agreement with the results of the workers at Pennsylvania State College but it has been checked and rechecked and it is felt that less than 0.1 percent HMX is produced under these conditions. Other amine nitrates (dimethylammonium nitrate possibly excluded) give fairly low yields of HMX. Since HMX may be obtained from DNPT when monomethylammonium nitrate is used, it is possible that DNPT is not the precursor of HMX in the Bachmann reaction; this would also indicate that HMX is produced by a synthesis process only in the Bachmann reaction. This is in agreement with the author's interpretation of Winkler's rate studies.

A third result is that it seems that a considerable quantity of a urea-formaldehyde polymer was produced when urea was added belatedly to a modified Bachmann reaction. This seems to indicate that the "fragments" giving rise to the second mole of RDX are either methylene glycol or a simple derivative of this compound. It also seems to indicate that the "catalytic" function of the ammonium or amine nitrate is (at least in part) to combine with methylol groups.

A fourth subject which has been ignored is that, in view of the fact of the production of RDX on the belated addition of ammonium nitrate, there is probably an isolatable precursor for this second mole of RDX. Several attempts were made to isolate this postulated precursor and these attempts are described in an appendix to this thesis.

Lastly, it will have been noticed that the anticipated results were not achieved when ammonium or amine nitrates were added belatedly to the DNPT conversion (i.e. good yields of HMX were still obtained). It is apparent that the reason for this behaviour is the slow conversion of DNPT to AcAn under the mild reaction conditions used. In other words, DNPT and/or PHX (see p.77) persisted in the reaction mixture for a long period of time and were converted to HMX on the addition of ammonium nitrate. This phenomenum strengthens the possibility (already mentioned) that the production of RDX on the belated addition of ammonium nitrate to a modified Bachmann reaction may not, in fact, be evidence for a synthesis process but may actually represent the conversion of uncompletely nitrated compounds (containing the six-membered ring) to RDX. This has already been discussed in some detail and new experiments, designed to test this point, are presented in the next section.

III. Ammonium Nitrate Consumption and Other Material Balances in the Bachmann Reaction

It has already been pointed out that the various proposed mechanisms for RDX formation in the Bachmann reaction are of two types: those mechanisms in which the two moles of RDX are formed by identical processes and those mechanisms in which the two moles of RDX are formed by different processes (see p. 94). It was also pointed out that the product formed might be different with respect to the distribution of the ammonium nitrate nitrogen depending on which type of mechanism represents the actual case (see pp. 13 & 94). In the ideal reaction (see equation 3, p. 62), if two molecules of RDX arise from one molecule of hexamine by identical processes, then each molecule of RDX must contain one amino nitrogen atom which originated in the ammonium nitrate (Case I); if, however, the two molecules of RDX arise by different processes, this rule need not apply and a likely alternative would be the case in which one molecule of RDX has two ammonium nitrate amino nitrogen atoms and the other molecule, none at all (Case II).

In Case I, the RDX produced should be equivalent to the ammonium nitrate consumed since each molecule of RDX contains one ammonium nitrate amino nitrogen. In Case II, the RDX produced would not be expected to be equivalent to the ammonium nitrate consumed since it is unlikely that both moles of RDX would be produced to an equal extent. Davy, Chemical Control Superintendent, Holston Ordnance Works, has made the following statement (91):

> "Material balance calculations on the pilot plant operations show that the ammonium nitrate not recovered is equivalent to the RDX yield obtained (within experimental error). If one mole of RDX is produced by nitrolysis of hexamine maintaining one six-membered ring intact, and the other mole of RDX by reaction of the remainder of the hexamine molecule with ammonium nitrate and acetic anhydride, the two different processes must give the same yield in order that the material balance be satisfied. Since that seemed unlikely, it appeared probable that both moles of RDX are formed by the same path."

In view of the evidence obtained in this laboratory (presented in the previous section) favouring Case II, it was considered necessary to re-investigate the consumption of ammonium nitrate in the Bachmann reaction.

A more thorough theoretical examination of the problem showed that the equivalence between RDX production and ammonium nitrate consumption as determined by Davy is neither a necessary nor a sufficient condition for the existence of Case I. It is not a necessary condition since "the ammonium nitrate not recovered" is not necessarily a measurement of the ammonium nitrate actually consumed in the production of RDX. First, "the ammonium nitrate not recovered" may be greater than the actual consumption due to RDX production since ammonium nitrate may be consumed in reactions leading to the formation of nitramines other than RDX (eg. isolable products such as HMX* or inisolable, low-molecular weight products) or may be destroyed in the reaction mixture (eg. by the

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* In a later paper (16), Davy states that one mole of ammonium nitrate is consumed when one mole of HMX is produced from one mole of hexamine. Hence the ammonium nitrate consumed should be equivalent to the RDX(B) produced.

action of acetic anhydride or acetyl nitrate). Secondly, "the ammonium nitrate not recovered" may be less than the actual consumption due to RDX production since ammonium nitrate, or other ammonium salts or ammonia derivatives which analyse as ammonium nitrate, may be generated by the hydrolysis of by-products after dilution or may result from the incomplete nitration of all of the hexamine introduced. Again, the equivalence of the RDX production to the ammonium nitrate consumption is not a sufficient condition for the existence of Case I since, even if ammonium nitrate were neither destroyed nor generated in the mother liquor through side-reactions, it is possible that the two reactions of catalysed nitrolysis and synthesis (indicated by Case II) may proceed to an equal extent. Thus the most general statement that can be made with regard to this problem is that if it can be shown that the RDX production is equivalent to the ammonium nitrate consumption over a wide range of conditions, and if it can be shown that ammonium nitrate is neither destroyed or generated by side-reactions, then it is likely that Case I is indicative of the reaction mechanism.

Since Davy's experiments were conducted over a narrow range of conditions (optimum conditions) it was considered that a more extensive investigation* of ammonium nitrate consumption would contribute to the understanding of the mechanism of the Bachmann reaction. Two investigations were started simultaneously, one at the University of Pennsyl-

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* The RDX Committee (Canada, U.S.) at a meeting held in Kingsport, Tennessee, on Sept. 30, 1943, suggested that this investigation be undertaken.

vania, the other in this laboratory. The results of both investigations are considered in this thesis.

Carmack (at the University of Pennsylvania) investigated the consumption of ammonium nitrate as the mole ratio of ammonium nitrate was varied between 0.00 and 2.87 moles per mole of hexamine (92); he later studied the effect of holding time for low-temperature Bachmann runs (93,94) and investigated the gaseous products of the reaction and subsequent simmering process with a view to establishing the fate of all of the amino nitrogen introduced into the reaction mixture (95,96). In this laboratory, the investigation was extended to include the measurement of yields other than RDX and material consumptions other than ammonium nitrate and the study of independent reaction variables other than the mole ratio of ammonium nitrate. In general the following measurements were made: the yields of RDX, HMX and BSX and the concentration in the mother liquor of formaldehyde, ammonia, free nitric acid, total nitrate ion, acetic acid and acetic anhydride. The following independent variables were studied:

(1) the effect of varying the mole ratio of ammonium nitrate,

(2) the effect of simultaneously varying the mole ratios of ammonium nitrate and acetic anhydride,

(3) the effect of temperature (for zero moles of ammonium nitrate),

(4) the effect of temperature (for the full quantity of ammonium nitrate),

(5) the effect of varying the holding time before dilution (for full quantity of ammonium nitrate at 40°C.),*

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* This list includes the work of Carmack in order that it may serve as a "table of contents" for the succeeding sections.

(6) the effect of varying the holding time after dilution (for zero moles of ammonium nitrate at 40°C.),

(7) the effect of withholding ammonium nitrate (reaction temperature 40°C., holding temperature 70°C.),

(8) the effect of withholding ammonium nitrate (reaction temperature 70°C., holding temperature 70°C.),

(9) the effect of belatedly adding monomethylammonium nitrate to a modified Bachmann reaction (reaction temperature 40°C., holding temperature 70°C.), and

(10) the effect of other miscellaneous variables including the variation of nitric acid mole ratio and the holding time before dilution at 70°C.; this section also includes a short discussion of Carmack's work on the gaseous products of the Bachmann reaction. *

While the results obtained in this laboratory show good agreement with those obtained at the University of Pennsylvania (where duplicate series were carried out), the interpretations of these results differ widely. Carmack believes that there is an equivalence between the RDX produced and the ammonium nitrate consumed. In this conclusion he supports the views of Davy and the hypothesis that the two moles of RDX produced in the Bachmann reaction are formed by similar processes. The conclusion reached by this researcher stands in subalternate or contradictory relationship to that of Carmack and Davy: in general, there is no equivalence between the RDX produced and the ammonium nitrate consumed; there may be an equivalence over a narrow range of conditions (optimum conditions), but even these data are open to question since it can be shown that "ammonium nitrate" can be generated by the hexamine (ammonium nitrate may be recovered even when none is introduced). There is no evidence that ammonium nitrate is destroyed in the mother liquor to any appreciable extent but the fact that not all of the amino nitrogen can be accounted for in terms of solid reaction products and volatile ammonia or amines casts doubt on any statement so explicit as that of Carmack and Davy. The view of this researcher, then, is that no positive conclusion can be reached with regard to the equivalence and that the possibility of a mechanism where the two moles of RDX are produced by different processes is not excluded.

In the succeeding pages, the results of the material balance experiments are discussed. It is found that all data may be explained in terms of the proposed "catalysed nitrolysis-synthesis" mechanism.

A. Effect of Ammonium Nitrate Concentration on Yields and Material Balances

In this section, the results of extensive investigations dealing with the consumption and recovery of the various reagents used in the Bachmann reaction are given. Particular attention has been directed to the ammonia consumption as the ammonium nitrate concentration was increased from zero to four moles per mole of hexamine, but material balances are also presented for formaldehyde, nitric acid and acetic anhydride.

Experimental

1. Experimental and Analytical Procedures

Bachmann Procedure:- The procedure adopted for the Bachmann run was that of a continuous three-feed addition (previously described p.121). The reagents used were 0.660 moles of acetic anhydride, 0.000 to 0.400 moles of ammonium nitrate dissolved in 0.433 moles of 97 percent nitric acid, and 0.100 moles of hexamine dissolved in 0.382 moles of acetic acid. In addition, the pot was charged with 0.084 moles of acetic acid, 0.010 moles of acetic anhydride, and with an estimated 2 1/2 percent (for low ammonium nitrate concentrations) to 1 percent (for high ammonium nitrate concentrations) of the ammonium nitrate-nitric acid solution otherwise added. Throughout the addition, the hexamine-acetic acid solution was retarded 5 percent in relation to the other reagents. The reaction temperature and holding temperature were 69 - 71°C. The addition time was 12 minutes and the holding time was 20 minutes. The reaction mixture was diluted with 700 ml. of cold water and was filtered after standing for at least 24 hours. The crude product was air dried to constant weight and the filtrate and wash waters were mixed, their combined volume measured and a sample saved for analysis.

After this series of experiments was started, several new procedures were reported which are said to give greater reproducibility of results than does this procedure. It was nevertheless considered wiser not to change since this would have necessitated repetition of many of the completed runs. This procedure gave, in general, a reproducibility of considerably better than 5 percent in all analyses. This is illustrated below by a comparison of a set of duplicate runs:

Ammonium nitrate introduced	0.2680	0.2680
RDX produced	0.1446	0.1450
HMX produced	0.0051	0.0050
BSX produced	0.0159	0.0173
Formaldehyde in mother liquor	0.0750	0.0761
Ammonia in mother liquor	0.1078	0.1135
Total nitric acid in mother liquor . . .	0.1675	0.1635

The quantities used in this series of runs did not meet the optimum conditions as determined by other workers in this field. The acetic anhydride was low by at least half a mole per mole of hexamine, and the nitric acid by about one-third of a mole. The RDX yields were, in consequence, about 5 percent low.

RDX(B)[*]:- RDX(B) was determined by fuming off one-half of the crude product in 70 percent nitric acid under standard conditions and correcting for loss of RDX(B) by means of a fume off calibration curve (see Figure 2). The standard conditions called for complete solution of the crude product in seven times its weight of 70 percent nitric acid and holding at a temperature of over 100°C. for three minutes after the height of the fume off. The resulting solution was diluted with five volumes of cold water and the RDX(B) allowed to crystallize out at room temperature for at least 48 hours. The filtered product was air dried.

Weight RDX(B) = 2·(Weight fumed-off product + c)

or Weight RDX(B) = 2f·(Weight fumed-off product)

where c and f may be determined graphically.

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[*] RDX(B) = RDX + HMX (see also p. 47)

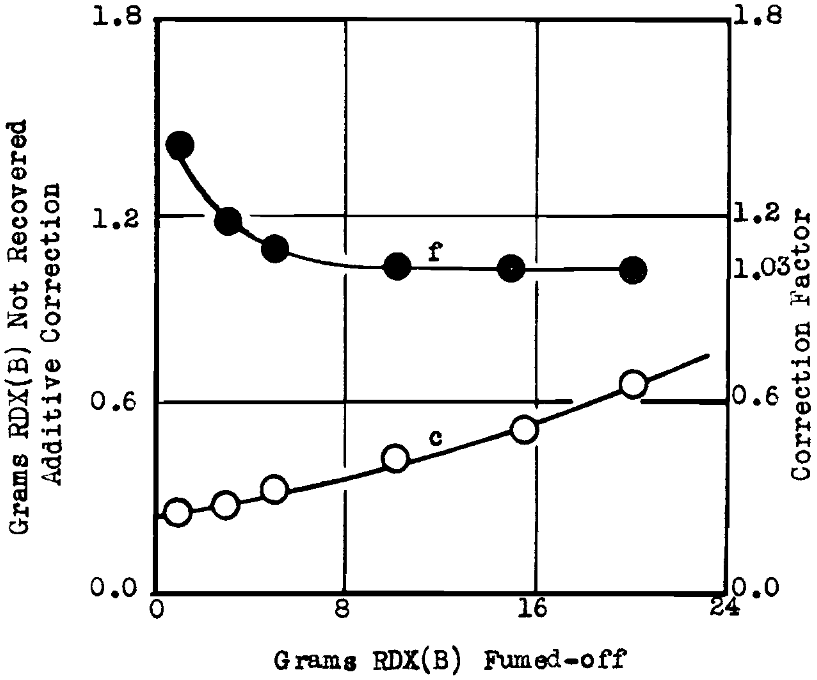

Figure No. 2

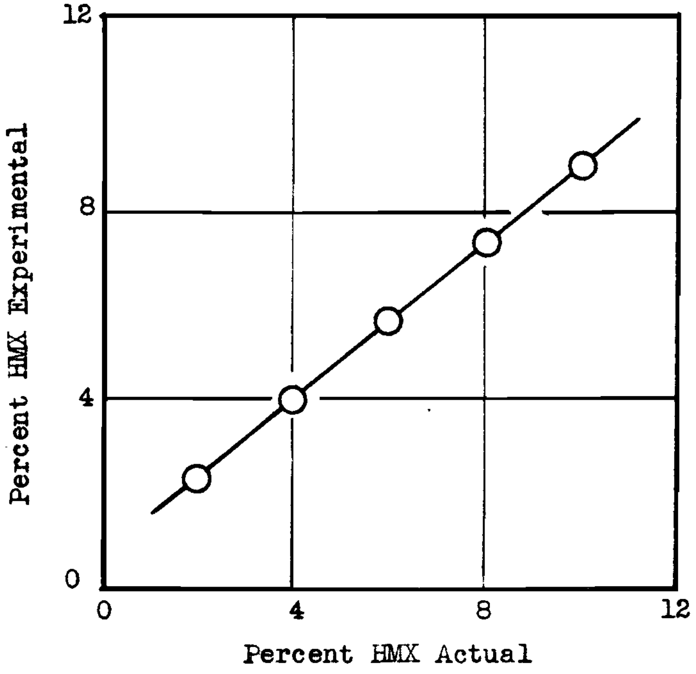

Figure No. 3

Duplicate determinations agreed with one another to better than one part per thousand. It is believed that the fume off is superior to the simmer since the RDX(B) is dissolved during the destruction of the BSX and there is no possibility that by-products can escape destruction due to occlusion.

BSX:- The yield of BSX was obtained by difference:

$$\text{Moles BSX} = \frac{\text{Weight crude product} - \text{Weight RDX(B)}}{322}$$

HMX and RDX:- HMX in the RDX(B) was determined by the alkaline hydrolysis method of Winkler and Epstein. Four grams of fumed-off product was dissolved in 300 ml. acetone and thermostatted at 25°C. To this was added 150 ml. of 0.380 N. sodium hydroxide at 25°C. After stirring for two minutes, the whole was allowed to stand in the thermostat for eighteen additional minutes. The reaction was terminated by the addition of 5 ml. of glacial acetic acid. The acetone was distilled off and the HMX was allowed to crystallize for about 10 hours at room temperature. The filtered product was dried at 110°C. for one hour and weighed. The result, calculated as percent HMX in RDX(B), was corrected by means of a calibration curve (see Figure 3).(See Ref.58).

$$\text{Moles HMX} = \frac{\text{Percent HMX in RDX(B) (corr.)} \times \text{Weight RDX(B)}}{29600}$$

$$\text{Moles RDX} = \frac{\text{Weight RDX(B)} - \text{Weight HMX}}{222}$$

Great care must be exercised in applying this method. While, in general, duplicates agreed to better than 5 percent, several times they differed by as much as 100 percent for no apparent reason.

Formaldehyde:- Formaldehyde in the mother liquor was determined by steam distilling a suitable portion of the diluted mother liquor and analysing the distillate for formaldehyde by the method of Romijin and Signer (97,98). The steam distillation was carried out on 50 ml. of the diluted mother liquor to which had been added 50 ml. water and 0.5 ml. sulfuric acid. Of this solution, 75 ml. was distilled over into 100 ml. of distilled water contained in a 500 ml. Erlenmeyer flask, the snout of the condenser being below the surface of the water. To the residue in the distilling flask was added 75 ml. water and the distillation was repeated. This process was continued until 375 ml. of distillate had been obtained. This distillate was then diluted to either 500 ml. or 1000 ml. in a volumetric flask, depending on the formaldehyde concentration. The formaldehyde was determined by adding 25 ml. approximately one-tenth normal standard iodine solution to 25 ml. of the dilute formaldehyde solution, titrating the resulting solution with dilute alkali until it was pale yellow in colour, allowing to stand for ten minutes, acidifying with 5 ml. strong hydrochloric acid and titrating the excess iodine with approximately one-tenth normal standard sodium thiosulfate solution using starch as an indicator.

$$\text{Moles Formaldehyde in Mother Liquor} = \frac{(25.00 - mn)\cdot NV}{2500}$$

where m = volume standard N/10 sodium thiosulfate used,
n = number ml. standard N/10 iodine equivalent to one ml. standard N/10 sodium thiosulfate,

N = normality standard N/10 iodine solution, and
V = volume of diluted mother liquor.

Duplicate determinations on the same distillate agreed to within one part per thousand while duplicate determinations on different distillates of the same mother liquor agreed to within five parts per thousand.

It was recently observed in this laboratory that the formaldehyde could be determined directly in the undistilled mother liquor. This has considerable theoretical significance since it shows that the formaldehyde is free in the diluted mother liquor, not in chemical combination with nitrogen as in hexamine or nitramines.

Ammonia:- Ammonia in the mother liquor was determined on the residue from the above steam distillation by diluting this residue to about 300 ml. with water, adding 25 ml. of 50 percent sodium hydroxide and distilling over about 200 ml. into an excess (25 ml.) of approximately one-tenth normal standard hydrochloric acid solution. The excess hydrochloric acid was titrated with approximately one-tenth normal standard sodium hydroxide solution using methyl red as an indicator.

$$\text{Moles Ammonia in Mother Liquor} = \frac{(25.00 - m'n')\cdot N'V}{5000}$$

where m' = volume standard N/10 sodium hydroxide used,
n' = number ml. standard N/10 hydrochloric acid equivalent to one ml. standard N/10 sodium hydroxide, and
N' = normality standard N/10 hydrochloric acid solution.

Duplicate determinations differed as widely as 5 percent, particularly when the ammonia value was low. The ammonia could not be determined directly by distillation of the alkaline mother liquor without previous acid distillation due to the interference of formaldehyde. Neither could the ammonia be accurately determined if the preliminary steam distillation were carried out in the absence of a few drops of sulfuric acid. It appears that, while most of the ammonia was present as ammonium nitrate, some was present as ammonium acetate and that ammonia could be slowly distilled from the neutral solution. Thus if the steam distillation were carried out in the absence of sulfuric acid, some of the ammonia would appear in the distillate as hexamine. This was shown by precipitation of the iodine complex. It can be seen that this procedure would cause an error in the formaldehyde determination as well.

Nitric Acid:- Nitric acid in the mother liquor falls into two categories: free and combined nitric acid. The free nitric acid is that which can be directly titrated with alkali; the combined nitric acid is that which is present in the form of salts as, for example, in ammonium nitrate.

Free Nitric Acid:- The free nitric acid in the mother liquor was determined by titrating 100 ml. of the diluted mother liquor with approximately one normal standard sodium hydroxide solution.

The standard alkali was added rapidly until the pH of the solution was about 1.75 (Beckmann pH Meter); the alkali was then added in a number of small constant volumes (e.g. 5 drops), the pH being determined after each addition. This procedure was continued until the pH of the solution approximated 2.75. The change in pH (ΔpH) was calculated for each addition, and the addition which gave the greatest value for ΔpH was considered to be the end point of the titration. The end point for a typical run is illustrated graphically in Figure 4.

$$\text{Moles } \underline{\text{free}} \text{ Nitric Acid} = \frac{m''N''V}{100000}$$

where m'' = volume standard N/1 sodium hydroxide used, and
N'' = normality standard N/1 sodium hydroxide.

The method of differential titration is considered by this researcher to be superior to the method of Bachmann of the University of Michigan (61) for solutions which vary so widely in quantity (0-3 moles per mole of hexamine) and quality (ammonium and methylammonium*) of nitrates present. Since the nitric acid excess in these series of runs was small (less than 0.06 moles in most cases), the error in its estimation was correspondingly large. A deviation of 10 percent might well be expected although, in practice, deviations of greater than 5 percent were not encountered. It should be remarked, at this point, that there is a lower limit to the size of the addition unit

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* In a later section this procedure is applied to modified Bachmann runs in which methylammonium nitrate is used.

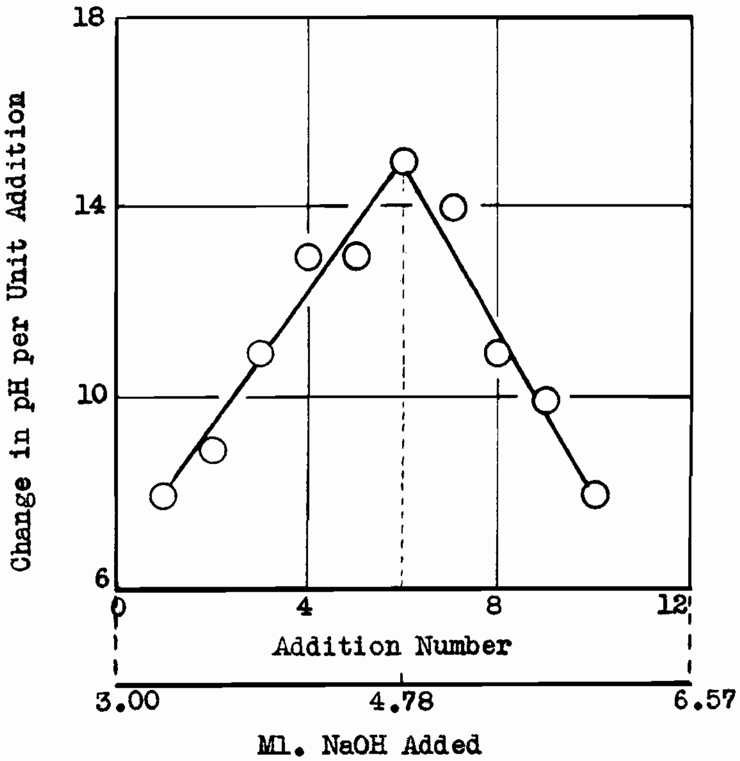

Figure No.4

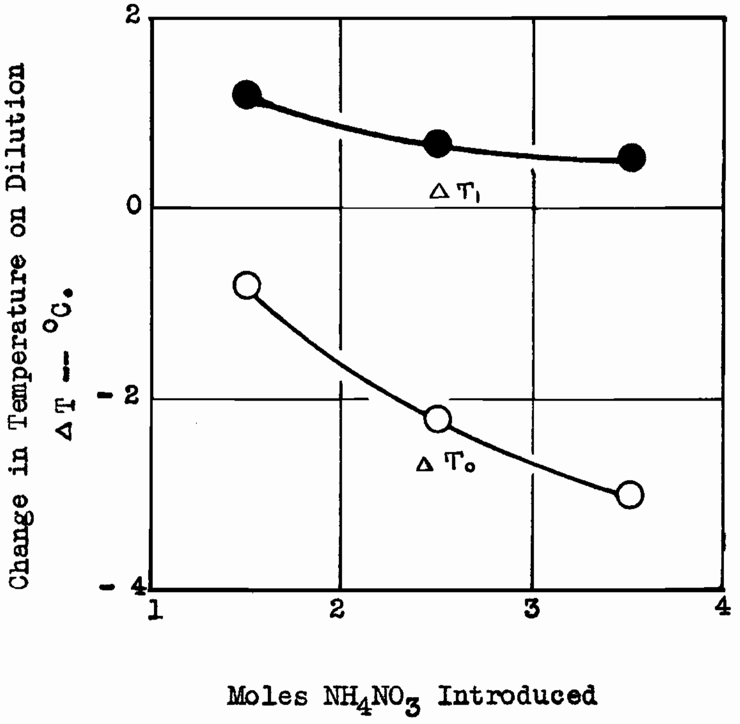

Figure No. 5

used in setting up Figure 4: if this portion were too small, the curve would flatten out and a poor end point would be obtained. Many titrations did not give the sharp end point of the one illustrated above and, in these cases, it was necessary to carry out a careful mathematical analysis in order to determine the end point.

Total Nitric Acid (i.e. Nitrate Ion);- Total nitric acid in the mother liquor was determined by nitron precipitation. To 10 ml. of the diluted mother liquor was added 70 ml. of distilled water and 7 drops of sulfuric acid. This solution was brought to boiling and one gram of nitron dissolved in 10 ml. of 5 percent acetic acid was added. The resulting mixture was allowed to cool for one hour in the air and for two hours in an ice bath. The nitron nitrate was then filtered off on a weighed, scintered-glass crucible, washed with part of the filtrate and with 10 ml. of ice water in 2 ml. portions. The scintered-glass crucible and its contents were then dried at 105°C. for one hour, cooled and weighed.

Moles <u>total</u> Nitric Acid = 0.000266 WV

where W = weight of nitron nitrate.

Some criticism has been directed at this method of analysis due to the solubility of nitron nitrate in cold water, to the insolubility of nitron nitrite and to the occlusion of nitron acetate. While these objections are founded on sound principles, in practice duplicates agree to better than ten parts per thousand, and the results obtained by use of this method have led to important theoretical considerations. Errors lose much of their significance when analytical conditions are carefully controlled.

Combined Nitric Acid:- Combined nitric acid was determined by difference:

Moles combined Nitric Acid =
Moles total Nitric Acid - Moles free Nitric Acid.

Acetic Anhydride[*]: - The material balance of the acetic acid - acetic anhydride part of the system under study could have been satisfactorily made without determining the quantity of unreacted acetic anhydride present at the end of the reaction. This, however, is an interesting factor and was investigated for several concentrations of ammonium nitrate.

After a number of new methods were explored (potentiometric titration with water, titration with aniline using trinitrobenzene as an indicator, and differential titration with aniline and water using phenolphthalein as indicator), it was decided that the temperature-rise method[**] presented the greatest possibilities. Since sampling of a two phase system can never be entirely satisfactory, it was deemed

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[*] Acetic acid is not considered to react and, in the material balance calculations, it is supposed that it is recovered quantitatively.

[**] The original method, based on the heat of hydrolysis of acetic anhydride in the presence of sulfuric acid, was developed at the St. Maurice Chemicals Co., Shawinigan Falls, P.Q.

necessary to perform the analysis on a complete run. Actually three, and preferably four, runs (separate and distinct from the runs on which the other material balances were carried out) were necessary to determine the acetic anhydride excess at any one concentration of ammonium nitrate. These runs are detailed in the following paragraphs.

1. To a regular run, cooled to 25°C. without dilution, was added 3 ml. of anhydrous sulfuric acid. When temperature equilibrium (at 25°C.) had been attained between the well-stirred pot and the well-stirred water bath, 25 ml. of water at 25°C. was added and the change in temperature was observed. This change in temperature, ΔT_{oe}, was considered to be due to the heat of dilution of the system, ΔT_o, and to the heat of hydrolysis, ΔT_e, of the acetic anhydride excess, e ml.

$$\Delta T_{oe} = \Delta T_o + \Delta T_e$$

2. To a regular run, cooled to 25°C. without dilution, were added 3 ml. of acetic anhydride and 3 ml. of anhydrous sulfuric acid. When temperature equilibrium had been established (as previously), 25 ml. of water at 25°C. was added and the change in temperature was observed. This change in temperature, $\Delta T_{o(e+3)}$, was considered to be due to the heat of dilution of the system, ΔT_o, and to the heat of hydrolysis, $\Delta T_{(e+3)}$, of the acetic anhydride excess, (e+3) ml.

$$\Delta T_{(e+3)} = \Delta T_{oe} + \Delta T_3$$

$$\Delta T_1' = \frac{\Delta T_{o(e+3)} - \Delta T_{oe}}{3}$$

where $\Delta T_1'$ = change in temperature due to the hydrolysis of 1 ml. acetic anhydride.

3. To a regular run, cooled to 25°C. without dilution, were added 5 ml. of acetic anhydride and 3 ml. of anhydrous sulfuric acid. When temperature equilibrium had been established, 25 ml. water at 25°C. was added and $\Delta T_{o(e+5)}$ was obtained where

$$\Delta T_{o(e+5)} = \Delta T_{oe} + \Delta T_5$$

$$\Delta T_1'' = \frac{\Delta T_{o(e+5)} - \Delta T_{oe}}{5}$$

The purpose of this run was to check the additivity of temperatures (intensity factor) in relation to the additivity of the heats of hydrolysis (capacity factor). Had $\Delta T_1'$ and $\Delta T_1''$ differed by more than experimental error, a correction would have had to be introduced to compensate for the change in specific heat or the change in heat losses with change in temperature. Since $\Delta T_1'$ and $\Delta T_1''$ were not found to differ, this run could have been omitted.

4. This run was a simulated rather than a true run. A synthetic mixture containing zero excess anhydride was made up by weighing out the quantities of pure RDX, BSX, ammonium nitrate, nitric acid and acetic acid as determined for that particular type of run by the other material balance analyses. This mixture was heated to 70°C. for 20 minutes and then cooled to 25°C. and treated as run No. 1 above. The change of temperature, ΔT_0, in this case was regarded as being due solely to the heat of dilution of the system. In this connection, the ammonium nitrate

concentration is very important since the ΔT_o factor (which is actually a temperature depression) seems to be largely due to the heat of solution of undissolved ammonium nitrate.

Now: $$\Delta T_e = \Delta T_{oe} - \Delta T_o$$

and $$e = \frac{\Delta T_e}{\Delta T_1}$$

where $$\Delta T_1 = \frac{\Delta T_1' + \Delta T_1''}{2}$$

when $\Delta T_1'$ and $\Delta T_1''$ agree within experimental error.

Calculating e to moles of acetic anhydride:

$$\text{Moles Acetic Anhydride} = \frac{e \times 1.082}{102.1}$$

$$= \frac{0.3180\ (\Delta T_{oe} - \Delta T_o)}{3\ \Delta T_{o(e+5)} + 5\ \Delta T_{o(e+3)} - 8\ \Delta T_{oe}}$$

In an actual case:

$\Delta T_{oe} = +3.30^\circ C.$ $\Delta T_{o(e+3)} = +6.85^\circ C.$

$\Delta T_o = -0.68^\circ C.$ $\Delta T_{o(e+5)} = +9.25^\circ C.$

$\Delta T_1' = 1.18^\circ C.$ and $\Delta T_1'' = 1.19^\circ C.$

and Moles Acetic Anhydride = 0.0355

Due to the very considerable amount of work involved in each determination, only a few cases were investigated. At the time that the work was carried out, the significance of the ammonia recovery curve was not fully appreciated, and values for ΔT_o must have been in considerable error due to the false quantity of ammonium nitrate added to the blank runs. This must have been particularly true for runs carried out with less than two moles of ammonium nitrate per mole of hexamine. It is possible that in a more extensive investigation, calibration curves could be set up. An example of this is given in Figure 5.

As mentioned previously, whether or not the unreacted acetic anhydride is determined, the material balance on the acetic acid-acetic anhydride part of the system can be made by titrating the diluted mother liquor for acetic acid. This titration was carried out with approximately one normal standard sodium hydroxide solution on 10 ml. of the mother liquor, diluted to 125 ml. with distilled water. The end point was taken as pH 8.9 as determined by the pH meter. This represents the pH of approximately one-tenth normal solution of sodium acetate in water. It may be that at this pH, the ammonium nitrate present was hydrolysed to a limited extent, but since the titration was carried out rapidly and since the ammonium nitrate concentration was small at the high dilutions used (about 0.005 N), this possibility was discounted. It is a favourable sign that no "fading" of the end point was observed at these dilutions.

Moles Acetic Anhydride in the diluted Mother Liquor as Acetic Acid*

$$= \frac{\frac{m''N''V}{1000} - A - 0.466}{2}$$

where m'' = volume of standard N/1 sodium hydroxide, and

A = moles free nitric acid present (as previously determined).

The quantity 0.466 represents the acetic acid introduced into the system as such.

---

* Actually represents acetic anhydride not consumed. See footnote on p. 202.

By taking into account the quantity of unreacted acetic anhydride present at the end of the run, a new figure is obtained representing the amount of acetic anhydride hydrolysed to acetic acid before dilution.

Moles Acetic Anhydride Hydrolysed to Acetic Acid before Dilution

$$= \frac{\frac{m''N''V}{1000} - A - 0.466}{2} - B$$

where B = moles unreacted acetic anhydride (previously determined).

It should be noted that in Table V, the figure shown is the latter wherever a value is given for the unreacted acetic anhydride. Otherwise it is the former.

An alternate method for the determination of acetic anhydride present in the diluted mother liquor as acetic acid consists in adding an excess of approximately one normal standard sodium hydroxide solution (25 ml.) to 10 ml. of the mother liquor (diluted to 125 ml.), boiling to get rid of the ammonia and back-titrating with approximately one normal standard hydrochloric acid solution to an end point of pH 8.9. In this case the calculations resolve to:

Moles Acetic Anhydride in the Diluted Mother Liquor as Acetic Acid

$$= \frac{\frac{(25.00 - m''''n'''')N''V}{1000} - C - 0.466}{2}$$

and

Moles Acetic Anhydride Hydrolysed to Acetic Acid before Dilution

$$= \frac{\frac{(25.00 - m''''n'''')N''V}{1000} - C - 0.466}{2} - B$$

where m'''' = volume standard N/1 hydrochloric acid used,

n'''' = number ml. standard N/1 sodium hydroxide equivalent to 1 ml. standard N/1 hydrochloric acid, and

C = moles total nitric acid present (as previously determined).

In those runs which have a value reported for free nitric acid, first method was used for the acetic acid titration, in others, the alternate method was used.

The agreement between the two methods is only fair, the second method giving values about 4 percent higher than the first. One reason for this lies in the fact that any of the acetic acid present as ammonium acetate will not be titrated by the first method. In the second method, there is a very good possibility that in the hot alkaline solution formaldehyde may be oxidized to formic acid thus using up some of the alkali. From Table V it will be apparent that both methods give a material balance that is at least 2 percent high. Any one of several possibilities may account for this. Any nitrous acid present in the diluted mother liquor will appear as acetic acid. It is possible that some formaldehyde is oxidized to formic acid in the Bachmann reaction itself, although this does not show in the formaldehyde balance. And again, it is possible that the nitrous oxide (with which the diluted mother liquor is saturated) gives rise to a titratable acid of the $H_2N_2O_2$ type. Any one or a combination of the possibilities would account for the high acetic anhydride balance.

On the basis of the above calculating formulae, the difference

$$\frac{(25.00-m''''n'''')N''V \quad - m''N''V}{1000}$$

should represent the combined nitric acid. It is interesting to observe that it actually coincides more closely with the "ammonia recovered" factor. These two, as is shown later, are not identical. This difference, then, indicates a method for determining the quantity of ammonia in the mother liquor other than the one used in this series of experiments. This alternate method, however, depends on a small difference in two large titrations and can thus never be as accurate as the alkaline distillation method.

The experiments of Carmack (92) were conducted under essentially the same conditions and his analytical procedures, while not identical, were comparable to those used in this laboratory.

The Bachmann procedure was a standard three-feed addition. The initial charge was 30 ml. of acetic acid and 30 ml. of acetic anhydride and to this were added simultaneously, equivalently and continuously over a period of twelve and a half minutes a solution of 33.6 g. (0.240 moles) hexamine dissolved in 52.5 ml. of acetic acid, 150 ml. (1.400 moles) of acetic anhydride and a solution of varying amounts of ammonium nitrate in 75 g. (1.19 moles) of 97 percent nitric acid. The temperature was maintained at 73-75°C. during the course of the addition and for ten minutes thereafter. The reaction mixture was then drowned in 600 ml. of hot distilled water and simmered on a steam bath for one and a half to two hours with stirring. The filtered product was considered to be RDX(B) containing five percent HMX and having an average molecular weight of 225.8. Hence

$$\text{Moles RDX(B)} = \frac{\text{Weight simmered product}}{225.8}$$

Ammonia in the diluted mother liquor was determined on an aliquot portion of the filtrate. Acetic acid and formaldehyde were expelled by prolonged boiling with the occasional addition of water; the residual solution was made alkaline with sodium hydroxide and distilled into boric acid.

In this laboratory formaldehyde, ammonia and nitric acid analyses were carried out in duplicate. HMX determinations were carried out in duplicate wherever possible. The Bachmann runs themselves were generally carried out in duplicate - the number of runs for a given case being indicated in the table of results.

2. Experimental Results

The results obtained in the above-described series of Bachmann runs are summarized in Table V. The results obtained in comparable experiments at the University of Pennsylvania(92) are presented in Table VI. All data have been calculated on the basis of one mole of hexamine.

TABLE V

BACHMANN REACTION:-EFFECT OF AMMONIUM NITRATE CONCENTRATION ON YIELDS AND MATERIAL BALANCES; TEMP. 70°C.

(CALCULATED TO ONE MOLE OF HEXAMINE)

RUN NUMBER	NH_4NO_3 INTRODUCED	AVERAGE OF	RDX + HMX	HMX IN RDX-B	RDX	HMX	BSX	FORMALDEHYDE (6)			AMMONIA (4 + X)			NITRIC ACID (4·33 + X + Y)					ANHYDRIDE (6·7)				AMMONIUM NITRATE CONSUMED			MOLES RDX+HMX PRODUCED / MOLES NH_4NO_3 CONSUMED			MOLES RDX PRODUCED / MOLES NH_4NO_3 CONSUMED			$\frac{\text{MOLES } NH_3 \text{ NOT RECOVERED}}{\text{MOLES } HNO_3 \text{ NOT RECOVERED}}$	$\frac{\text{MOLES } NH_3 \text{ IN MOTHER LIQUOR}}{\text{MOLES COMB. } HNO_3 \text{ IN MOTHER LIQUOR}}$	MOLES HNO_3 CONSUMED × 0·25
								IN MOTHER LIQUOR	FOR	AC-COUNTED	IN MOTHER LIQUOR	FOR	AC-COUNTED	IN MOTHER LIQUOR FREE	IN MOTHER LIQUOR COMB.	IN MOTHER LIQUOR TOTAL	FOR	AC-COUNTED	UN-REACTED	INTO ACETIC ACID	FOR	AC-COUNTED	APPARENT	CORRECTED										
	MOLES		MOLES	%	MOLES	MOLES	MOLES	MOLES	MOLES	%	MOLES	MOLES	%	MOLES	MOLES	MOLES	MOLES	%	MOLES	MOLES	MOLES	%	MOLES	MOLES	%	UNCORR.	CORR. I	CORR. II	UNCORR.	CORR. I	CORR. II			
1	0·00	2	0·06	7·2	0·06	·003	0·61	3·05	5·67	95	0·51	2·52	63			1·05	3·06	69		6·50	7·11	106	(-) 0·51	0·00	—	(-) 0·12	—	—	(-) 0·12	—	—	1·07		
2	0·25	2	0·15	5·1	0·14	·006	0·61	2·79	5·66	95	0·49	2·75	65			0·96	3·22	69		6·61	7·22	108	(-) 0·24	0·23	96	(-) 0·63	0·65	0·39	(-) 0·58	0·61	0·35	1·02		
3	0·49	4	0·24	6·6	0·23	·012	0·62	2·55	5·73	96	0·45	3·02	67	0·46	0·36	0·82	3·39	69		6·27	6·89	103	(+) 0·04	0·47	96	(+) 6·00	0·49	0·37	(+) 5·75	0·47	0·37	0·97	1·25	1·00
4	0·74	2	0·39	8·0	0·37	·024	0·57	2·26	5·74	96	0·41	3·32	70			0·93	3·84	74		6·53	7·10	106	0·33	0·71	96	1·18	0·55	0·46	1·12	0·52	0·44	1·06		
5	0·98	2	0·60	8·2	0·56	·037	0·53	2·02	5·98	100	0·37	3·80	76			0·81	4·24	78		6·64	7·17	107	0·61	0·95	97	0·98	0·63	0·57	0·92	0·59	0·53	1·00		
6	1·23	2	0·75	10·9	0·69	·064	0·46	1·76	5·92	99	0·31	4·02	77			0·78	4·49	79		6·76	7·22	108	0·92	1·21	98	0·82	0·62	0·57	0·75	0·57	0·52	1·02		
7	1·47	2	1·08	9·6	1·00	·080	0·31	1·33	5·88	98	0·23	4·47	82	0·42	0·23	0·65	4·89	83	0·31	6·17	6·79	101	1·24	1·46	99	0·87	0·74	0·70	0·81	0·68	0·64	0·98	1·00	1·00
8	1·72	2	1·31	8·3	1·23	·083	0·24	0·98	5·95	99	0·20	4·93	86	0·53	0·10	0·63	5·36	87	0·36	6·20	6·80	101	1·52	1·68	98	0·86	0·78	0·74	0·81	0·73	0·70	0·99	2·00	0·97
9	1·95	6	1·45	6·5	1·38	·072	0·17	0·88	5·98	100	0·30	5·23	88	0·48	0·22	0·70	5·63	88	0·04	6·65	6·86	102	1·65	1·80	92	0·88	0·81	0·77	0·84	0·77	0·73	0·95	1·36	0·98
10	2·20	2	1·51	5·2	1·45	·060	0·15	0·78	5·97	100	0·54	5·58	90			1·16	6·20	93					1·66	1·79	81	0·91	0·84	0·81	0·87	0·81	0·78	1·41		
11	2·44	2	1·53	9·1	1·42	·107	0·15	0·74	5·98	100	0·62	5·74	89			1·06	6·18	90	0·01	6·61	6·77	101	1·82	1·94	79	0·84	0·79	0·76	0·78	0·73	0·70	1·00		
12	2·68	2	1·49	4·5	1·45	·051	0·17	0·76	5·98	100	1·11	6·14	89			1·65	6·68	94					1·57	1·70	63	0·95	0·88	0·84	0·92	0·85	0·81	1·23		
13	2·91	5	1·50	4·4	1·45	·050	0·16	0·78	5·99	100	1·25	6·30	91	0·57	1·26	1·83	6·88	91	0·01	6·59	6·76	101	1·66	1·79	62	0·90	0·84	0·81	0·87	0·81	0·78	1·30	0·99	0·95
14	3·16	2	1·54	4·9	1·48	·057	0·13	0·76	5·94	99	1·51	6·56	92	0·57	1·44	2·01	7·06	93		6·53	6·66	99	1·65	1·78	56	0·93	0·87	0·83	0·90	0·83	0·80	1·11	1·05	0·95
15	3·40	2	1·56	5·2	1·50	·062	0·12	0·78	5·98	100	1·66	6·75	91	0·56	1·56	2·12	7·21	92	0·00	6·93	7·05	105	1·74	1·87	55	0·90	0·83	0·80	0·86	0·80	0·76	1·03	1·06	0·95
16	3·88	1	1·56	4·8	1·50	·057	0·14	0·78	6·03	100	2·29	7·41	94			2·58	7·70	93	0·00	6·98	7·12	106	1·59	1·72	44	0·98	0·91	0·87	0·94	0·87	0·83	0·76		

X = MOLES AMMONIUM NITRATE INTRODUCED

Y = 0·11 MOLES FOR RUNS 1-4,
0·09 " " " 5-8,
0·06 " " " 9-12,
0·04 " " " 13-16.

TABLE VI

BACHMANN REACTION:- EFFECT OF AMMONIUM NITRATE CONCN. ON RDX YIELD AND AMMONIUM NITRATE CONSUMPTION - 75°C. (CARMACK)

RUN NUMBER	NH_4NO_3 INTRODUCED	AVERAGE OF	RDX(B)	AMMONIA (4+x)			AMMONIUM NITRATE CONSUMED	RDX(B) PRODUCED / NH_4NO_3 CONSUMED	HEXAMINE CONVERTED TO LINEAR COMPOUNDS	HEXAMINE CONVERTED TO CYCLIC COMPOUNDS	TOTAL HEXAMINE CONVERTED
				IN MOTHER LIQUOR	TOTAL ACCOUNTED FOR						
	MOLES		MOLES	MOLES	MOLES	%	MOLES		%	%	%
1	0·00	1	0·07	0·70	0·91	23	-0·70	-0·10	77	3	80
2	0·26	1	0·13	0·64	1·03	24	-0·38	-0·34	80	7	87
3	0·52	1	0·28	0·59	1·43	32	-0·07	-4·00	77	14	91
4	0·78	1	0·45	0·50	1·85	39	+0·28	+1·61	72	23	95
5	1·04	1	0·61	0·45	2·28	45	0·59	1·04	68	31	99
6	1·30	1	0·92	0·42	3·18	60	0·88	1·04	52	46	98
7	1·56	1	1·09	0·49	3·76	67	1·07	1·02	44	54	98
8	1·82	1	1·22	0·52	4·18	72	1·30	0·94	39	61	100
9	2·08	2	1·39	0·62	4·79	79	1·46	0·95	31	69	100
10	2·35	1	1·37	0·92	5·03	79	1·43	0·96	31	69	100
11	2·61	1	1·32	1·24	5·20	79	1·37	0·97	33	67	100
12	2·87	2	1·47	1·29	5·70	83	1·58	0·94	27	74	101

x = Moles Ammonium Nitrate Introduced

Discussion

The results of this investigation are discussed in the following pages under these general headings:

1. Variation in yields of solid products,
2. Recovery of reagents from the mother liquor,
3. Material balances, and
4. Miscellaneous considerations concerning the reaction mechanism.

1. Variation in Yields of Solid Products

RDX:- As the ammonium nitrate concentration is increased from zero to two moles per mole of hexamine, the RDX yield increases rapidly from a small value to about 1.4 moles. A further increase in the mole ratio of ammonium nitrate results in a slow, linear increase in the yield of RDX (Figure No. 6).

HMX:- As the ammonium nitrate concentration is increased, the HMX yield increases from a small value to a maximum of about 0.1 moles in the region of 2.0-2.5 moles of ammonium nitrate. A further increase in the mole ratio of ammonium nitrate results in a fairly rapid decrease in the yield of HMX. The percent HMX in the RDX(B) follows the same general trend as does the absolute yield of HMX but there are indications that the maximum occurs at a somewhat lower concentration of ammonium nitrate (Figure No. 7). These results agree with those of Winkler(58).

RDX(B):- As the ammonium nitrate mole ratio is increased, the yield of RDX(B) increases to a maximum in the region of 2.5 moles of ammonium

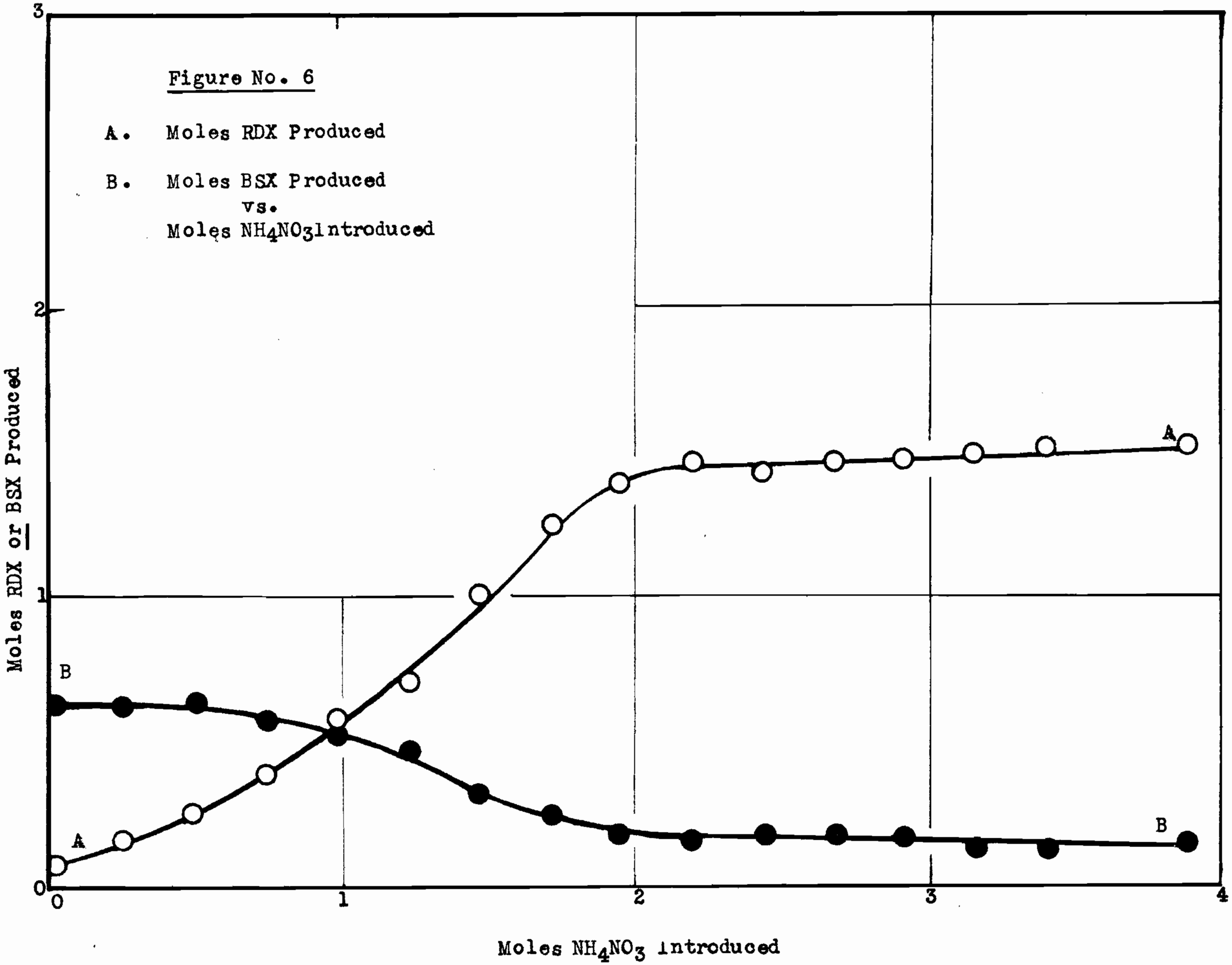

Figure No. 6

A. Moles RDX Produced

B. Moles BSX Produced
vs.
Moles NH_4NO_3 Introduced

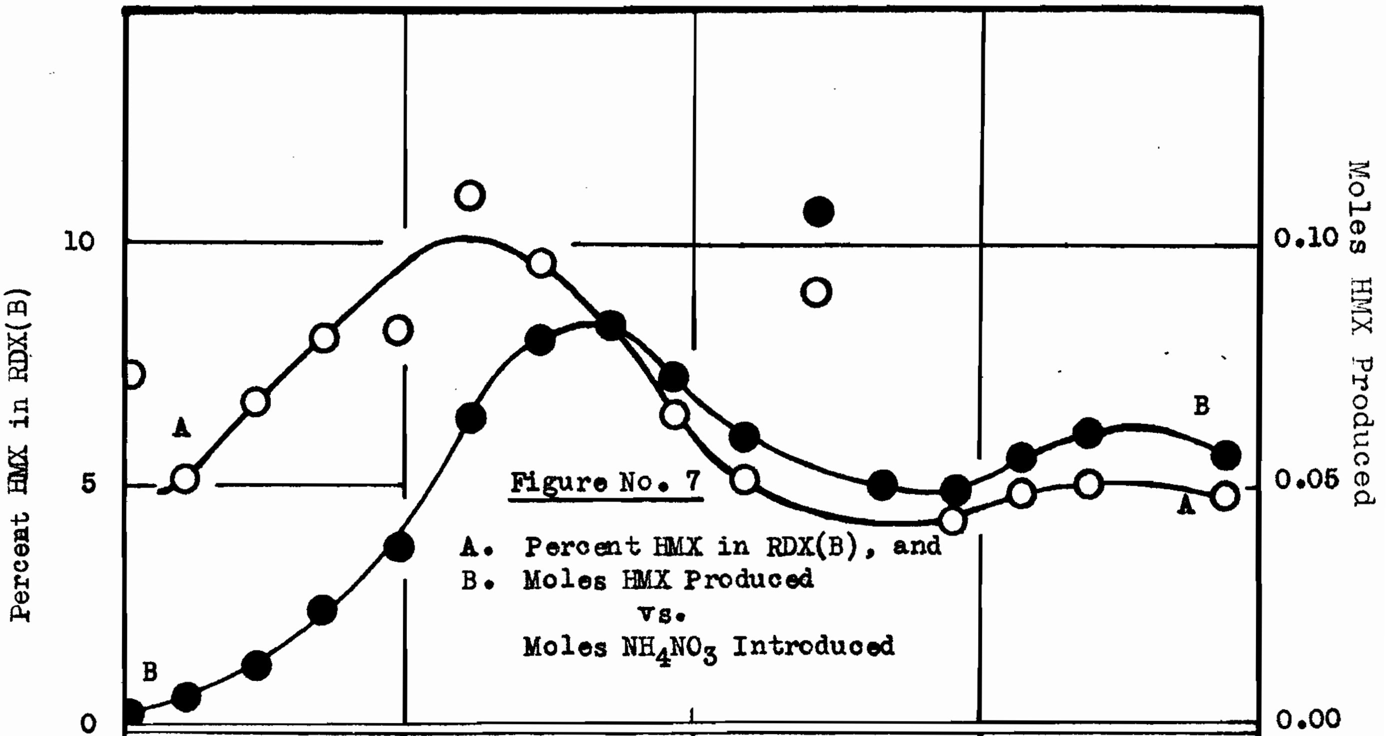

Figure No. 7

A. Percent HMX in RDX(B), and
B. Moles HMX Produced
vs.
Moles NH_4NO_3 Introduced

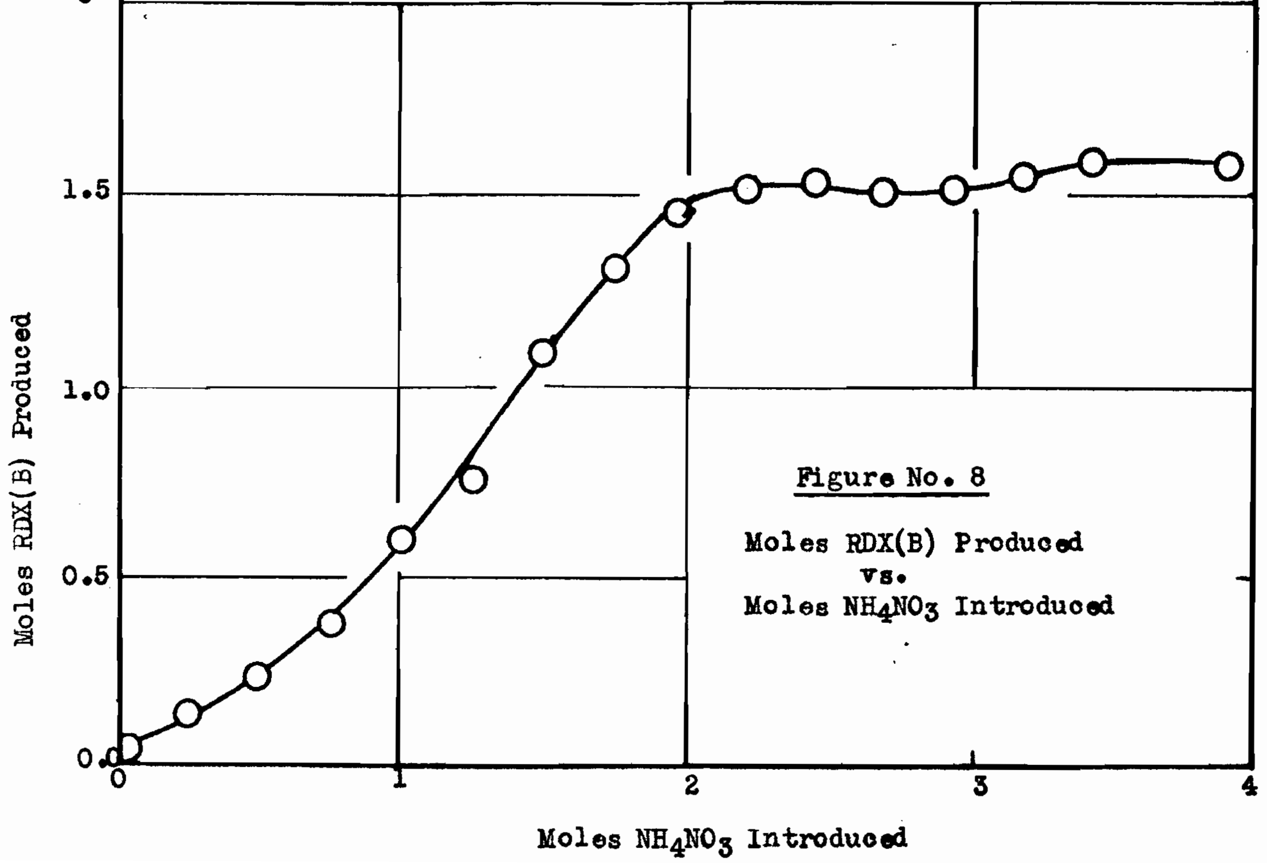

Figure No. 8

Moles RDX(B) Produced
vs.
Moles NH_4NO_3 Introduced

nitrate, falls to a minimum at about 2.9 moles and then rises again. This is illustrated in Figures Nos. 8 and 10. Essentially the same behaviour was observed by Carmack(92) (Figures Nos. 9 and 11).

There is considerable disagreement concerning the presence of a minimum value of the RDX(B) yield beyond the two mole concentration of ammonium nitrate. This behaviour has been observed by McLean (99) (Figure No. 10) and by Winkler(64) at McGill University, as well as by Wright at the University of Toronto(59) (Figure No. 11). Carmack's results (Table VI) also indicate the existence of the minimum (Figure No. 11) but the reproducability of his experiments is not good(92). On the other hand, Holston Ordnance Works has been unable to confirm this result in their pilot-plant work and Bachmann(61), in his extensive laboratory-scale studies, failed to observe a minimum. Furthermore, Winkler, on the basis of new data, altered his original views(58).

On the basis of experiments herein reported, it seems that the early maximum in the RDX(B) yield curve is caused by the maximum in the yield of HMX (which occurs somewhat earlier than the RDX maximum), that the depression is caused by the decrease in HMX yield and that the subsequent rise is due to the slow increase in the yield of RDX. This explanation is based on an examination of Figures Nos. 6, 7 and 8.

BSX:- As the ammonium nitrate concentration is increased from 0.0 to 0.5 moles per mole of hexamine, the BSX yield remains constant. As the ammonium nitrate mole ratio is further increased to two moles, the yield of BSX decreases fairly rapidly. Beyond this point the decrease in yield is slow and may be linear (Figure No. 6).

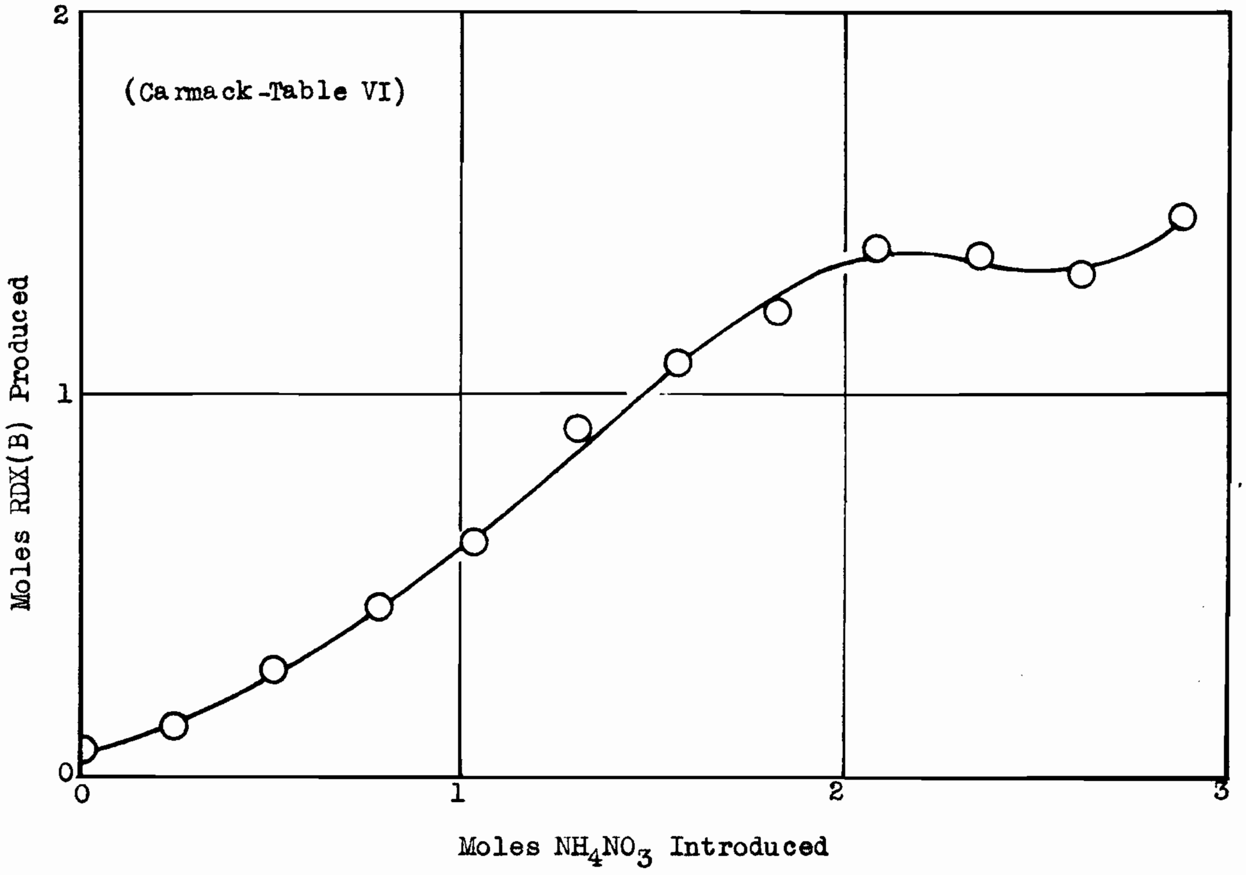
(Carmack-Table VI)
Moles RDX(B) Produced
0
1
2
0
1
2
3
Moles NH_4NO_3 Introduced

Figure No. 9

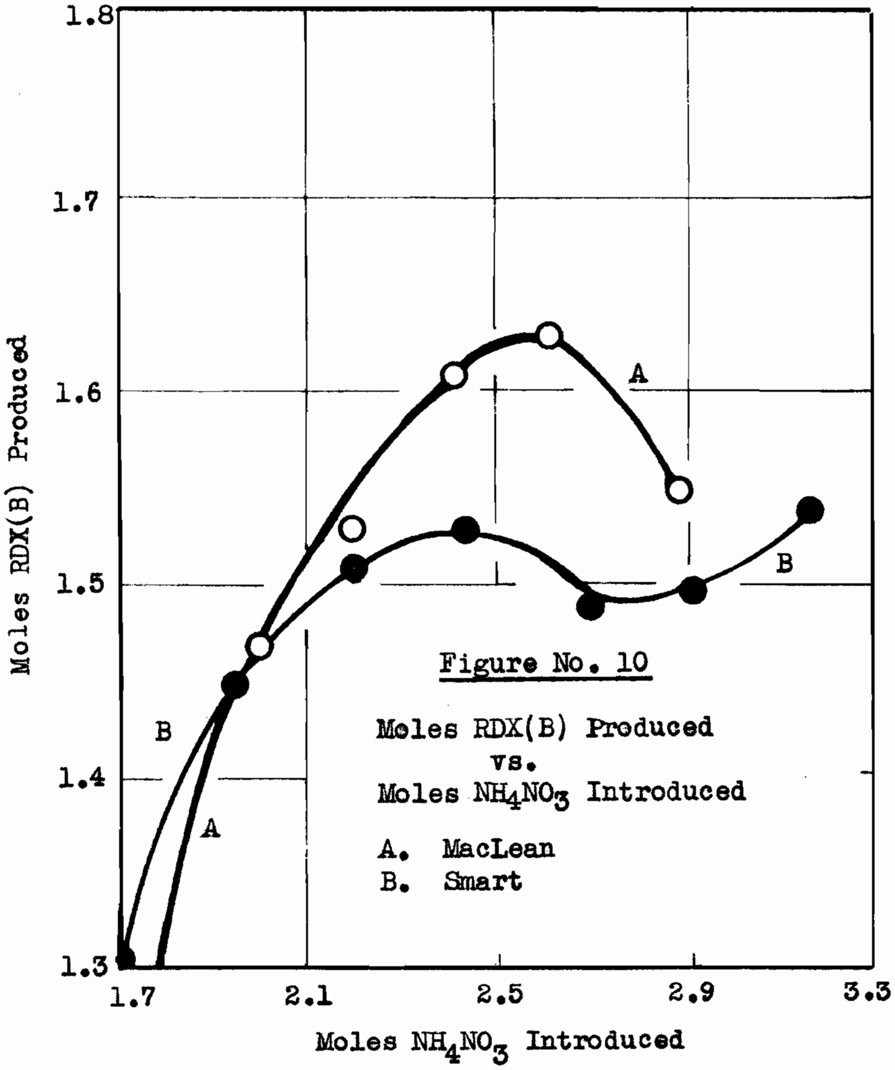

Figure No. 10

Moles RDX(B) Produced
vs.
Moles NH_4NO_3 Introduced

A. MacLean
B. Smart

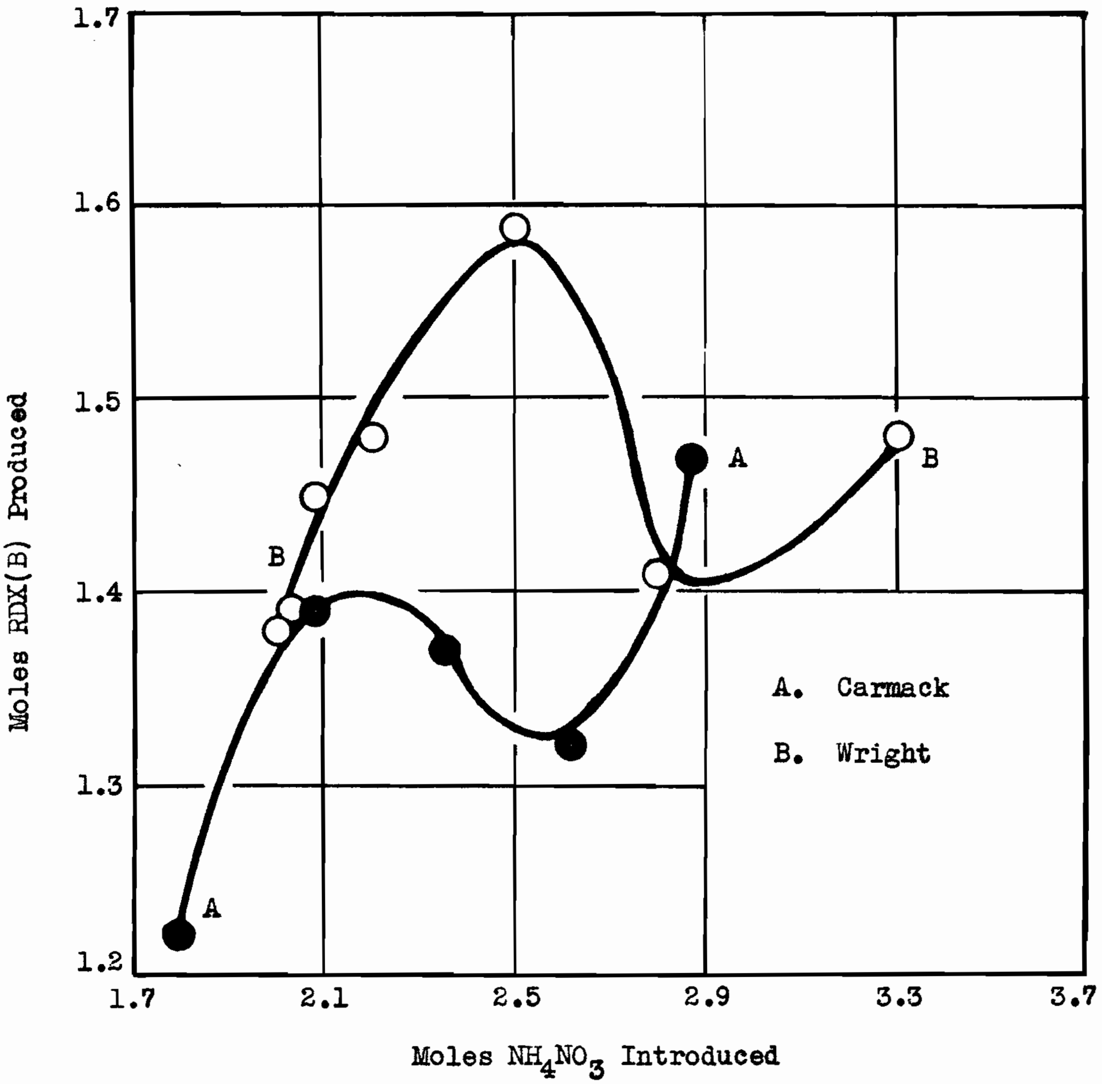
1.7
1.6
1.5
1.4
1.3
1.2
1.7
2.1
2.5
2.9
3.3
3.7
Moles RDX(B) Produced
Moles NH_4NO_3 Introduced
A
B
A
B
A. Carmack
B. Wright

Figure No. 11

2. Recovery of Reagents from the Mother Liquor*

<u>Formaldehyde</u>:- As the ammonium nitrate concentration is increased, the amount of formaldehyde which can be recovered from the mother liquor decreases very rapidly (and linearly) from a value of about three moles per mole of hexamine at zero moles of ammonium nitrate to a constant value of about 0.75 moles at high ammonium nitrate concentrations. This minimum value is reached in the region of two moles of ammonium nitrate (Figure No. 12). The existence of the minimum suggests that, even under ideal reaction conditions, some of the formaldehyde originally present in the hexamine cannot be converted to RDX or HMX. If this consideration is valid, the maximum theoretical yield of RDX may be represented as 87.5 percent on the formaldehyde basis. This implies that, during the degradation of hexamine (supposing a two-stage mechanism), formaldehyde may be split off in such a way that it cannot be converted to solid products by a synthesis process, even in the presence of an excess of ammonium nitrate.

With regard to the increased RDX yield, the decreased BSX yield and the decreased formaldehyde recovery, it is interesting to note that: (1) at low concentrations of ammonium nitrate (i.e., less than 0.5 moles), the RDX yield increases rapidly at the expense of the recoverable formaldehyde but not at the expense of the BSX yield; (2) at high concentrations

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* In this section, the term "recovery" signifies the quantity of a given compound which can be shown to be present in the diluted (or undiluted) mother liquor. In referring to the <u>total</u> recovery of a reagent (as in material balances), the terms "<u>total</u> recovery" and "amount of reagent accounted for" are used.

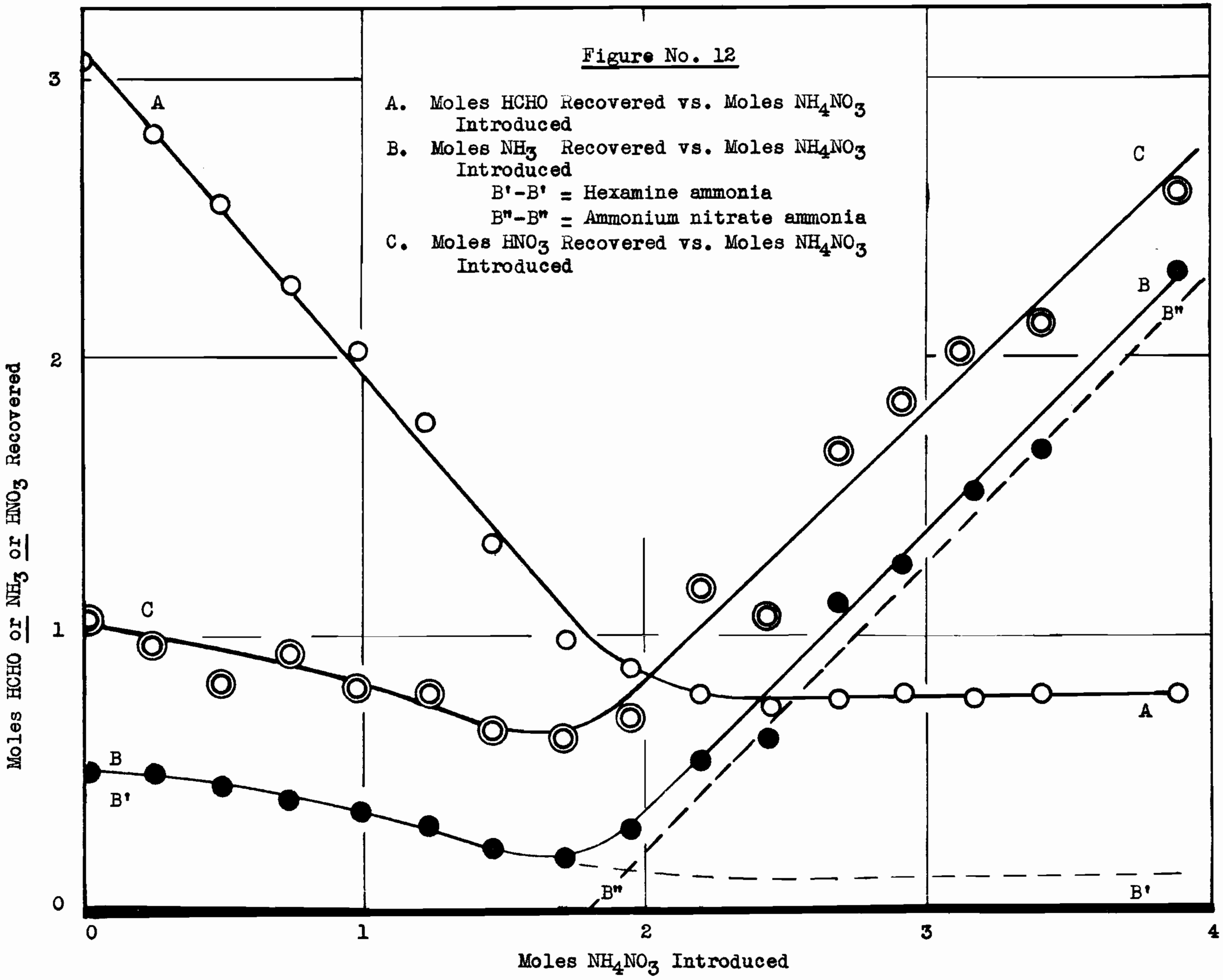

Figure No. 12

A. Moles HCHO Recovered vs. Moles NH_4NO_3 Introduced
B. Moles NH_3 Recovered vs. Moles NH_4NO_3 Introduced
B'-B' = Hexamine ammonia
B"-B" = Ammonium nitrate ammonia
C. Moles HNO_3 Recovered vs. Moles NH_4NO_3 Introduced
A
B
B'
B"
C
0
1
2
3
4
Moles HCHO or NH_3 or HNO_3 Recovered
Moles NH_4NO_3 Introduced

of ammonium nitrate (i.e., above two moles), the RDX yield increases slowly at the expense of the BSX but not at the expense of the recoverable formaldehyde; and (3) at intermediate concentrations of ammonium nitrate, the RDX yield increases rapidly at the expense of both the BSX and formaldehyde. In terms of the "catalysed nitrolysis - synthesis" mechanism, this implies that small concentrations of ammonium nitrate do not affect the nitrolysis step (giving BSX) to any great extent, the RDX being produced chiefly by a synthesis process; an excess of ammonium nitrate, on the other hand, improves the efficiency of the catalysed nitrolysis step (giving RDX, as contrasted with the uncatalysed nitrolysis step giving BSX) but does not result in increased synthesis, this process being comparatively efficient over the whole range of concentrations studied.

Ammonia:- The curve representing the recovery of ammonia is one of considerable importance since it forms the basis for the evaluation of the ammonium nitrate consumption and of the ratio of RDX production to ammonium nitrate consumption.

The first observation that can be made with regard to the curve (Figure No. 12) is that, when no ammonium nitrate is introduced, about 0.5 moles of ammonia is recovered from the mother liquor per mole of hexamine introduced. Secondly, as ammonium nitrate is introduced into the system in increasing quantities, less ammonia is recovered from the mother liquor. And, lastly, the amount of ammonia recovered from the mother liquor continues to decrease as the mole ratio of ammonium nitrate is increased until upwards of 1.75 moles of ammonium nitrate is being introduced (a theoretical excess considering the yields of RDX obtained) but from this point onwards, excess ammonium nitrate can be quantitatively recovered.

The results obtained in similar experiments at the University of Pennsylvania are shown in Figure No. 13. While, in general, the shape and significance of the curve seem to be the same as that shown in Figure No. 12, the curve is not as well defined and in almost every case the quantity of ammonia recovered is higher than for a corresponding case in Figure No. 12. The higher ammonia recovery as determined by Carmack may be accounted for by the slight differences in procedure used in the two laboratories. Carmack, in his experiments, destroyed the BSX by hydrolysis in the mother liquor without attempting to isolate it. In this way any ammonia arising during the decomposition of the BSX would be caught or, alternately, any ammonium nitrate occluded in the BSX would be recovered. In this laboratory, however, the BSX was isolated in the form of the crude solid product and was later destroyed in a fume-off procedure; ammonia from the above-mentioned sources would not be accounted for. While it has been stated that BSX gives no ammonium salts on hydrolysis (only oxides of nitrogen), the results presented here indicate otherwise. Alternately, it may be that the crude product contains some (hitherto unisolated) compound which can give ammonia on hydrolysis.

Now, it is evident that the ammonia recovered from the mother liquor

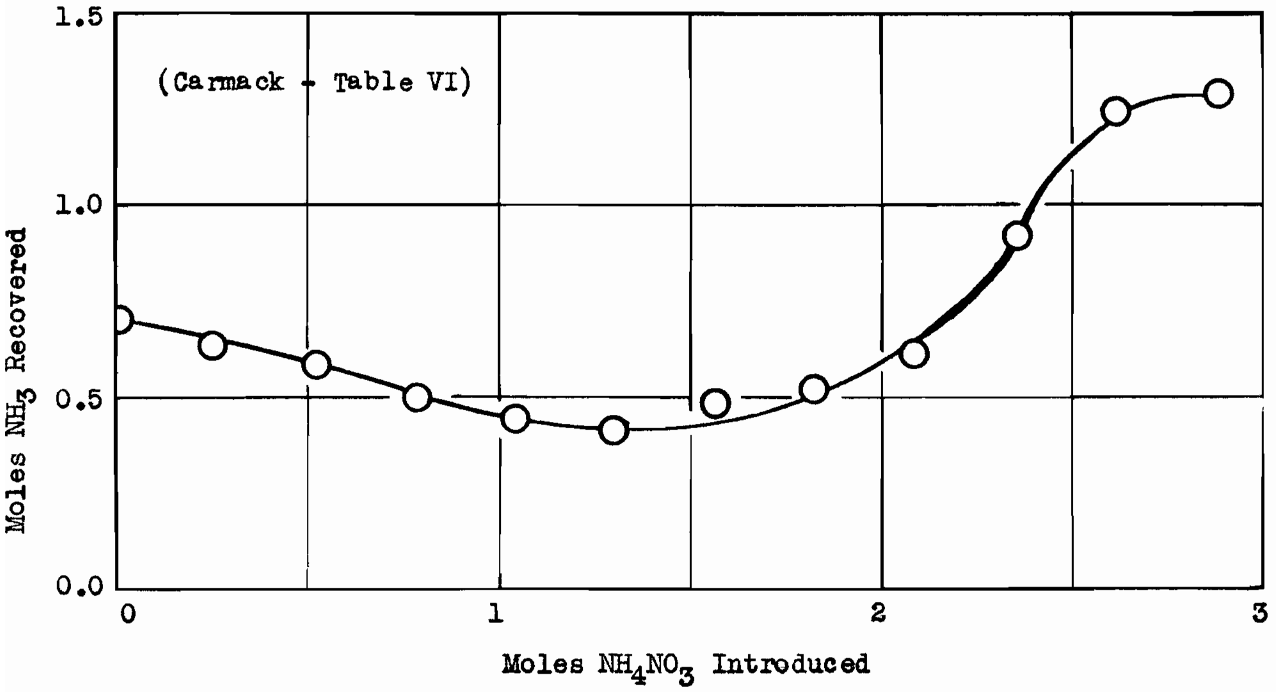

Figure No. 13

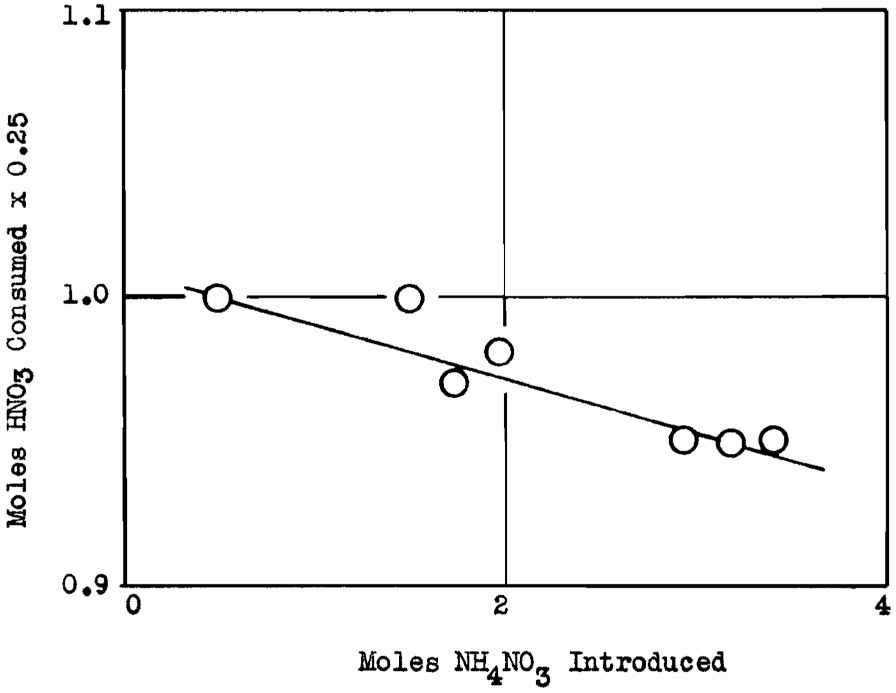

Figure No. 14

when no ammonium nitrate is introduced must originate in the hexamine molecule. It is further evident that, since the quantity of ammonia recovered decreases, the quantity of "hexamine ammonia" appearing in the diluted mother liquor must decrease. This decrease does not take place abruptly, however, and in fact there seems no reason* to believe that this value has decreased to zero even in the region of large excesses of ammonium nitrate.

These considerations are important since, as was stated previously (p. 157), if ammonium nitrate (or a substance analysing as ammonium nitrate) is generated in the Bachmann reaction, the ratio of RDX production to ammonium nitrate consumption will not be significant unless the ammonia generated can be quantitatively taken into account. At low concentrations of ammonium nitrate it is certain that amino nitrogen originating in the hexamine may be distilled from the alkaline mother liquor and would normally (i.e., in the treatment of Davy(16) and Carmack(92)) be considered as "ammonium nitrate not consumed". Whether this same thing occurs (on a reduced scale) at higher concentrations of ammonium nitrate or not seems to be a matter for controversy.

In the opinion of the author, "ammonium nitrate" is generated by the hexamine (in either the undiluted or diluted mother liquor) over the whole range of ammonium nitrate concentrations studied and, hence, the equivalence between RDX production and ammonium nitrate consumption as

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* See, however, the argument of Carmack(92) presented on p. 218.

determined by Davy and Carmack is not valid. The reasons for this belief are two in number. The first is based on an examination of the ammonia recovery curve (Figure No. 12): neither in the work of Carmack nor in the work herein reported has it been shown that the ammonia recovery drops to zero for any concentration of ammonium nitrate; in fact, it seems that the ammonia recovery curve would level off and become parallel to the X-axis if the reaction liquor could continue to consume all of the ammonium nitrate introduced. As it is, the ammonia recovery curve (B) can be resolved into two component curves, one representing amino nitrogen from the hexamine (B') and the other representing amino nitrogen from the ammonium nitrate (B"). This resolution indicates that (1) at low concentrations of ammonium nitrate all of the ammonium nitrate introduced is consumed, (2) at high concentrations, excess ammonium nitrate can be quantitatively recovered and (3) at all concentrations of ammonium nitrate hexamine amino nitrogen can be distilled from the mother liquor. The first two indications may be readily accepted and in their acceptance is some weight of justification for the third.

The second reason for the above-stated belief is based on the unexpected and unpredicted relationship between the formaldehyde recovery and the ammonia recovery (Figure No. 15). In the region of high formaldehyde recovery (i.e., when mole ratio of ammonium nitrate introduced is low), the quantities of ammonia and formaldehyde in the mother liquor decrease simultaneously and in direct proportion to one another. This proportionality holds rigidly in the region of ammonium nitrate deficiency (i.e. 0.00-1.75 moles per mole of hexamine) but, at the point where an

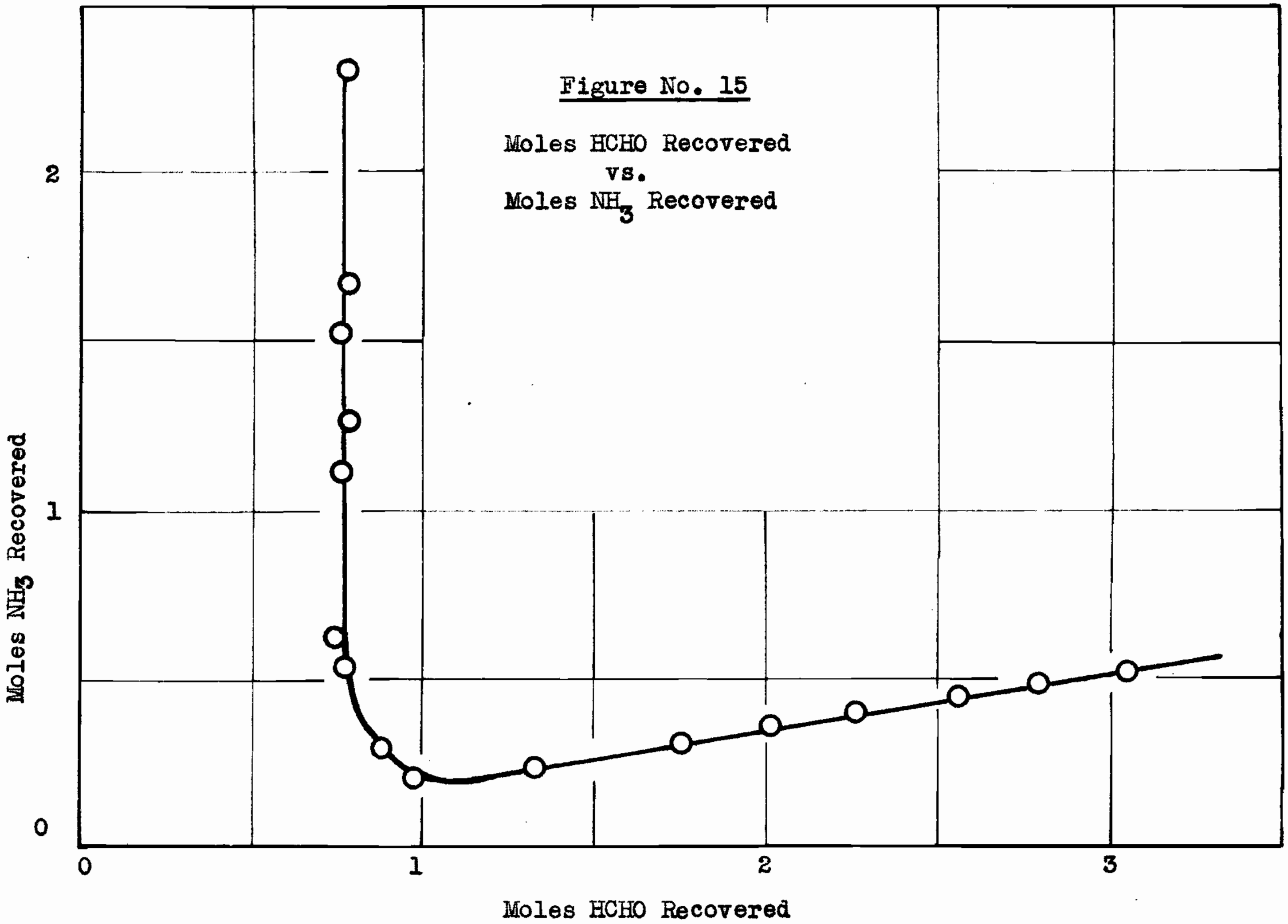

Figure No. 15

Moles HCHO Recovered
vs.
Moles NH_3 Recovered

excess of ammonium nitrate is established, the curve is discontinuous. It is apparent that this discontinuity may be directly attributed to the establishment of an ammonium nitrate excess and, this being so, it may be stated that the amount of formaldehyde recovered from the mother liquor is proportional to the amount of amino nitrogen recovered which originated in the hexamine. Thus, since the formaldehyde curve falls to a minimum value, the hexamine amino nitrogen curve (B') must do the same. Further analysis of the experimental data will show that the relationship of the recovered formaldehyde to the recovered ammonia is not unique. Several other variables may be shown to be related to the formaldehyde recovery, the ammonia recovery and to one another; among these are the production of BSX, the quantity of amino nitrogen not accounted for and the quantity of nitric acid not accounted for.

It should be pointed out that one assumption is implicit in the above arguments; that the mechanism of RDX formation is the same at low and at high concentrations of ammonium nitrate. This assumption is necessary in order that graphs showing well-defined trends may be extrapolated from the region of ammonium nitrate deficiency to the region of ammonium nitrate excess. That there is no discontinuity in mechanism seems to be indicated by the fact that there is no discontinuity in the magnitude of dependent variables while there is discontinuity in the magnitude of independent variables.

Carmack believes that "ammonium nitrate" is generated (hexamine incompletely nitrated) in the reaction liquor only at low concentrations of ammonium nitrate and hence that the equivalence between RDX production and ammonium nitrate consumption is valid in the region of ammonium nitrate excesses. His reason for so believing is based on an interpretation of the ammonia balance in the reaction and will be discussed later (see p.217).

It has been stated that if "ammonium nitrate" is generated by the hexamine, a correction must be applied if the ratio of RDX production to ammonium nitrate consumption is to be valid. In view of the foregoing discussion, an emperical correction may be formulated as follows:

$$C_x = C_o \frac{f_x}{f_o}$$

where C_x = moles hexamine amino nitrogen* in the diluted mother liquor of a run to which x moles of ammonium nitrate is introduced,

C_o = moles hexamine amino nitrogen in the diluted mother liquor of a run to which zero moles of ammonium nitrate was introduced,

f_x = moles formaldehyde in the mother liquor of the former run, and

f_o = moles formaldehyde in the mother liquor of the latter.

The correction C_x should be subtracted from the quantity of ammonia recovered to obtain a value for the "ammonium nitrate not consumed". For this particular series of runs $C_x = 0.167 f_x$. The correction is small at high concentrations of ammonium nitrate.

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* That is, amino nitrogen which originated in the hexamine rather than in the ammonium nitrate.

The important question of ammonium nitrate consumption and other aspects of the ammonia recovery are discussed on pp.207 and 225.

Nitric Acid:- It has already been pointed out that nitric acid in the mother liquor may be present in the free state or in the form of a salt. In Figure No. 16, the recovery of free nitric acid, combined nitric acid and total nitric acid are plotted against the mole ratio of ammonium nitrate.

The quantity of free nitric acid recovered from the mother liquor increases slightly as the ammonium nitrate concentration is increased (Figure No. 16). This corresponds to a slight decrease in the amount consumed. This decrease is such that, at low ammonium nitrate concentrations, one mole of hexamine consumes 4.0 moles of nitric acid while, at high concentrations, one mole of hexamine consumes 3.8 moles of nitric acid (Figure No. 14). These results agree with those of Bachmann(61) who reported that between 3.8 and 3.9 moles of nitric acid are consumed in the normal Bachmann reaction.

The curve representing combined nitric acid (Figure No. 16) closely follows the curve representing recovered ammonia (Figure No. 17). While the former is displaced downwards somewhat over the whole range of ammonium nitrate concentrations, there seems little doubt that the ammonia and combined nitric acid exist together in the form of ammonium nitrate. The slight difference between the two curves is probably due to the incomplete precipitation of nitron nitrate. It was originally thought that the nitric acid and ammonia might be present in the form of hexa-

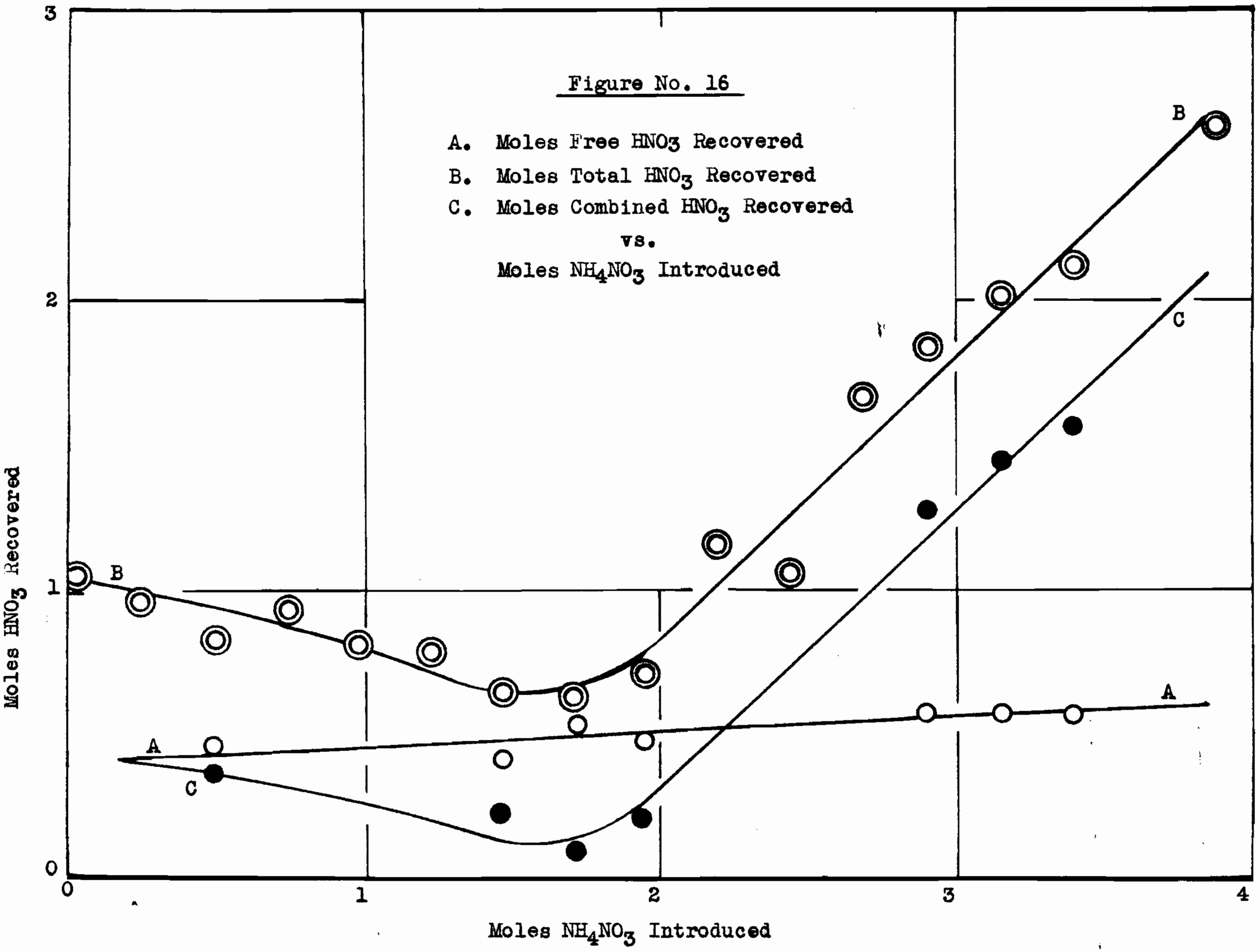

Figure No. 16

A. Moles Free HNO_3 Recovered

B. Moles Total HNO_3 Recovered

C. Moles Combined HNO_3 Recovered

vs.

Moles NH_4NO_3 Introduced

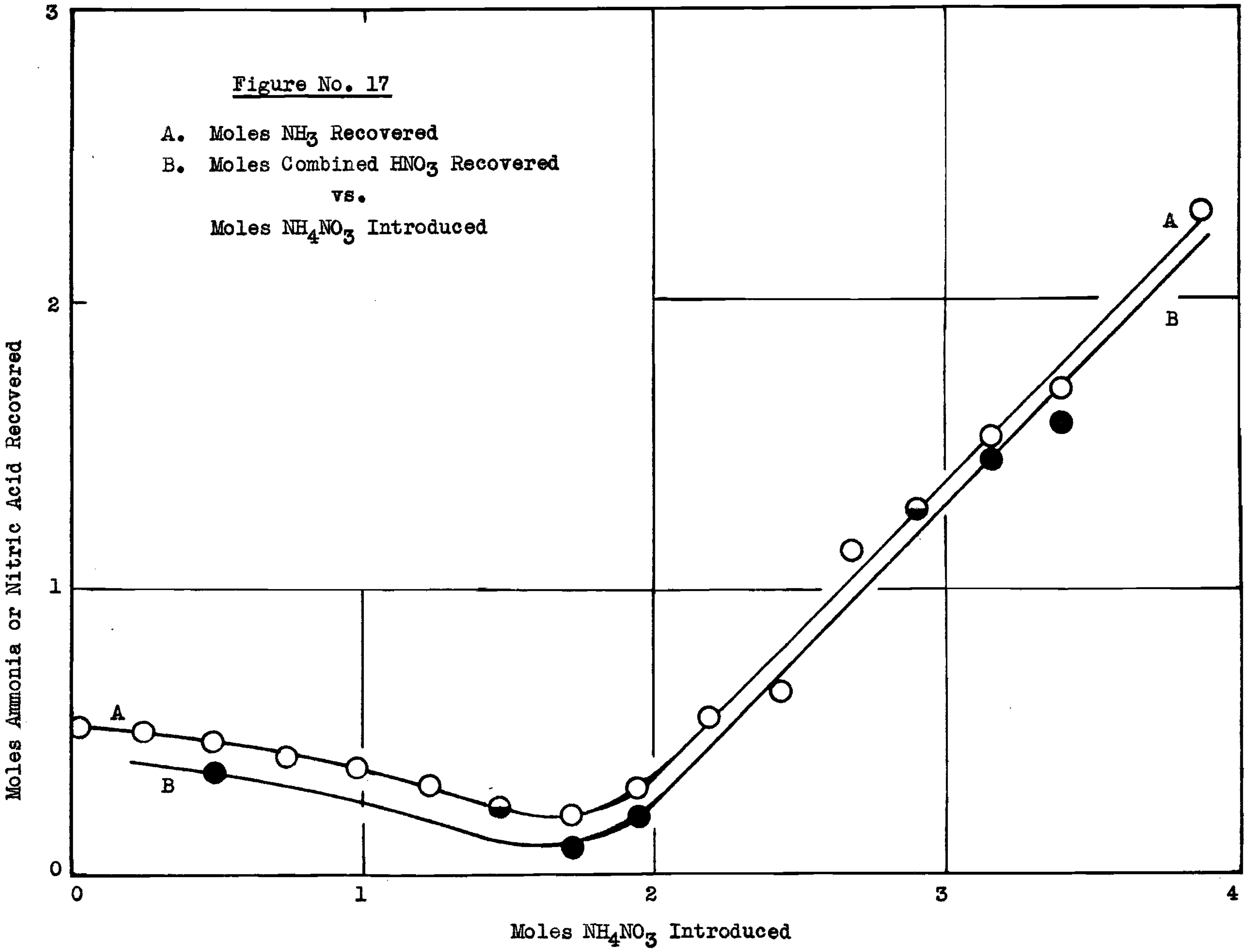

Figure No. 17

A. Moles NH_3 Recovered

B. Moles Combined HNO_3 Recovered

vs.

Moles NH_4NO_3 Introduced

mine dinitrate. In this case the ratio between the two would be 1:2 rather than 1:1. The values of the ratio are given in Table V. In four cases it approximates 1:1, in one case it is 1:2 and in two cases it is intermediate between the two other values. It might seem that this ratio is inconclusive, then, but it is noteworthy that those values of the ratio which deviate widely from unity are derived from the region of low ammonia and nitric acid recovery where small analytical errors are magnified when the quantities are calculated as ratios. In general, evidence is against the existence of hexamine as such in the diluted mother liquor and against the possibility of survival of hexamine in the Bachmann reaction.

Acetic Anhydride:- The acetic anhydride may be determined before dilution in which case a figure is obtained representing the acetic anhydride which does not react. The acetic anhydride may also be determined after dilution (as acetic acid) in which case a figure is obtained representing the acetic anhydride which is not consumed.*

The amount of unreacted acetic anhydride present in the undiluted reaction liquor was determined only in a few cases, and it may be that these results are in considerable error. It was apparent, however, that as the ammonium nitrate concentration is increased the amount of acetic anhydride not reacting decreased (Figure No. 18). No relationships other than this qualitative one are volunteered although they may well

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* The distinction between "reaction" and "consumption" lies in the fact that the former includes hydrolysis while the latter does not.

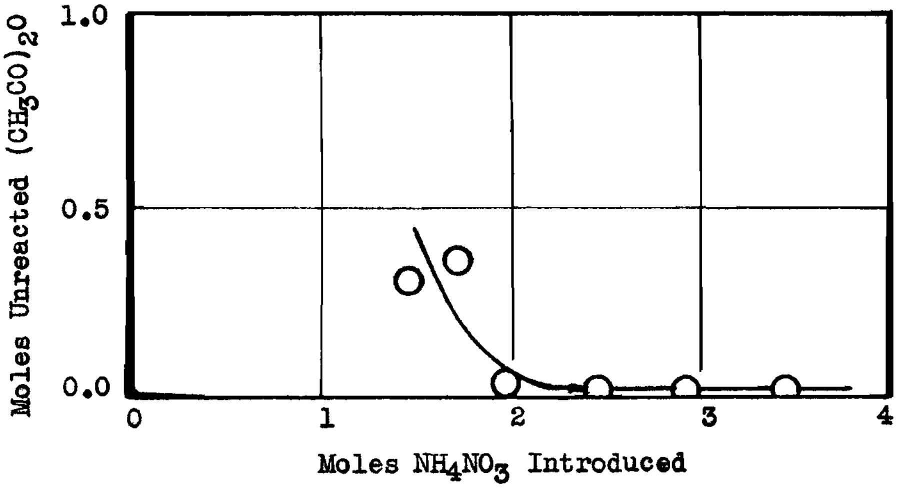


Figure No. 18

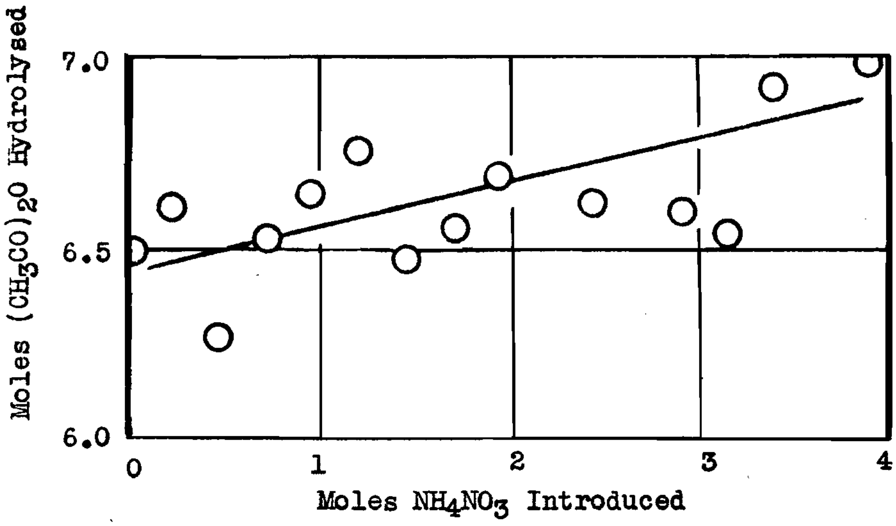


Figure No. 19

exist. One result of these analyses was the discovery that, at high concentrations of ammonium nitrate, insufficient quantities of anhydride were being introduced to ensure an excess at the end of the reaction. In view of this fact, a new series of runs was carried out in order to show the effect of excess anhydride. These experiments (hereinafter described) showed increased yields of RDX for high concentrations of ammonium nitrate but invalidated none of the arguments set forth here.

The amount of acetic anhydride not consumed during the reaction apparently increases as the ammonium nitrate concentration is increased (Figure No. 19). This behaviour, however, is poorly defined. The experimental error in the titration of acetic acid in the diluted mother liquor is high due to the presence of interfering substances (see p.177). This error is probably about five percent which is of the same order of magnitude as the expected decrease in anhydride consumption due to decreased BSX formation. In view of the apparent lack of trend of the points in Figure No. 19, the coefficient of correlation between the two variables was calculated and found to be 0.71. Further, the slope of the straight line which was considered to best define the variation was found to be about 0.075. This slope corresponds to a decrease in anhydride consumption of 0.30 moles. The decrease in BSX yield is about 0.50 moles.

3. Material Balances

<u>Formaldehyde</u>:- The total recovery of formaldehyde (i.e., the number of moles of formaldehyde accounted for) and the percent recovery were

calculated from the yield of RDX, the yield of BSX, the yield of HMX, and the quantity of formaldehyde recovered from the diluted mother liquor. The results of these calculations are given in Table V and the percent recovery is plotted as a function of the mole ratio of ammonium nitrate in Figure No. 20.

These results indicate that at high ammonium nitrate concentrations all of the formaldehyde introduced may be accounted for. At low concentrations, however, a slight loss of formaldehyde is incurred corresponding to about five percent of the formaldehyde introduced. The fact that formaldehyde can be quantitatively recovered at high mole ratios of ammonium nitrate is of considerable importance since, once established, it may be used to guage the accuracy of other analyses and can be used as the basis for new deductions.

It seems that there are two possible explanations for the loss of formaldehyde in runs of low ammonium nitrate concentration. The first is indicated by the results of a series of runs (hereinafter reported) in which the effect of variation in the holding time after dilution was investigated. It was found that certain, easily-decomposable by-products are present in the crude product of runs of low ammonium nitrate concentration. If the crude product is allowed to stand in contact with the diluted mother liquor, these by-products will completely decompose within three or four days at room temperature; the formaldehyde liberated in this decomposition remains in solution in the diluted mother liquor and will be titrated during the formaldehyde analysis. If, however, the

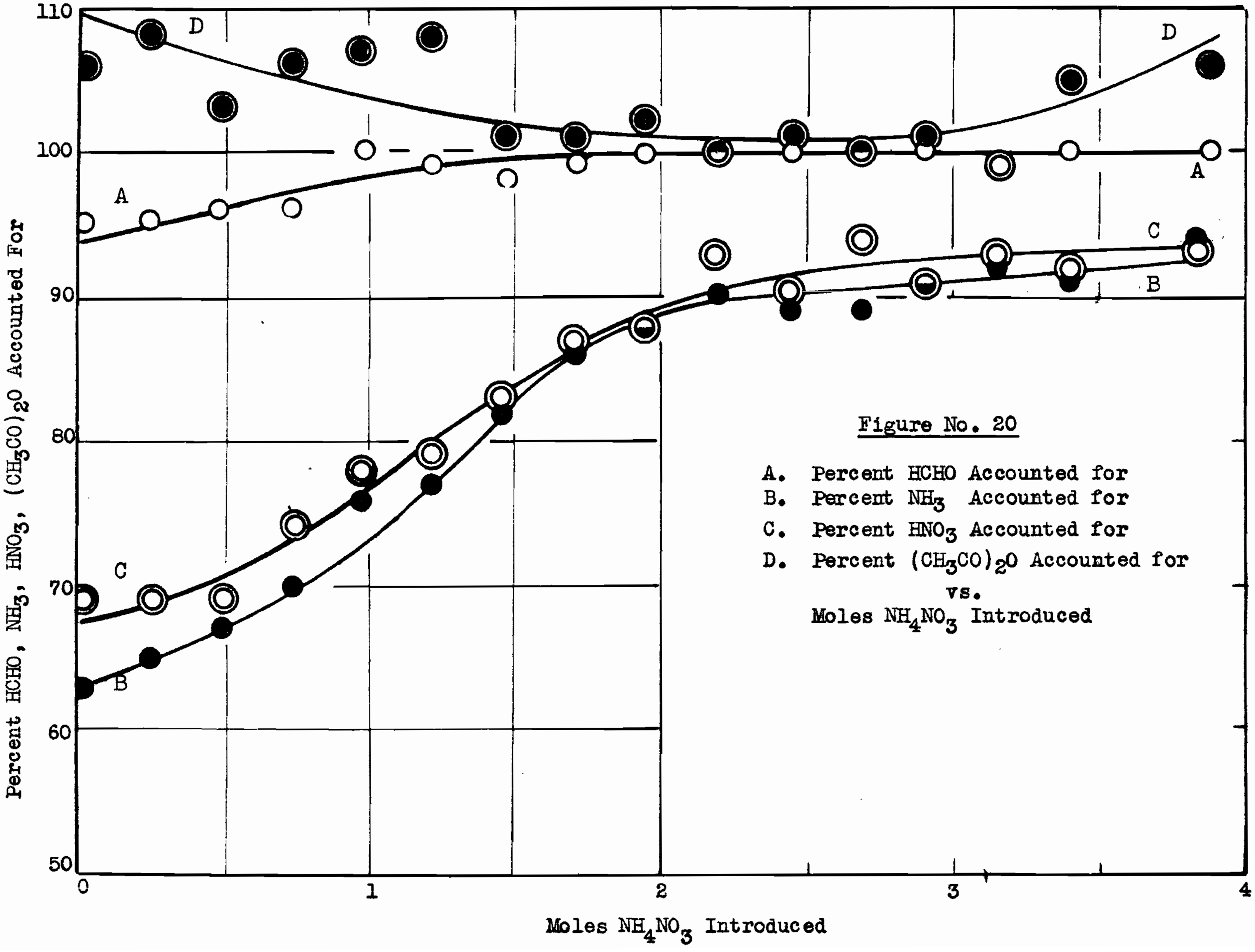


Figure No. 20

A. Percent HCHO Accounted for
B. Percent NH$_3$ Accounted for
C. Percent HNO$_3$ Accounted for
D. Percent (CH$_3$CO)$_2$O Accounted for

vs.

Moles NH$_4$NO$_3$ Introduced

crude product is filtered off before the by-product has completely decomposed, this by-product decomposes in the air and the liberated formaldehyde is lost to the system. At the time of the early material balance experiments, the significance of the long holding time after dilution was not fully appreciated and the diluted mother liquor was allowed to stand unfiltered for about one day only. Thus, in runs of low ammonium nitrate concentration, formaldehyde may have been lost to the air during the drying of the product.

The second possible explanation is indicated by the results of a series of runs (hereinafter presented) in which the effect of varying the reaction temperature was studied. It was found that for runs in which no ammonium nitrate whatsoever is present a slight loss of formaldehyde is incurred at high temperatures; thus at 60°C. all of the formaldehyde is accounted for, at 70°C. about 97 percent and at 80°C. only about 92 percent. Since the loss of formaldehyde seems to be associated with a diminution in yield of both RDX and BSX, one may conclude that the loss of formaldehyde is due to the oxidative destruction of hexamine or some closely related compound. Thus, in runs of low ammonium nitrate concentration, formaldehyde may have been lost by oxidation of the hexamine during the Bachmann reaction.

Ammonia:- The total recovery and the percent recovery of ammonia were calculated from the yield of RDX, the yield of BSX, the yield of HMX and the quantity of ammonia recovered from the diluted mother liquor, remembering that amino nitrogen is derived from both the hexamine and the ammonium nitrate. The results of these calculations are given in Table V and the percent ammonia accounted for is plotted as a function of the ammonium nitrate concentration in Figure No. 20.

In contrast to the recovery of formaldehyde, the ammonia recovery varies widely and is comparatively inefficient. At zero concentration of ammonium nitrate, only about 65 percent of the amino nitrogen introduced is recovered. The percent accounted for rises rapidly until, at the two mole level of ammonium nitrate, about 90 percent of the amino nitrogen introduced can be accounted for. As the mole ratio of ammonium nitrate is increased still further, only a slight increase in the percent recovery is observed. Essentially the same behaviour was found by Carmack (Figure No. 21). Somewhat the same picture is obtained if the quantity of amino nitrogen not recovered is plotted against the mole ratio of ammonium nitrate (Figure No. 22).

It is apparent from these observations that hexamine nitrogen is being lost to the system. It is also apparent that, as the ammonium nitrate concentration is increased, less hexamine amino nitrogen is lost to the system. The question arises, at this point, as to whether amino nitrogen originating in the ammonium nitrate is lost either during or subsequent to the reaction. It has already been pointed out that such a loss would invalidate the previously-determined ratios of RDX production to ammonium nitrate consumption since this loss was not quantitatively taken into account. Carmack(96) has shown that formaldehyde and formaldehyde-producing substances interfere with the recovery of ammonia

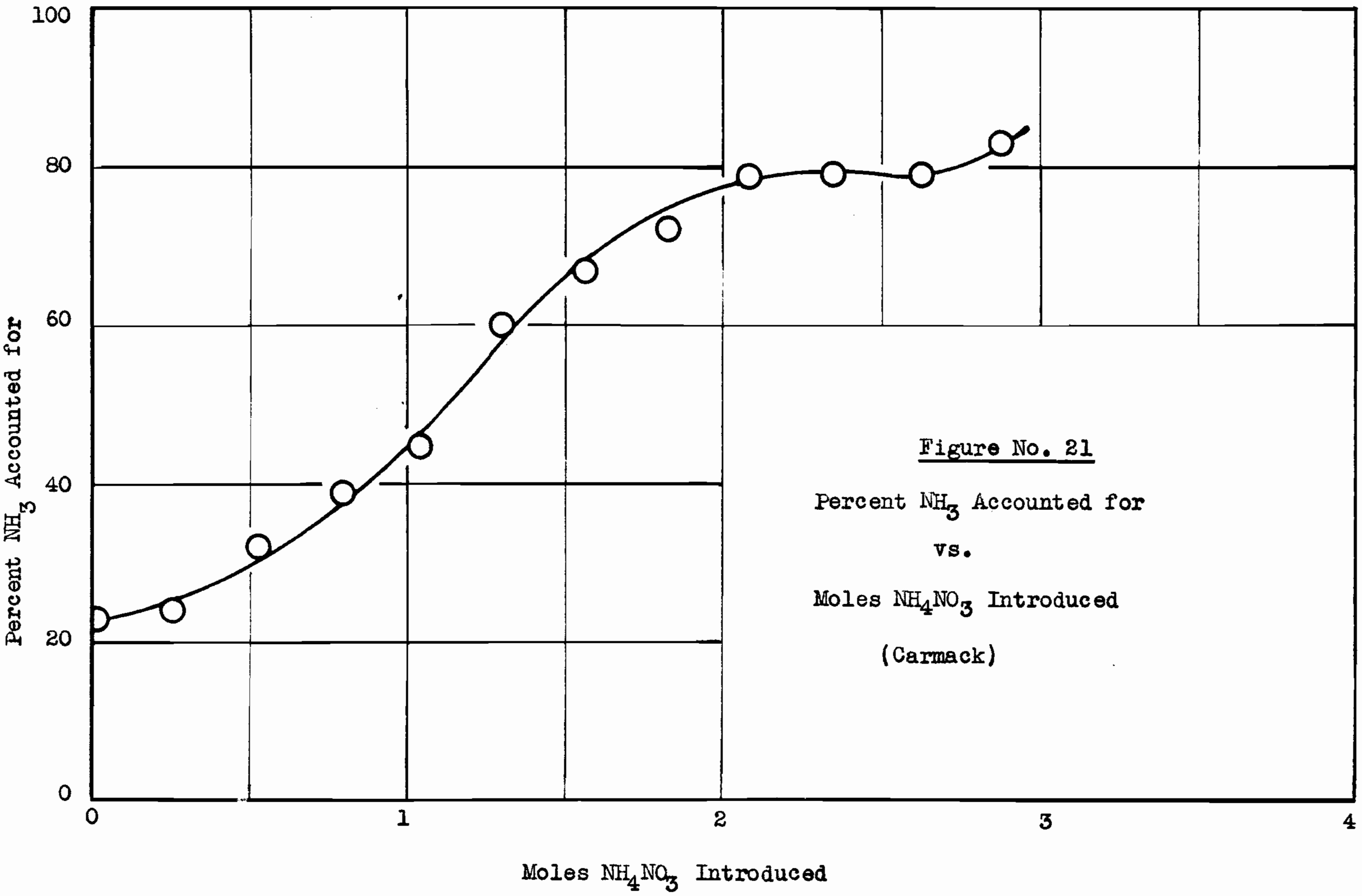


Figure No. 21

Percent NH_3 Accounted for

vs.

Moles NH_4NO_3 Introduced

(Carmack)

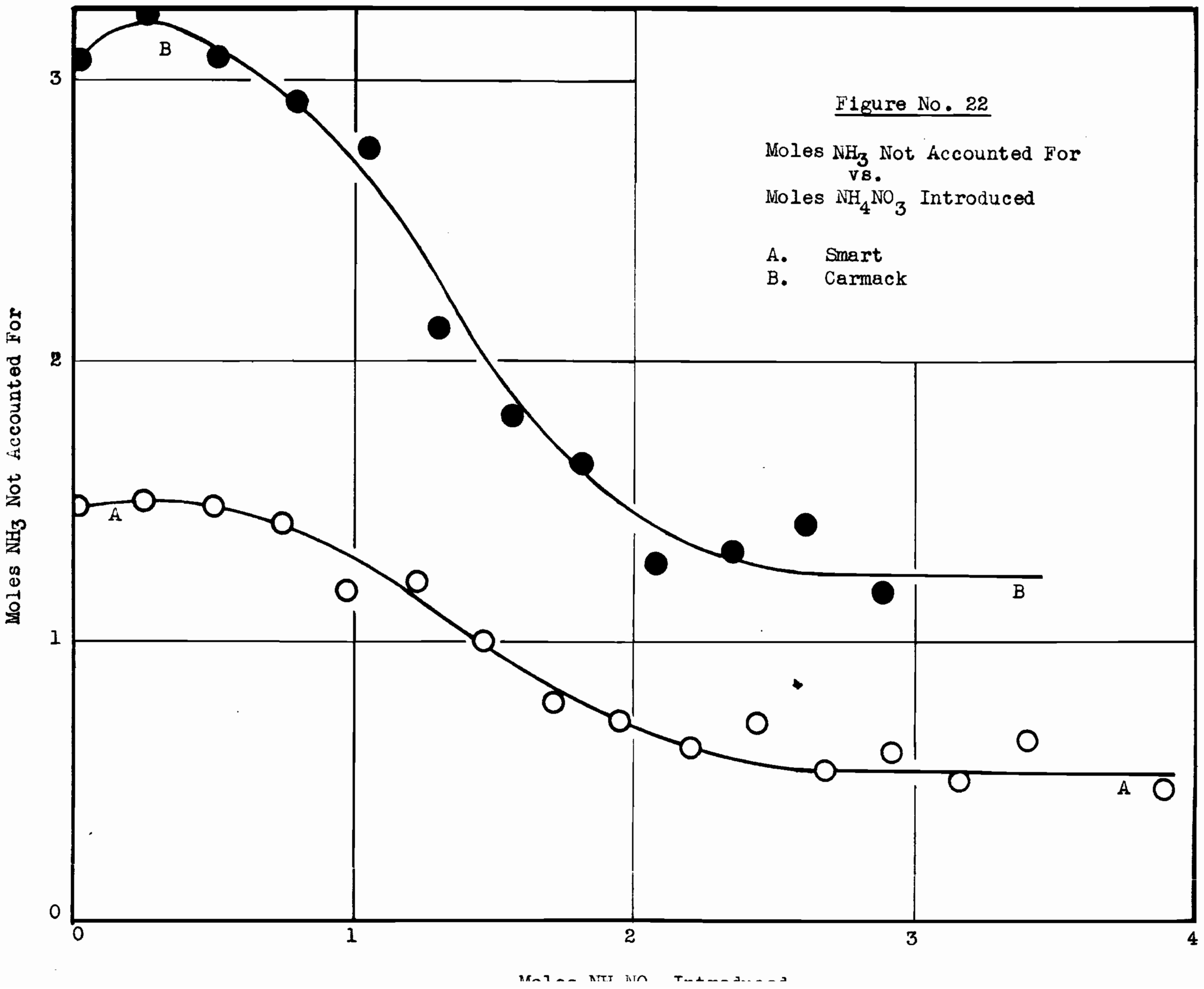


Figure No. 22

Moles NH_3 Not Accounted For
vs.
Moles NH_4NO_3 Introduced

A. Smart
B. Carmack

from the diluted mother liquor. This implies that, in runs of low mole ratios of ammonium nitrate (i.e., when a large amount of formaldehyde is available in the mother liquor), amino nitrogen which originated in the ammonium nitrate escapes analysis. The opinion has already been expressed by the author, however, that under these reaction conditions all ammonium nitrate introduced is consumed anyway. That ammonium nitrate can be destroyed by reaction with acetic anhydride is beyond question; that ammonium nitrate is destroyed by concentrations of acetic anhydride prevailing in the pseudo-continuous Bachmann reaction is extremely doubtful. The reasons for this belief are as follows:

(a) It has been shown (Figure No. 22) that, as the ammonium nitrate concentration is increased for a given concentration of acetic anhydride, less amino nitrogen is unaccounted for.

(b) As the acetic anhydride concentration is increased for a given concentration of ammonium nitrate, less amino nitrogen is lost to the system. (Compare Table V and Table VIII). (See also Figure No. 41.)

(c) The amount of amino nitrogen unaccounted for in the Bachmann reaction is roughly proportional to the quantity of BSX produced (Figure No. 23). This relationship would be unlikely if ammonium nitrate were being destroyed by the acetic anhydride.

The manner in which amino nitrogen is lost to the system forms an interesting topic for speculation. Closely linked with this is the

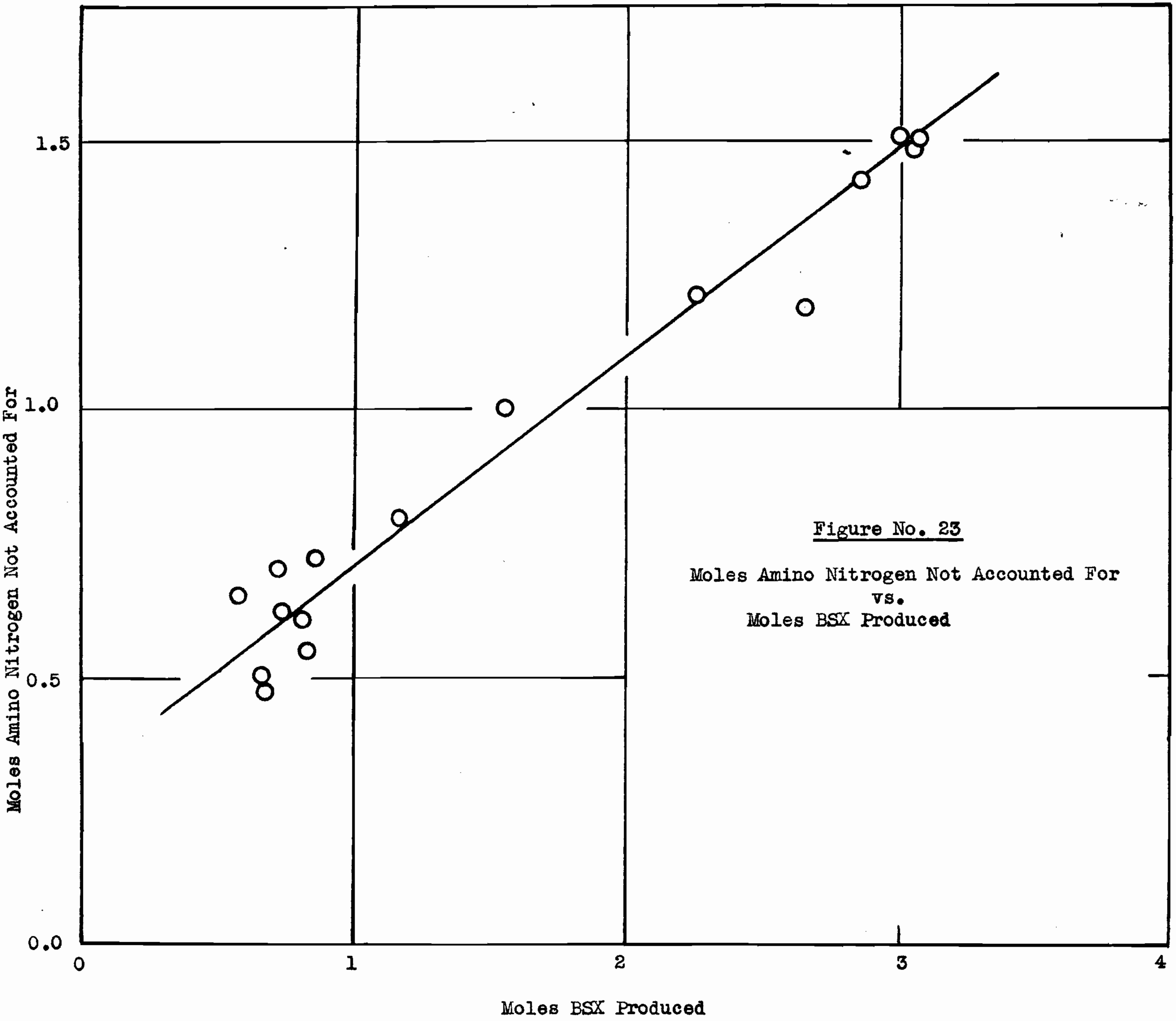
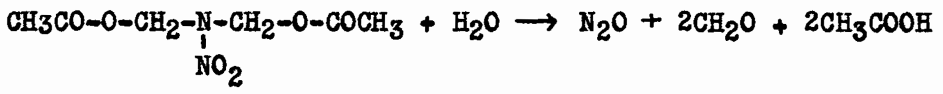


Figure No. 23

Moles Amino Nitrogen Not Accounted For
vs.
Moles BSX Produced

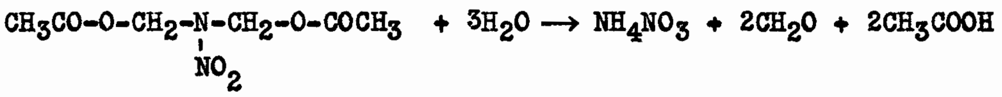
question of the presence of distillable amino nitrogen in the diluted mother liquor of a run to which no ammonium nitrate has been added.

In the opinion of the author, the amino nitrogen which cannot be accounted for in the material balance is lost to the system through the formation of inisolable nitramines which decompose upon dilution to give, in part, nitrous oxide, formaldehyde and acetic acid. This may be illustrated by the example of the diacetate of dimethylolnitramine:



$$\mathrm{CH3CO{-}O{-}CH_2{-}\underset{NO_2}{N}{-}CH_2{-}O{-}COCH_3} + \mathrm{H_2O} \longrightarrow \mathrm{N_2O} + \mathrm{2CH_2O} + \mathrm{2CH_3COOH} \quad \ldots\ldots\ 207$$

it is also the opinion of the author that the presence of distillable amino nitrogen in the diluted mother liquor of a run to which no ammonium nitrate is introduced can be accounted for by supposing an alternate type of decomposition for the diacetate of dimethylolnitramine (and similar compounds):



$$\mathrm{CH_3CO{-}O{-}CH_2{-}\underset{NO_2}{N}{-}CH_2{-}O{-}COCH_3} + \mathrm{3H_2O} \longrightarrow \mathrm{NH_4NO_3} + \mathrm{2CH_2O} + \mathrm{2CH_3COOH} \quad \ldots\ldots\ 208$$

While this type of decomposition is not general for nitramines, it has been reported that RDX is decomposed in dilute alkali to give ammonium nitrate along with nitrous oxide(100).

Some support for these postulated decompositions lies in the proportionality of (1) the amount of amino nitrogen unaccounted for, and (2) the amount of hexamine amino nitrogen in the diluted mother liquor to the calculated amount of easily-decomposable nitramines (Figures Nos.25 and 24). This latter factor is obtained by assuming that the two types

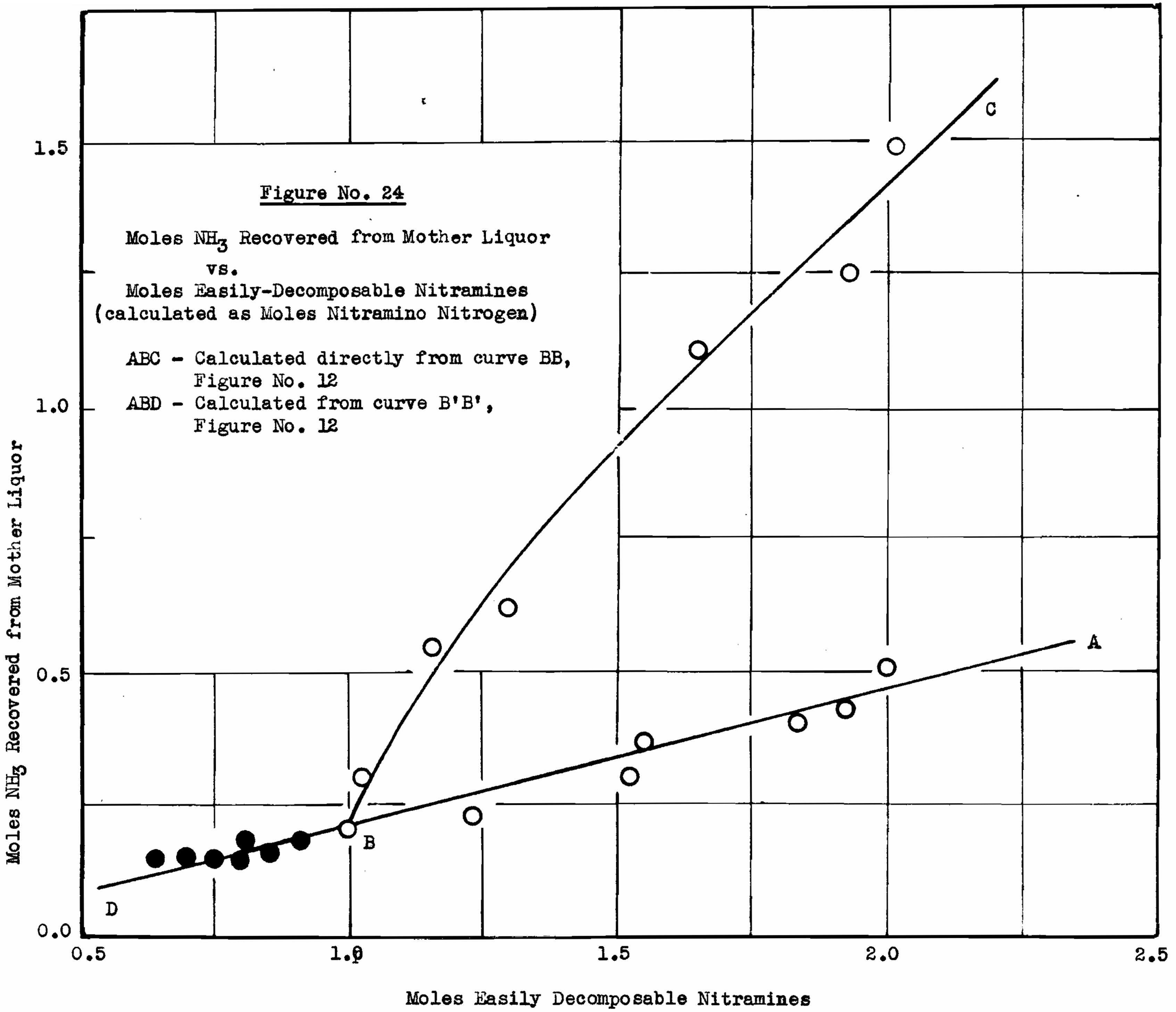


Figure No. 24

Moles NH_3 Recovered from Mother Liquor
vs.
Moles Easily-Decomposable Nitramines
(calculated as Moles Nitramino Nitrogen)

ABC - Calculated directly from curve BB, Figure No. 12

ABD - Calculated from curve B'B', Figure No. 12

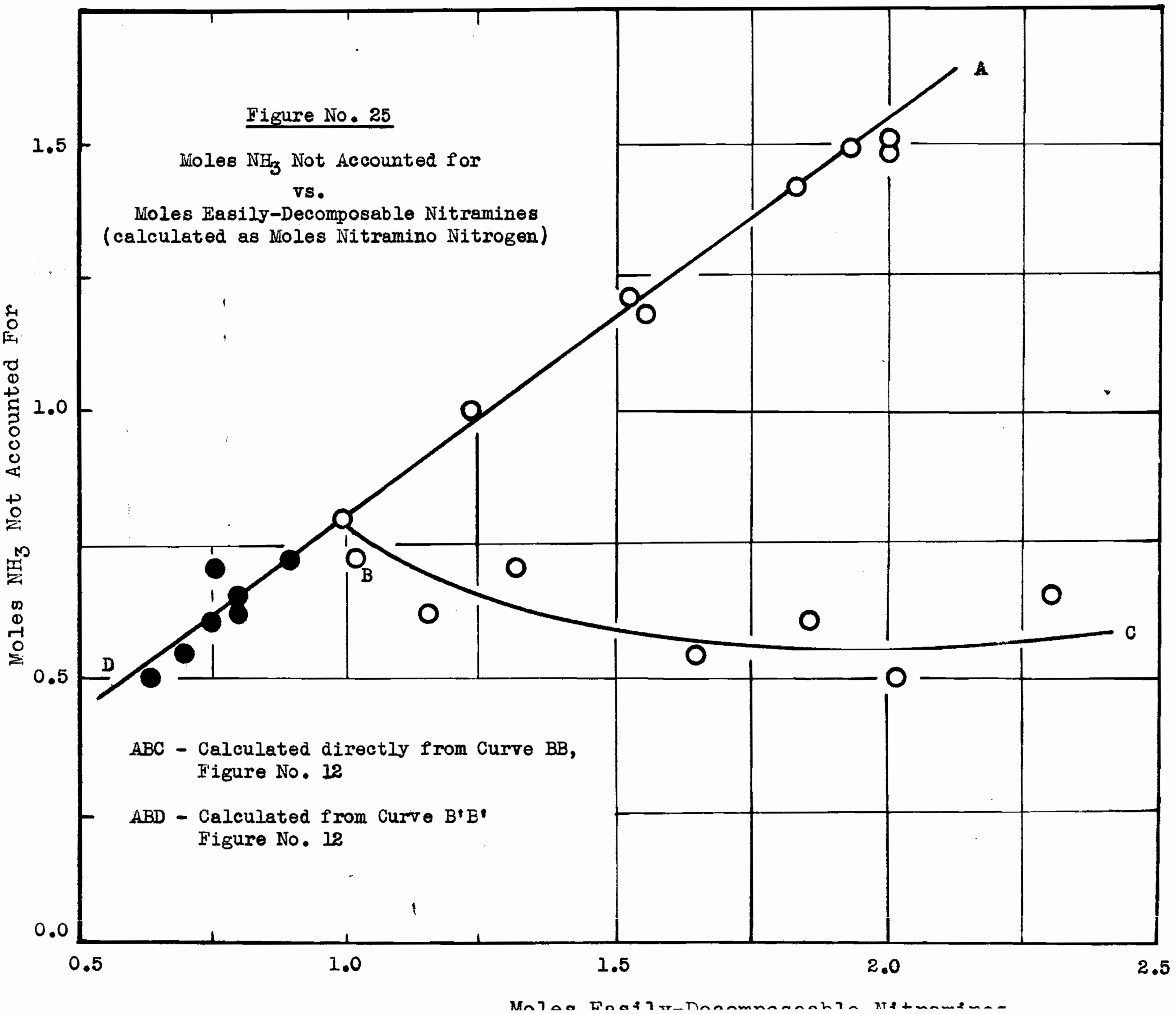


Figure No. 25

Moles NH_3 Not Accounted for
vs.
Moles Easily-Decomposable Nitramines
(calculated as Moles Nitramino Nitrogen)

ABC - Calculated directly from Curve BB, Figure No. 12

ABD - Calculated from Curve B'B' Figure No. 12

of decomposition shown above represent the fate of all of the easily-decomposable nitramines; the number of moles of hexamine amino nitrogen in the mother liquor plus the number of moles of amino nitrogen unaccounted for is thus taken as the number of moles of nitramino nitrogen present in the easily-decomposable nitramines.

Further explanation of Figures Nos. 24 and 25 is necessary. If, instead of the hexamine amino nitrogen in the mother liquor, the total amount of ammonia in the mother liquor is used, it will be observed that as the reaction passes from a condition of ammonium nitrate deficiency to a condition of ammonium nitrate excess, the curves in both Figures Nos. 24 and 25 show discontinuity. If, however, only the amino nitrogen arising from the hexamine is considered (as estimated from curve B' in Figure No. 12), the curve is not discontinuous and the proportionality holds throughout the range of ammonium nitrate concentrations investigated.

Further support for the postulated decomposition represented in equation 208 is found in Figure No. 15 where the amino nitrogen present in the diluted mother liquor is plotted as a function of the available formaldehyde in the mother liquor. Formaldehyde is produced in the decomposition of the postulated easily-decomposable nitramines and, while not all of the formaldehyde need be derived from this source, these two factors should be related. This relationship is observed in the proportionality of the quantity of hexamine amino nitrogen to the quantity of formaldehyde in the diluted mother liquor.

An alternate explanation for the loss of amino nitrogen lies in the postulation that hexamine is oxidized during the reaction to oxides of nitrogen. This is considered unlikely. Other explanations for the presence of amino nitrogen in the diluted mother liquors of runs to which little or no ammonium nitrate is introduced are possible. One of these explanations is that some of the hexamine introduced into the system survives the treatment with acetyl nitrate or the Bachmann reagents and generates ammonia or methyl amine at some stage subsequent to dilution. Winkler(90) has shown, however, that hexamine disappears in the reaction liquor extremely rapidly even at 35°C. Further, experiments involving the belated addition of ammonium nitrate indicate that no appreciable amount of hexamine survives treatment with acetyl nitrate. A second alternative is that some reaction by-product or intermediate containing unnitrated amino nitrogen may generate ammonia subsequent to dilution. This explanation is not without merit. In particular, it is possible the triacetate of trimethylolamine exists in the reaction liquor and that, due to its symmetry, it is able to resist the attack of nitrating agents.

Carmack, in his series of papers (92, 93, 94, 95, 96), discusses the ammonia balance in the Bachmann reaction in some detail. From the yield of RDX(B) and the quantity of ammonia recovered from the mother liquor, he has calculated the total number of moles of amino nitrogen recovered; by subtracting this from the number of moles of amino nitrogen introduced, a figure representing amino nitrogen unaccounted for was obtained. It was assumed that the amino nitrogen not recovered had escaped as nitrous oxide during the hydrolysis of the by-product linear nitramines and, on this basis, the percent hexamine converted to linear compounds was calculated. When this figure was added to the yield of RDX(B) (i.e. the percent hexamine converted to cyclic compounds), a new figure representing the percent conversion of hexamine to nitramines was obtained. Carmack found that at high mole ratios of ammonium nitrate (i.e. greater than two moles per mole of hexamine), all of the hexamine is converted to nitramines, but at low mole ratios, the conversion may be as low as 80 percent. This behaviour is shown in Table VI and in Figure No. 26. In the work reported herein, however, it was found that at high mole ratios of ammonium nitrate figures were obtained representing hexamine conversions considerably greater than 100 percent (Table VII and Figure No. 26(b)).

Carmack's discussion of the ammonia balance favours the validity of the equivalence between RDX production and ammonium nitrate consumption as determined by Davy, a point of view which is contested in this thesis. In the first place, it holds that, while at low ammonium nitrate concentrations hexamine is incompletely nitrated and the ratio between RDX and ammonium nitrate is meaningless, at high concentrations, the hexamine is completely nitrated and the ratio is significant. And secondly, Carmack points out that if hexamine conversions of greater than 100 percent are observed it is indicative of incomplete recovery of ammonia (or RDX). In view of these statements, the reasoning of Carmack was subjected to critical analysis.

It should first be emphasized that, while Carmack speaks of "hexamine incompletely nitrated" and this thesis of "ammonia generated by the hexamine", the difference in terminology or interpretation is not of

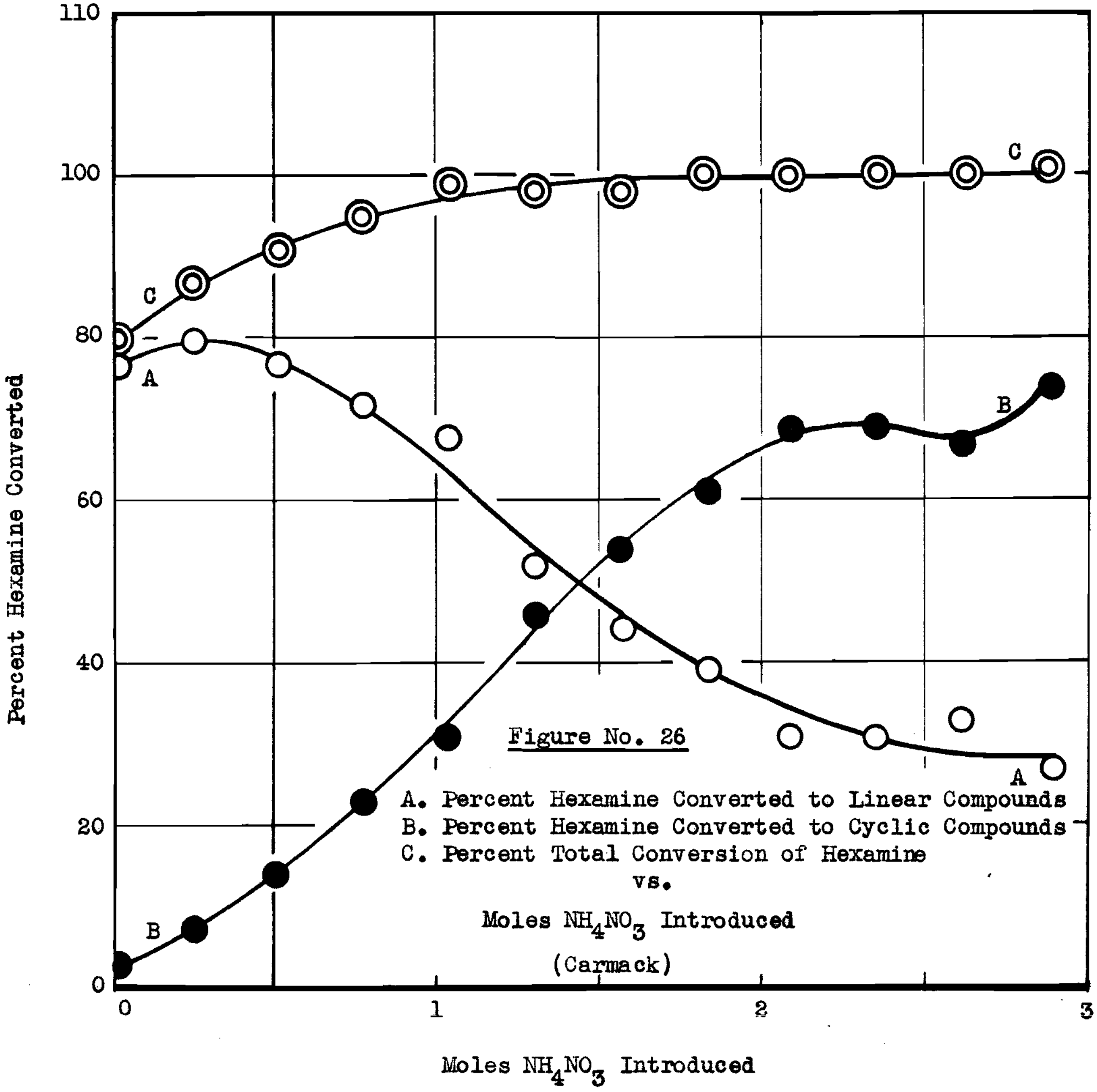


Figure No. 26

A. Percent Hexamine Converted to Linear Compounds
B. Percent Hexamine Converted to Cyclic Compounds
C. Percent Total Conversion of Hexamine
vs.
Moles NH_4NO_3 Introduced
(Carmack)

TABLE VIII

BACHMANN REACTION:-AMINO NITROGEN BALANCE BY THE METHOD OF CARMACK. SEE ALSO TABLE V

RUN NUMBER	AMINO NITROGEN ADDED			AMINO NITROGEN RECOVERED				AMINO NITROGEN LOST	HEXAMINE CONVERTED			TOTAL HEXAMINE CONVERTED	
	AS $(CH_2)_6N_4$	AS NH_4NO_3	TOTAL	AS NH_3	AS RDX	AS HMX	TOTAL		TO LINEAR NITRAMINES	TO RDX	TO HMX	BASED ON RDX(B)	BASED ON RDX
	MOLES			MOLES				MOLES	PERCENT			PERCENT	
1	4.00	0.00	4.00	0.51	0.18	0.01	0.70	3.30	82.5	3.0	0.3	86	86
2	4.00	0.25	4.25	0.49	0.42	0.02	0.93	3.32	83.0	7.0	0.6	91	90
3	4.00	0.49	4.49	0.45	0.69	0.05	1.19	3.30	82.5	11.5	1.2	95	94
4	4.00	0.74	4.74	0.41	1.11	0.10	1.62	3.12	78.0	18.5	2.4	99	97
5	4.00	0.98	4.98	0.37	1.68	0.15	2.20	2.78	69.5	28.0	3.7	101	98
6	4.00	1.23	5.23	0.31	2.07	0.26	2.64	2.59	64.8	34.5	6.4	106	99
7	4.00	1.47	5.47	0.23	3.00	0.32	3.55	1.92	48.0	50.0	8.0	106	98
8	4.00	1.72	5.72	0.20	3.69	0.33	4.22	1.50	37.5	61.5	8.3	107	99
9	4.00	1.95	5.95	0.30	4.14	0.29	4.73	1.22	30.5	69.0	7.2	107	100
10	4.00	2.20	6.20	0.54	4.35	0.24	5.13	1.07	26.8	72.5	6.0	105	99
11	4.00	2.44	6.44	0.62	4.26	0.43	5.31	1.13	28.3	71.0	10.7	110	99
12	4.00	2.68	6.68	1.11	4.35	0.20	5.66	1.02	25.5	72.5	5.1	103	98
13	4.00	2.91	6.91	1.25	4.35	0.20	5.80	1.11	27.8	72.5	5.0	105	100
14	4.00	3.16	7.16	1.51	4.44	0.23	6.18	0.98	24.5	74.0	5.7	104	99
15	4.00	3.40	7.40	1.66	4.50	0.25	6.41	0.99	24.8	75.0	6.2	106	100
16	4.00	3.88	7.88	2.29	4.50	0.23	7.02	0.86	21.5	75.0	5.7	102	97

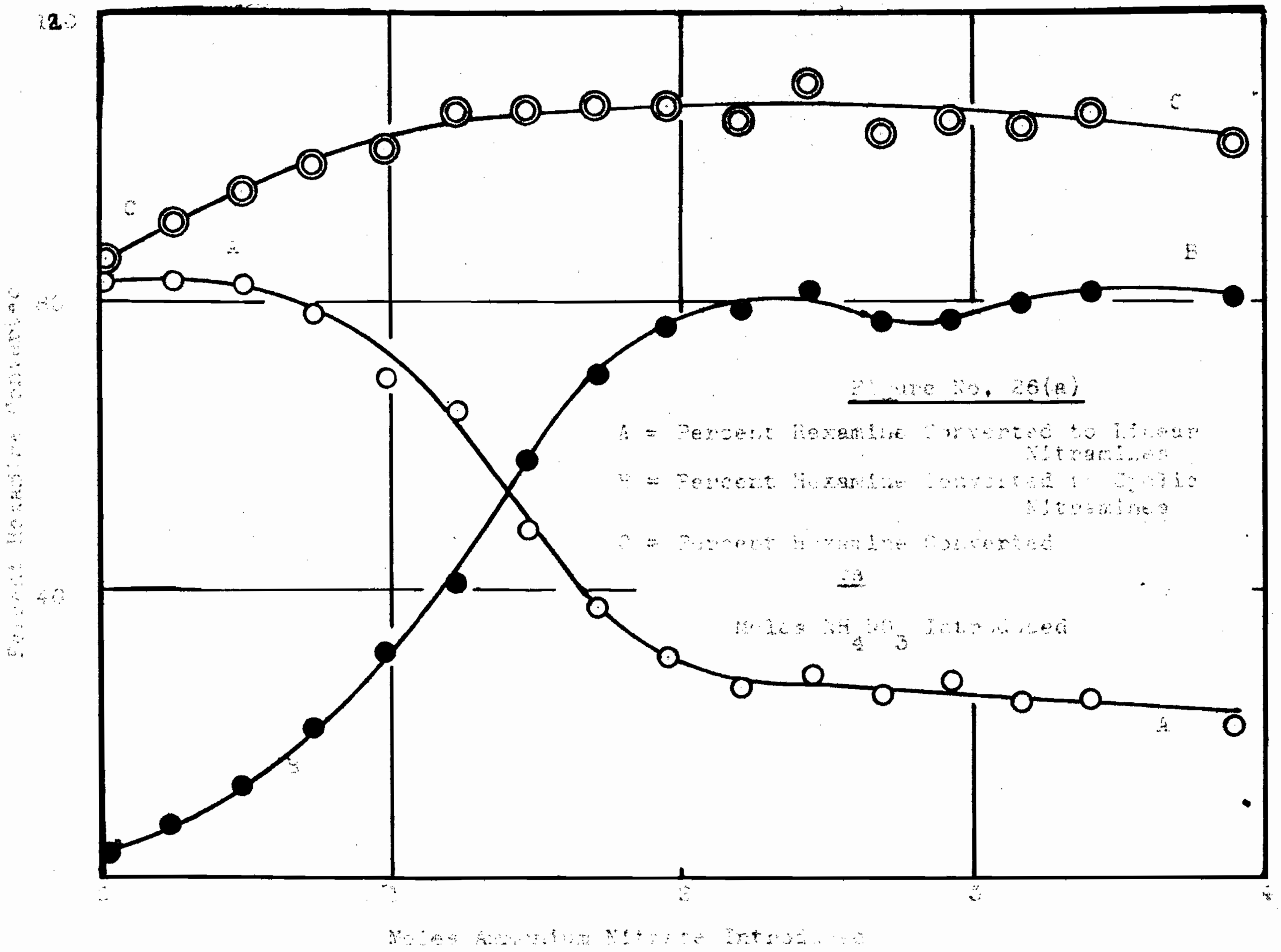


Figure No. 26(a)

fundamental importance. The important fact is that amino nitrogen which originated in the hexamine appears in the mother liquor.

In calculating his yield of linear nitramine, Carmack used the following basic equation:

$$\bar{N}(\text{hexamine}) + \bar{N}(\text{ammonium nitrate}) = \bar{N}(\text{RDX(B)}) + \bar{N}(\text{mother liquor}) + \bar{N}(\text{linear nitramines}) \quad \ldots\ldots \text{A}$$

where $\bar{N}$ = amino nitrogen,

and where the so-called linear nitramines are assumed to have quantitatively decomposed during the simmering process giving nitrous oxide. It is obvious that the amino nitrogen in the mother liquor originated in both the hexamine and ammonium nitrate (although in a given run either of these factors may be zero):

$$\bar{N}(\text{mother liquor}) = \bar{N}_{hex}(\text{mother liquor}) + \bar{N}_{an}(\text{mother liquor}) \quad \ldots\ldots \text{B}$$

where $\bar{N}_{hex}$(mother liquor) = hexamine amino nitrogen in the mother liquor, and

$\bar{N}_{an}$(mother liquor) = ammonium nitrate amino nitrogen in the mother liquor.

If it be assumed that the Davy mechanism is correct, then equation A may be written in the following form:

$$\bar{N}(\text{hexamine}) = \bar{N}(\text{RDX(B)}) + \bar{N}_{hex}(\text{mother liquor}) + \bar{N}(\text{linear nitramines}) \quad \ldots\ldots\ldots \text{C}$$

In this case, if the hexamine conversion is found to be quantitative, the quantity of ammonia generated by the hexamine must be zero and the ratio of RDX production to ammonium nitrate consumption will be valid for this particular run. Furthermore, in this case, if the hexamine conversion is found to be represented as being greater than 100 percent, loss of ammonia (or RDX) during analysis is implied. If, however, the mechanism of the reaction is assumed to be a two-stage process (e.g. nitrolysis and synthesis), the derivation of equation C from equation A is invalid, since, for example, RDX may be produced without the incorporation of two moles of hexamine amino nitrogen. In this case, the extent of the hexamine conversion as calculated by Carmack is not significant since it can fall below 100 percent when the nitrolysis reaction predominates and can rise above 100 percent when the synthesis reaction predominates.*

As a result of the critical analysis, then, it may be stated that Carmack's argument is not conclusive since he used his conclusion as a major premise. No explanation is volunteered for the fact that on calculation he obtains figures representing a quantitative conversion of hexamine. In this connection, however, it should be pointed out that in Table VII, when the calculated yield of linear nitramines is added to the yield of RDX (<u>not RDX(B)</u>), a quantitative conversion of hexamine is obtained. Had Carmack's method of calculation been sound, it would have indicated that, while RDX may be produced by the mechanism of Davy, HMX is produced by a synthesis process and by a synthesis process alone.

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* It should be pointed out, however, that the mere evaluation of the percent conversion will not alone tell the extent of the nitrolysis and synthesis steps since the N_{hex}(mother liquor) factor is also important in this respect.

In view of the fact that Carmack suggested that calculated hexamine conversions of greater than 100 percent were indicative of a loss of ammonia, it is interesting to observe that the quantities of ammonia recovered in experiments carried out in this laboratory were somewhat less than those reported by Carmack. It is believed that, in view of the foregoing discussion, these values are not in error due to ammonia loss, but are indicative of a higher overall conversion of hexamine to nitramines (in the terminology used by Carmack) or of an increased proportion of linear nitramines as compared with cyclic nitramines (on the basis of the explanations volunteered on p. 213). If Carmack's calculations had been valid, it would have indicated that linear nitramines yield ammonium nitrate during the simmer process or that the crude reaction product contains some as yet unidentified product which either has a free amine group or else can generate ammonia on hydrolysis.

Nitric Acid:- The total recovery and the percent recovery of nitric acid were calculated from the yield of RDX, the yield of BSX, the yield of HMX and the total quantity of nitric acid recovered from the diluted mother liquor. The results of these calculations are given in Table V and the percent nitric acid accounted for is plotted as a function of the mole ratio of ammonium nitrate in Figure No. 20.

It will be observed that the nitric acid and the amino nitrogen recovery curves parallel one another closely. It was subsequently found that the ratio of amino nitrogen unaccounted for to nitric acid unaccounted for is equal to unity no matter what the mole ratio of ammonium nitrate (Table V). The establishment of this value for the ratio enabled the prediction that the losses of amino nitrogen and nitric acid are related: nitric acid probably reacts with hexamine amino nitrogen to give, ultimately, nitrous oxide. This deduction is in accord with the earlier postulation (p.213) that amino nitrogen is lost to the system via the decomposition of inisolable, easily-hydrolysable nitramines into nitrous oxide, formaldehyde and acetic acid.

Acetic Anhydride:- The total recovery and the percent recovery of acetic anhydride were calculated from the yield of BSX and the quantity of acetic acid in the diluted mother liquor. The results of these calculations are given in Table V and in Figure No. 20. The curve representing the quantity of anhydride accounted for is irregular and in many cases it indicates that more anhydride can be recovered than was introduced into the reaction. The reasons for this condition have already been pointed out on p. 177. No explanation is volunteered for the general shape of the curve.

4. Miscellaneous Considerations Concerning the Reaction Mechanism

As has already been indicated, the principle objective of this research is the attempt to determine the validity of the equivalence between RDX production and ammonium nitrate consumption (as presented by Davy and Carmack).

In Table V, six different possible values of the ratio are given for each of the sixteen concentrations of ammonium nitrate studied. The first set of three values is based on the yield of RDX while the second set of three is based on the yield of RDX(B). The values of the two sets differ but little and the two are included mainly for the sake of completeness.

The first ratio of each set of three, "UNCORR." (Figure No. 28), is derived by using the value for the ammonium nitrate consumption as obtained directly by difference: ammonium nitrate introduced minus the amino nitrogen recovered from the diluted mother liquor. This value of the ammonium nitrate consumption is given in Table V and is plotted as a function of the mole ratio of ammonium nitrate in Figure No. 27. It will be observed that, since at low concentrations of ammonium nitrate more ammonia is recovered than is ammonium nitrate introduced, the value of the ammonium nitrate consumption (and hence the value of the ratio) is negative. The value of the ratio increases numerically to minus infinity, is discontinuous, decreases numerically from plus infinity to a minimum value of about 0.8 (at a concentration of 1.25 moles of ammonium nitrate per mole of hexamine) and then increases slightly to a value of about 0.9. That Carmack obtained the same result is shown in Table VI and in Figure No. 29.

The second ratio in each set of three, "CORR.I" (see Figures Nos. 30 and 31 for the ratios based on RDX and RDX(B) respectively), is derived by using the corrected value for the ammonium nitrate consumption. As was shown previously (p.198), the corrected value is equal to the uncorrected value plus a correction, $C_X = C_O \cdot f_X/f_O$, which is designed to compensate for the fact that some of the ammonia recovered

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Only the ratio based on RDX(B) is shown.

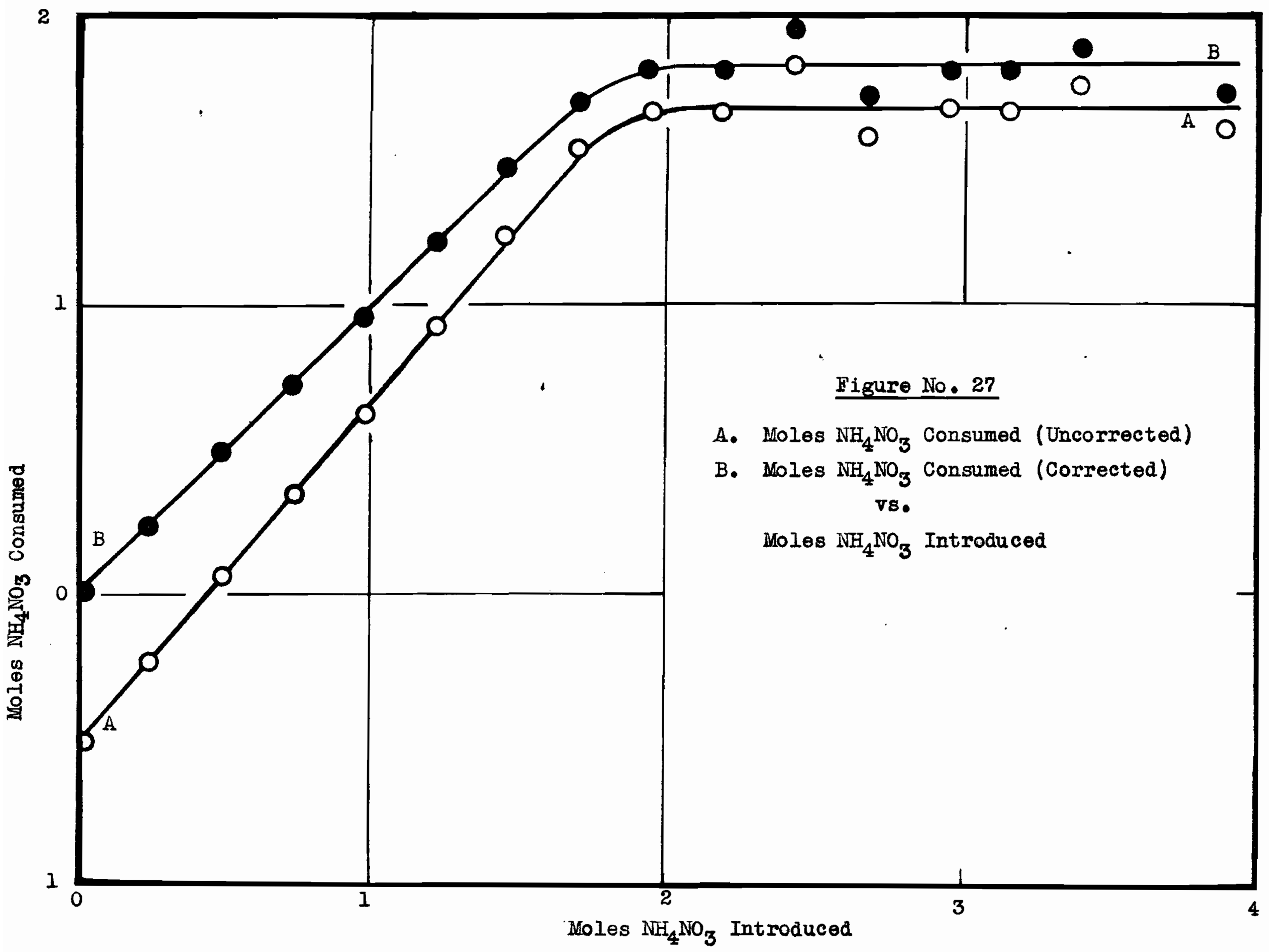

Figure No. 27

A. Moles NH_4NO_3 Consumed (Uncorrected)

B. Moles NH_4NO_3 Consumed (Corrected)

vs.

Moles NH_4NO_3 Introduced

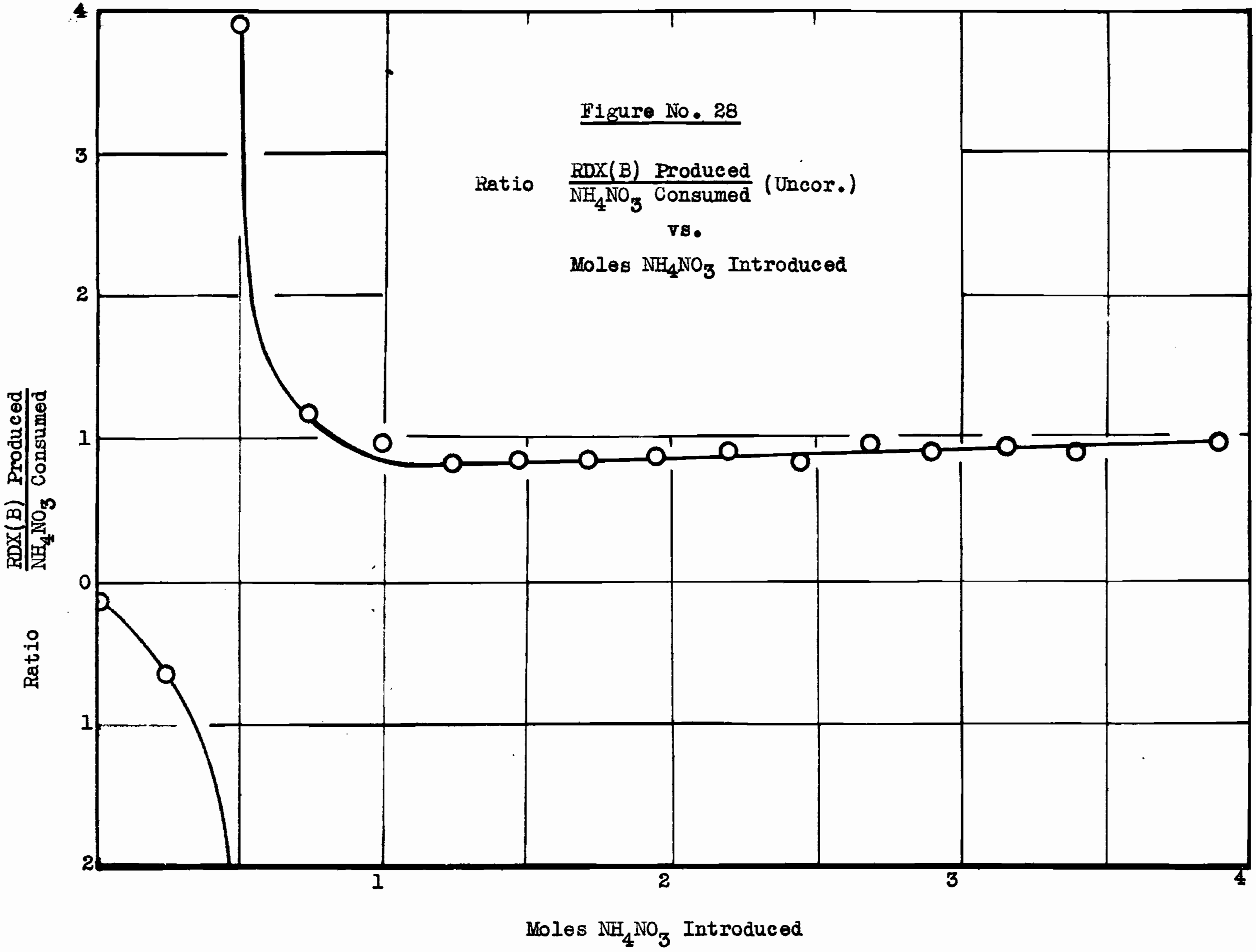

Figure No. 28

Ratio $\frac{RDX(B)\ Produced}{NH_4NO_3\ Consumed}$ (Uncor.)

vs.

Moles NH_4NO_3 Introduced

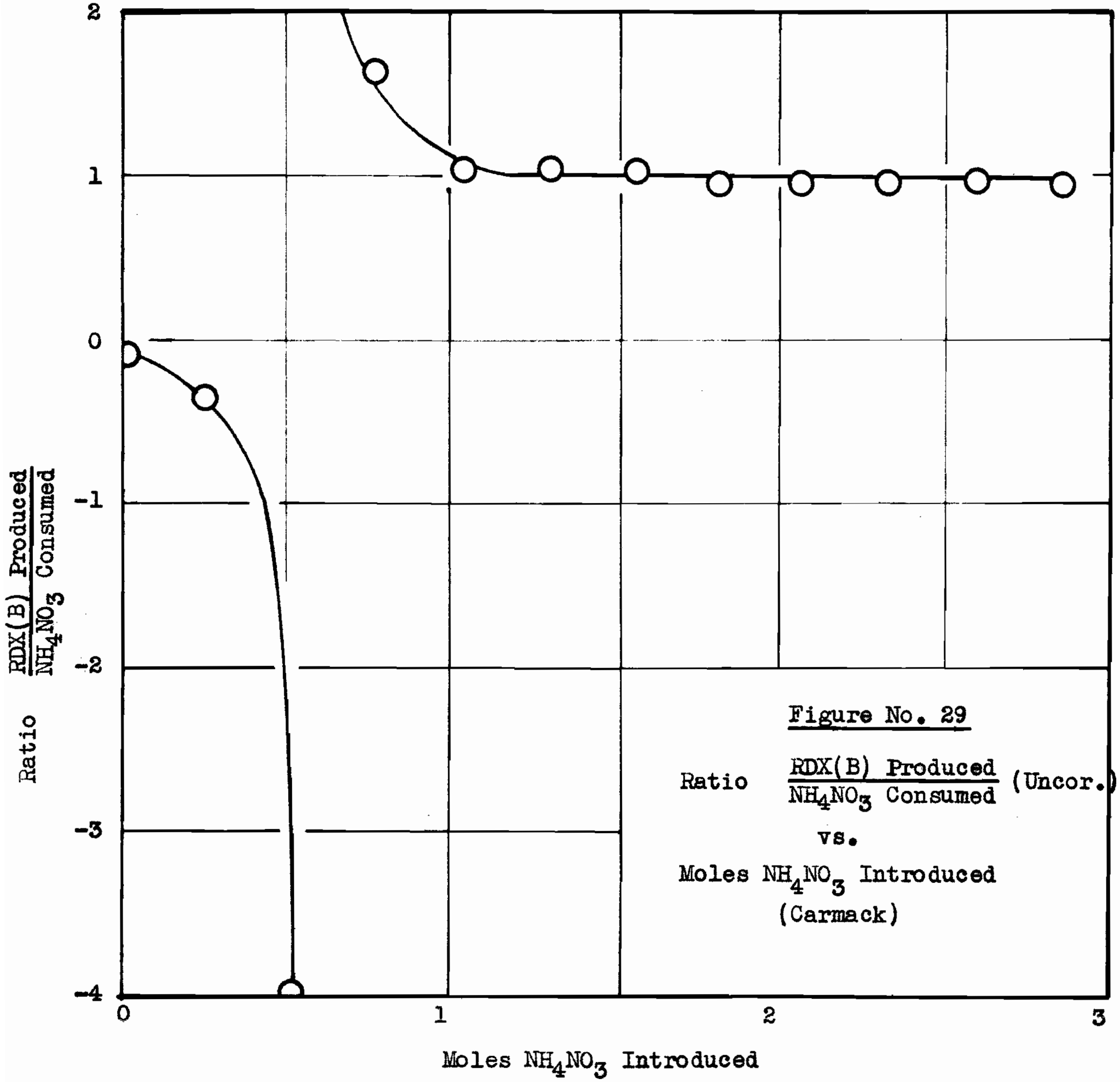

Figure No. 29

Ratio $\frac{RDX(B)\ Produced}{NH_4NO_3\ Consumed}$ (Uncor.)

vs.

Moles NH_4NO_3 Introduced

(Carmack)

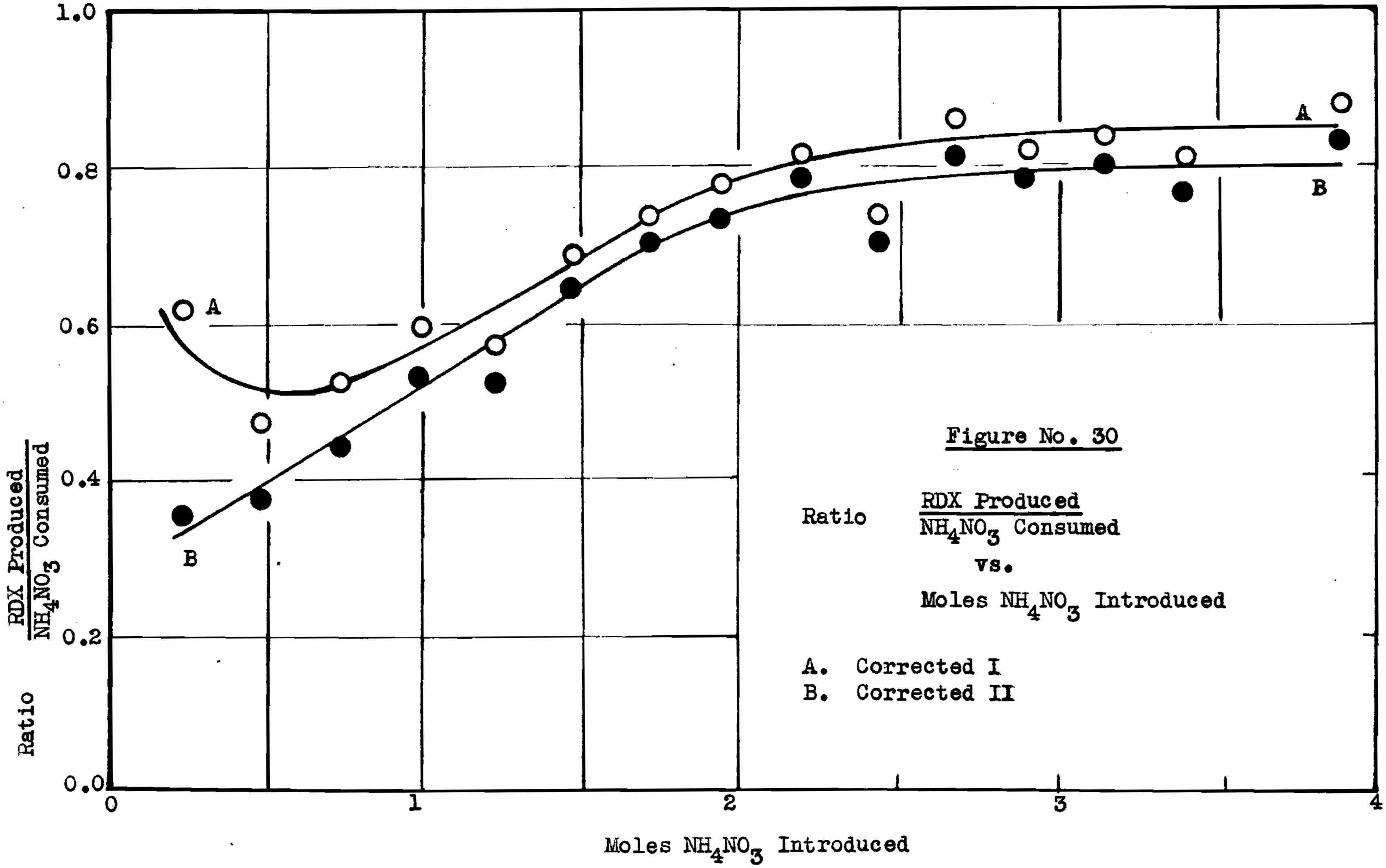

Figure No. 30

Ratio $\frac{\text{RDX Produced}}{NH_4NO_3 \text{ Consumed}}$

vs.

Moles NH_4NO_3 Introduced

A. Corrected I

B. Corrected II

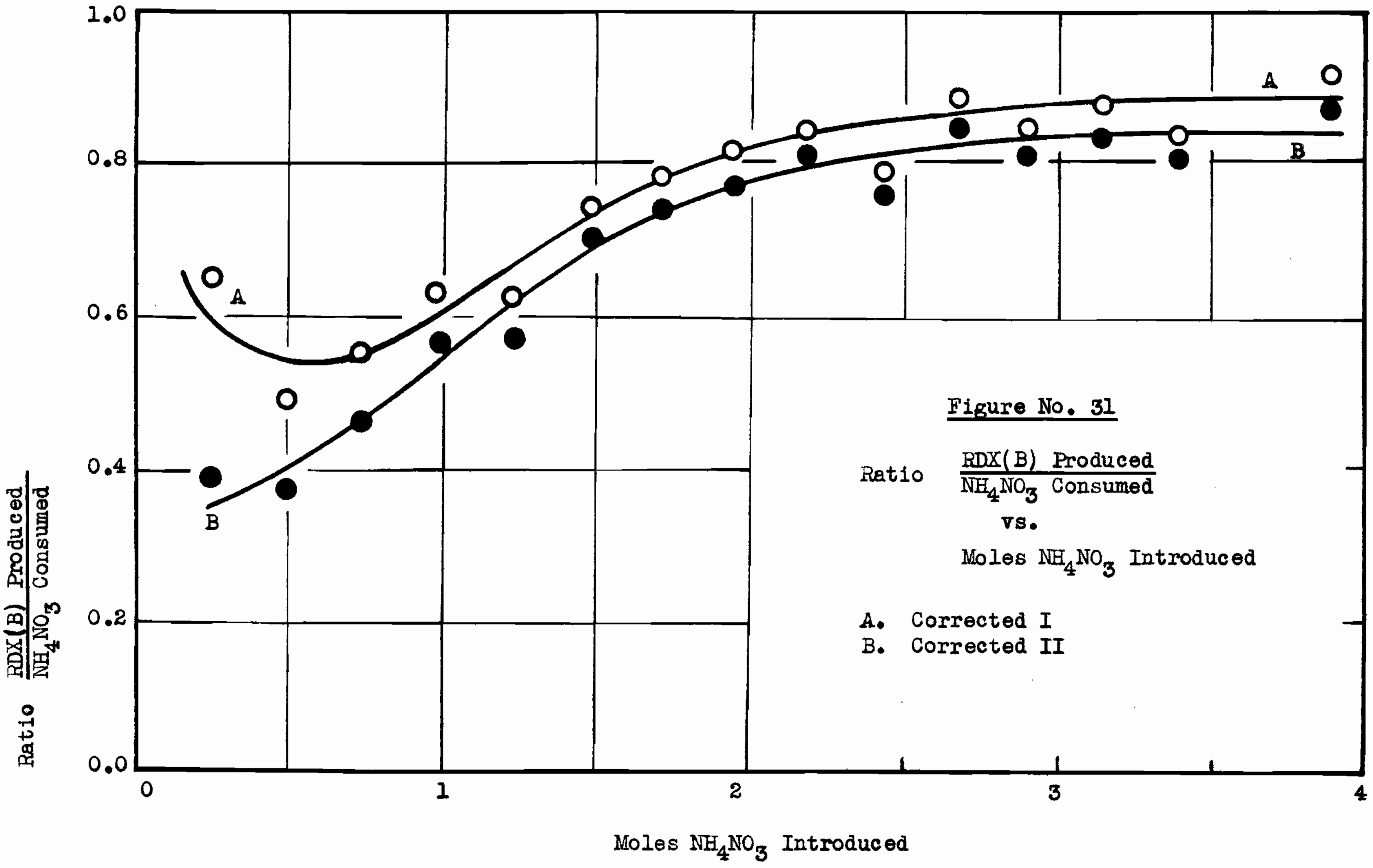

Figure No. 31

Ratio $\frac{\text{RDX(B) Produced}}{NH_4NO_3 \text{ Consumed}}$

vs.

Moles NH_4NO_3 Introduced

A. Corrected I
B. Corrected II

came from the hexamine rather than from the ammonium nitrate. The corrected value for the ammonium nitrate consumption is given in Table V and is plotted as a function of the mole ratio of ammonium nitrate in Figure No. 27.* Using this corrected value, the whole aspect of the ratio of RDX production to ammonium nitrate consumption is altered. The value of the ratio increases slowly from 0.5 to 0.8 as the mole ratio of ammonium nitrate is increased from zero to four moles per mole of hexamine.

The third ratio in each set of three, "CORR.II" (see Figures Nos. 30 and 31 for the ratios based on RDX and RDX(B) respectively), is derived by using the corrected value for the ammonium nitrate consumption as previously; an additional correction is made, however, by subtracting from the molar yield of RDX and RDX(B) a blank equal to the amount of RDX and RDX(B) produced in a run in which the mole ratio of ammonium nitrate is zero. The reason for this correction lies in the possibility that the RDX(B) produced in such a run arises by a different mechanism from the one which produces most of the RDX(B) when ammonium nitrate is present (e.g. direct nitrolysis). This correction removes irregularities in the ratio in the region of low ammonium nitrate concentrations. It may be that this correction is not justified at high mole ratios of ammonium nitrate, but it should be pointed out that the correction is small in this region anyway.

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* It should be pointed out that the corrected values of the ammonium nitrate consumption (as shown in Figure No. 27) provide strong justification for the correction itself and for the theoretical considerations already presented with regard to ammonia recovery: the curve representing these values shows that, at low concentrations of ammonium nitrate, all of the ammonium nitrate introduced is consumed. (See also Table V.)

The conclusion that can be reached by an examination of these data is that the ratio of RDX production to ammonium nitrate consumption is not equal to unity over any wide range of ammonium nitrate concentrations. Further, since ammonia may be recovered from the diluted mother liquor when no ammonium nitrate is introduced, even the most carefully determined values of the ratio are open to question. Again, while there is no direct evidence that ammonium nitrate is being destroyed or consumed in side-reactions, the fact that not all of the amino nitrogen can be accounted for in terms of solid reaction products or distillable amino nitrogen casts further doubt on any positive conclusion that may be drawn in this connection. And lastly, the arguments of Carmack in favour of an equivalence between RDX production and ammonium nitrate consumption may be shown to be inconclusive. In view of these facts, there seems to be little evidence to support any mechanism which assumes that the two moles of RDX are formed by identical or similar processes and these facts certainly do not exclude mechanisms which assume that the two moles of RDX are formed by different processes.

If one accepts a mechanism for the formation of RDX based on the two processes of "catalysed nitrolysis" and "synthesis", the values of the ratio of RDX production to ammonium nitrate consumption as herein determined and corrected may take on real significance. While it is not possible to evaluate accurately the quantities of RDX produced in the Bachmann reaction by nitrolysis, catalysed nitrolysis and by synthesis, these may be estimated by an analysis of the yield of RDX and the value of the above ratio. The rule in this respect is: the higher the value of the ratio, the more efficient is the catalysed nitrolysis process with respect to the synthesis process. The values given in Table V confirm previous discussions: the catalysed nitrolysis process is inefficient at low mole ratios of ammonium nitrate but the synthesis process is efficient at all concentrations of ammonium nitrate.

B. Effect of Simultaneously Varying the Ammonium Nitrate and Acetic Anhydride Concentrations

It has been pointed out (p. 204) that in the preceding series of runs insufficient acetic anhydride was introduced to ensure the presence of an excess at high mole ratios of ammonium nitrate. Three additional runs were carried out to show the effect of restoring the anhydride excess and are herein reported. In run 11 Table V, the ammonium nitrate mole ratio was 2.44 and the acetic anhydride mole ratio was 6.70. The three new runs have ammonium nitrate mole ratios of 2.91, 3.40 and 3.88 and acetic anhydride mole ratios of 7.20, 7.70 and 8.20 respectively.

The experimental and analytical procedures used were identical with those reported in the previous section. No analyses for total nitrate, free nitric acid, acetic anhydride or acetic acid were carried out.

The results of this series of experiments are presented in Table VIII and are discussed briefly in the following paragraphs.

TABLE VIII

BACHMANN REACTION:-EFFECT OF SIMULTANEOUSLY VARYING THE AMMONIUM NITRATE AND ACETIC ANHYDRIDE CONCENTRATIONS ON YIELDS AND MATERIAL BALANCES. TEMP. 70°C.

(CALCULATED TO ONE MOLE OF HEXAMINE)

RUN NUMBER	NH_4NO_3 INTRODUCED	$(CH_3CO)_2O$ INTRODUCED	AVERAGE OF	RDX(B)	HMX IN RDX(B)	RDX	HMX	BSX	FORMALDEHYDE (6 MOLES)			AMMONIA (4+X MOLES)			NH_4NO_3 CONSUMED			MOLES RDX(B) PRODUCED / MOLES NH_4NO_3 CONSUMED			MOLES RDX PRODUCED / MOLES NH_4NO_3 CONSUMED			HEXAMINE CONVERSION		
									IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR		APPARENT	CORRECTED								TO LINEAR NITRAMINES	TO CYCLIC NITRAMINES	TOTAL
	MOLES	MOLES		MOLES	%	MOLES	MOLES	MOLES	MOLES	MOLES	%	MOLES	MOLES	%	MOLES	MOLES	%	UNCORR	CORR I	CORR II	UNCORR	CORR. I	CORR. II	%	%	%
1	2·44	6·70	2	1·53	9·1	1·42	0·109	0·15	0·74	5·98	100	0·62	5·74	89	1·82	1·94	79	0·84	0·79	0·76	0·78	0·73	0·70	29	82	111
2	2·91	7·20	1	1·56	4·3	1·52	0·051	0·13	0·79	6·22	104	1·31	6·70	96	1·60	1·73	60	0·98	0·90	0·87	0·95	0·88	0·85	15	81	96
3	3·40	7·70	1	1·64	4·6	1·58	0·057	0·08	0·73	6·02	100	1·64	6·88	92	1·76	1·88	56	0·93	0·87	0·84	0·90	0·84	0·81	19	85	104
4	3·88	8·20	1	1·50	3·3	1·46	0·038	0·13	0·82	5·89	98	2·38	7·30	91	1·50	1·64	42	1·00	0·92	0·88	0·98	0·89	0·86	24	77	101

X = MOLES AMMONIUM NITRATE INTRODUCED

Discussion

1. Variation in Yields of Solid Products

For a given ammonium nitrate concentration, an increase in the mole ratio of acetic anhydride results in increased yields of RDX and RDX(B) (Figures Nos. 32 and 36), but there is an indication that the anhydride concentration is optimal. This does not agree with the results reported by other workers.

The yield of HMX and the concentration of HMX in the RDX(B) decrease slightly as the acetic anhydride mole ratio is increased (Figures Nos. 33 and 34). The yield of BSX decreases as the acetic anhydride concentration is increased (Figure No. 35).

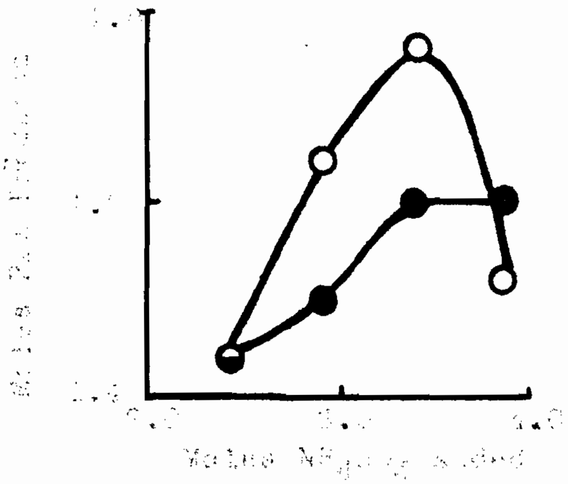
In terms of a mechanism based on the two processes of catalysed nitrolysis and synthesis, these results indicate that the increased yields of RDX are due to the increased efficiency of the catalysed nitrolysis step in the presence of an excess of acetic anhydride.

2. Recovery of Reagents from the Mother Liquor

The quantity of formaldehyde recovered from the diluted mother liquor probably does not vary appreciably as the acetic anhydride concentration is increased (Figure No. 37). The quantity of ammonia recovered from this source, too, varies but little as the acetic anhydride mole ratio is increased (Figure No. 39).

3. Material Balances

The formaldehyde balances in this series of runs are less satis-



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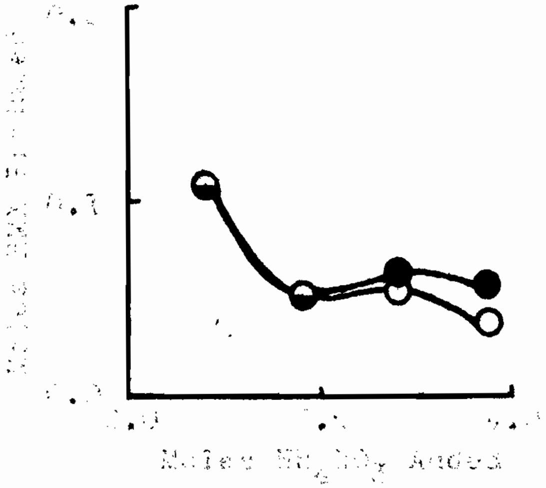

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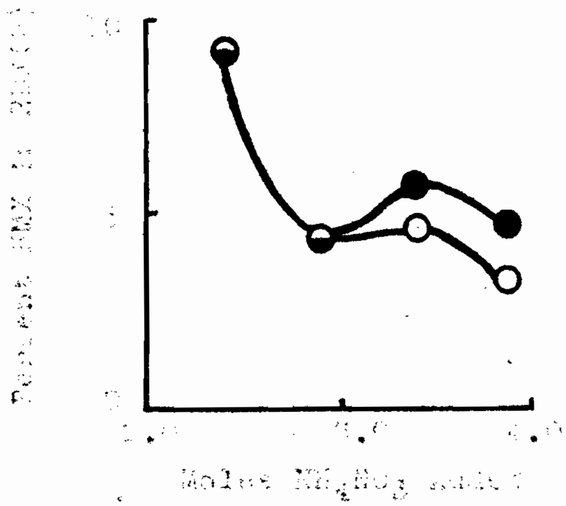

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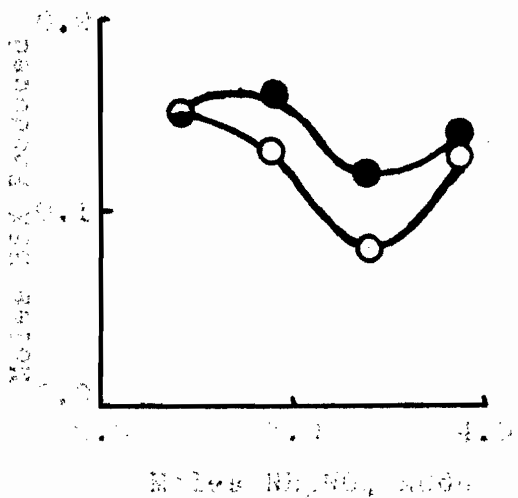

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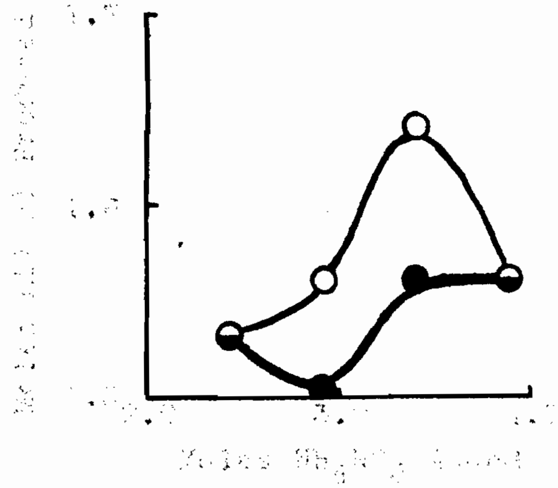

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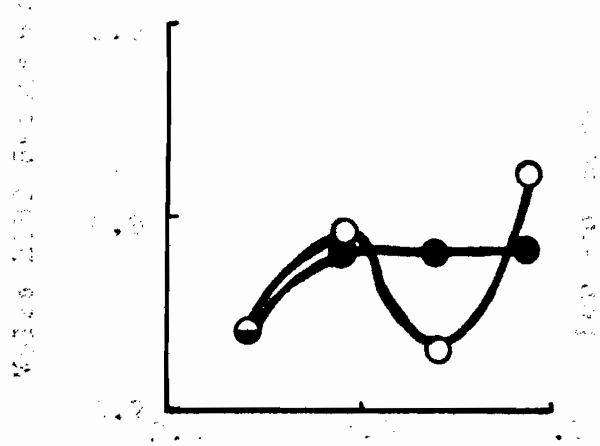

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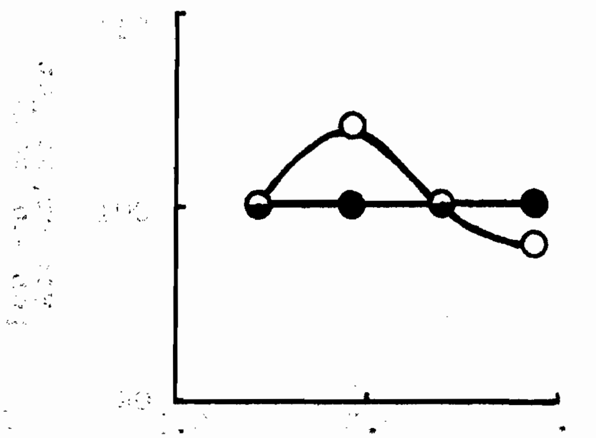

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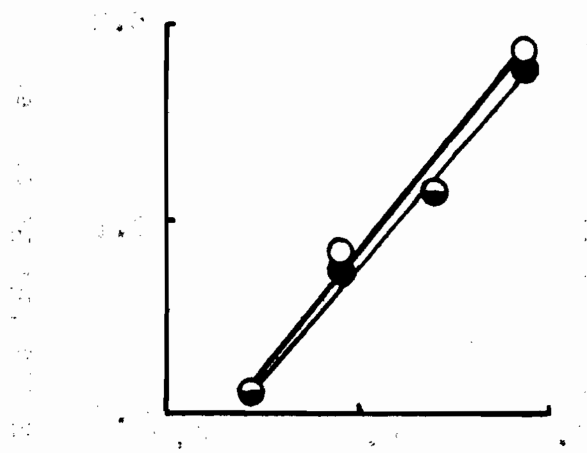

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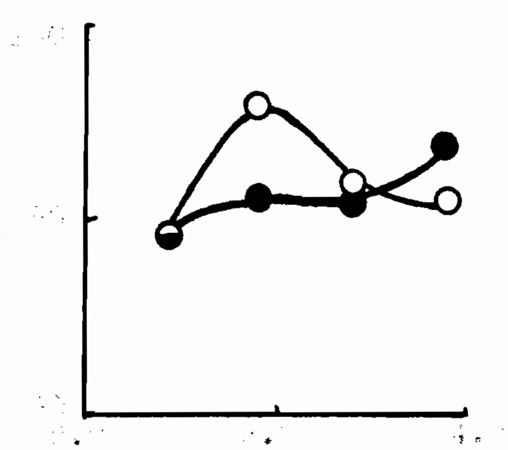

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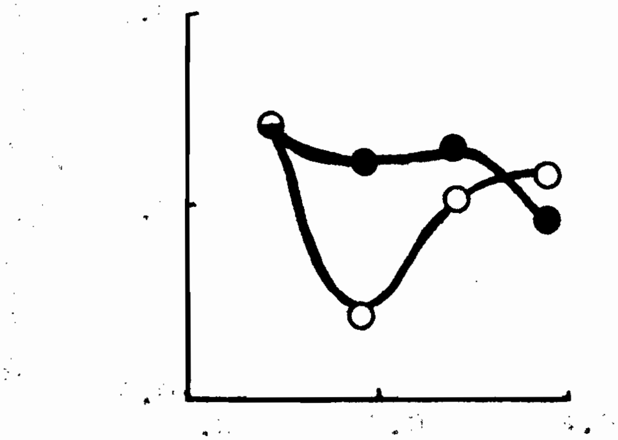

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factory than in the previous series. Of the three runs, one indicates a balance of 104 percent and another, 98 percent (Figure No. 38). No explanation other than that of experimental inaccuracy is volunteered for this behaviour.

The ammonia balance, too, is somewhat irregular but it seems that more amino nitrogen can be accounted for in terms of solid products and distillable amino nitrogen when the acetic anhydride concentration is increased (Figure No. 40). This same picture is presented by Figure No. 41 where the moles amino nitrogen not accounted for is plotted as a function of the ammonium nitrate mole ratio. In run 2 Table VIII, 96 percent of all of the amino nitrogen introduced could be accounted for: this represents one of the highest recoveries recorded in this laboratory.

The percent hexamine converted to linear nitramines, the percent hexamine converted to cyclic nitramines and the percent total conversion of hexamine were calculated according to Carmack (92) (See also p. 217). It was found that, in general, at higher concentrations of acetic anhydride a smaller percentage of the hexamine introduced was converted to linear nitramines and a greater percentage to cyclic nitramines (Figures Nos. 42 and 43). The calculated percent total conversion of hexamine was somewhat irregular but was invariably less than in the runs at lower mole ratios of acetic anhydride (Figure No. 44). In terms of Carmack's views, this indicates better recovery of RDX and of distillable amino nitrogen from the mother liquor. In terms of the views presented in

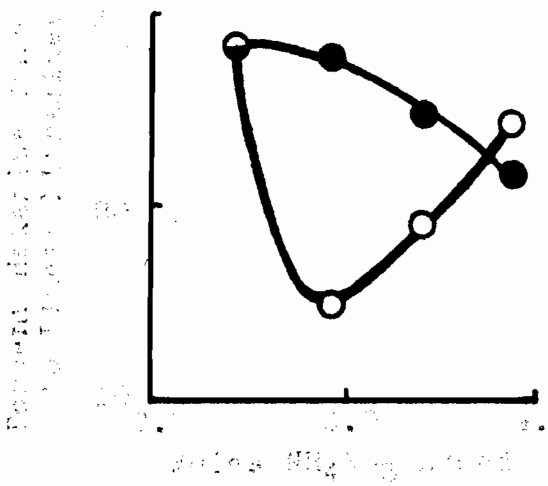
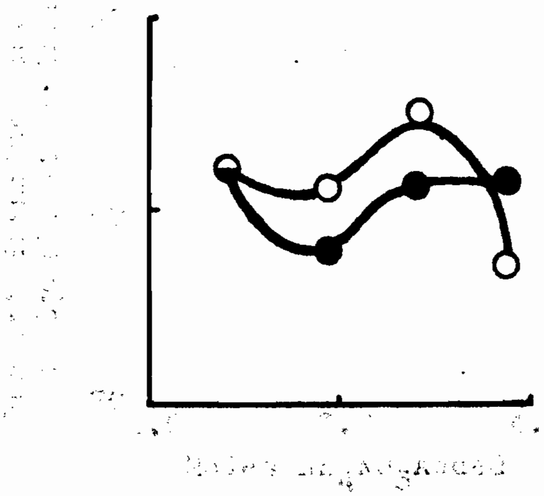


Figure No. 41



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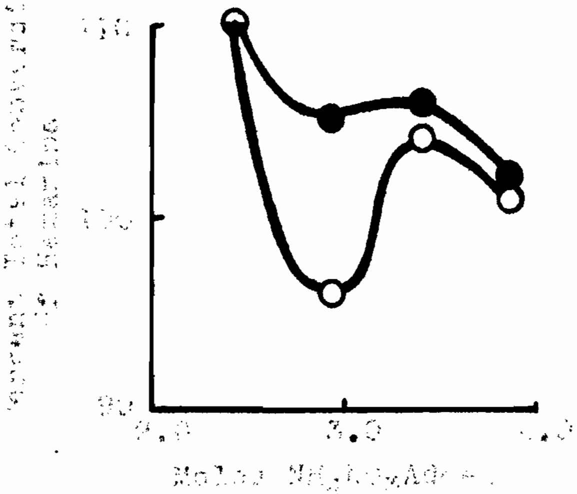

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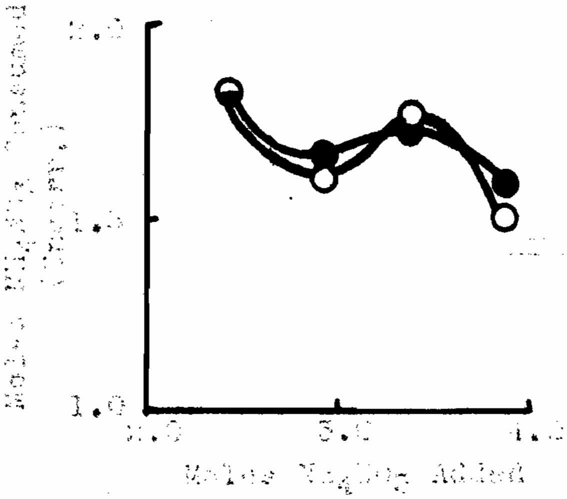

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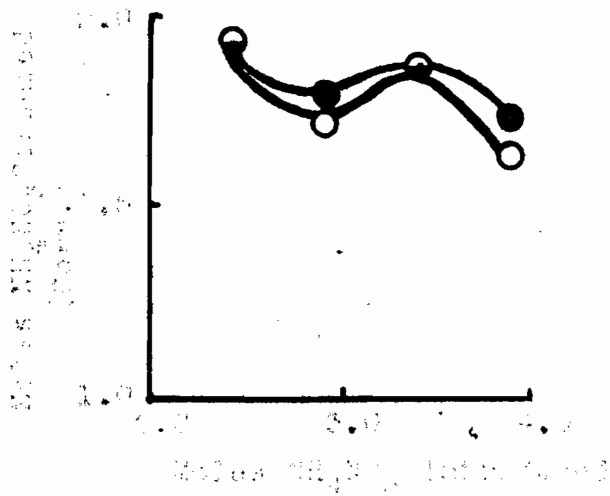


Figure No. 45

the preceding section, however, it is indicative of -

(1) decreased production of amino nitrogen during the hydrolysis of linear by-products, or

(2) increased efficiency of the catalysed nitrolysis process as compared with the synthesis process.

This latter interpretation is supported by other data presented in this section.

4. Miscellaneous Considerations Concerning the Reaction Mechanism

As the acetic anhydride mole ratio is increased for a given concentration of ammonium nitrate, the apparent consumption of ammonium nitrate (i.e. uncorrected) and the corrected consumption of ammonium nitrate decrease very slightly (Figures Nos. 45 and 46). Further, as the mole ratio of anhydride is increased, all values (i.e. corrected and uncorrected) of the ratio of RDX production to ammonium nitrate consumption increase (Figures Nos. 47-50). In runs 2 and 4 (Table VIII) the uncorrected values of the ratio approach unity. These values support the arguments of Carmack, particularly since they correspond to the "near quantitative" conversions of hexamine as calculated above. In defence of the stand adopted in this thesis (i.e. that no equivalence exists over any wide range of operating conditions), it should be pointed out that an increase in the efficiency of the catalysed nitrolysis process with respect to the synthesis process would account for both the higher ratio and for the calculated percent total conversion of hexamine.

Thus, while the experiments with increased quantities of acetic anhydride changed the yields of solid products somewhat and altered the

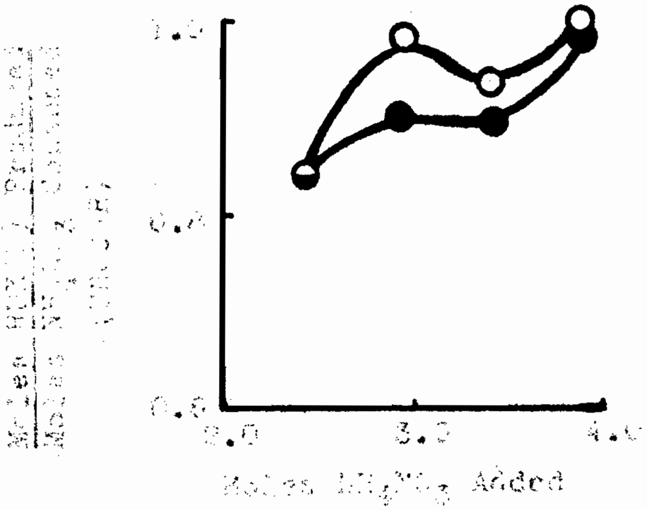


Figure No. 47

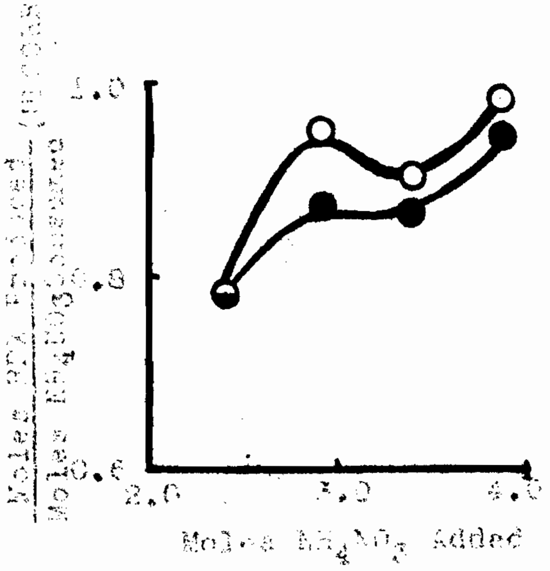


Figure No. 48

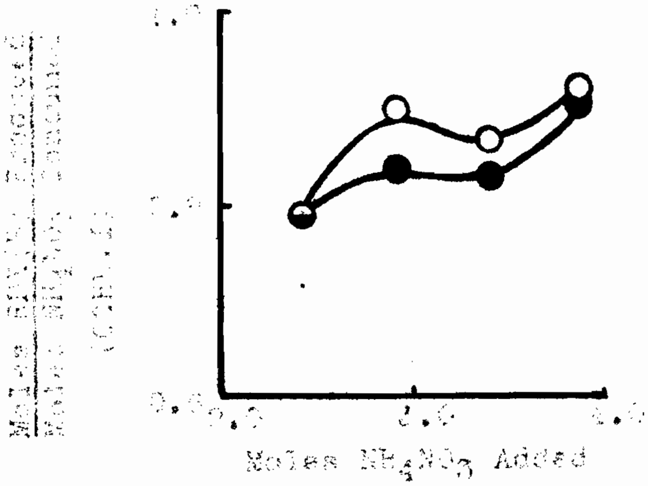


Figure No. 49

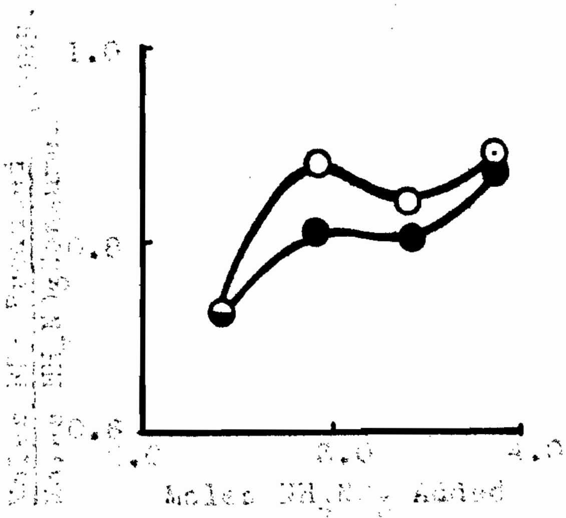


Figure No. 50

ratio of RDX production to ammonium nitrate consumption, they in no way invalidated any of the theoretical considerations previously advanced.

C. Effect of Temperature when Zero Moles of Ammonium Nitrate introduced

In this series of experiments, the effect of varying the reaction temperature between 40°C. and 80°C. for runs of zero mole ratio of ammonium nitrate is investigated.

The experimental and analytical procedures used were identical with those reported in Section A above except that the temperature of the Bachmann reactions was modified as indicated in Table IX and that, after dilution of the reaction liquor, at least three days were allowed to elapse before filtration. The results of these experiments are presented in Table IX and are discussed in the succeeding paragraphs.

Discussion

1. Variation in Yields of Solid Products

As the reaction temperature is increased (for runs to which no ammonium nitrate is added), the yield of RDX (and RDX(B)) decreases (Figure No. 51). The yield which is always very small decreases more rapidly at higher temperatures.

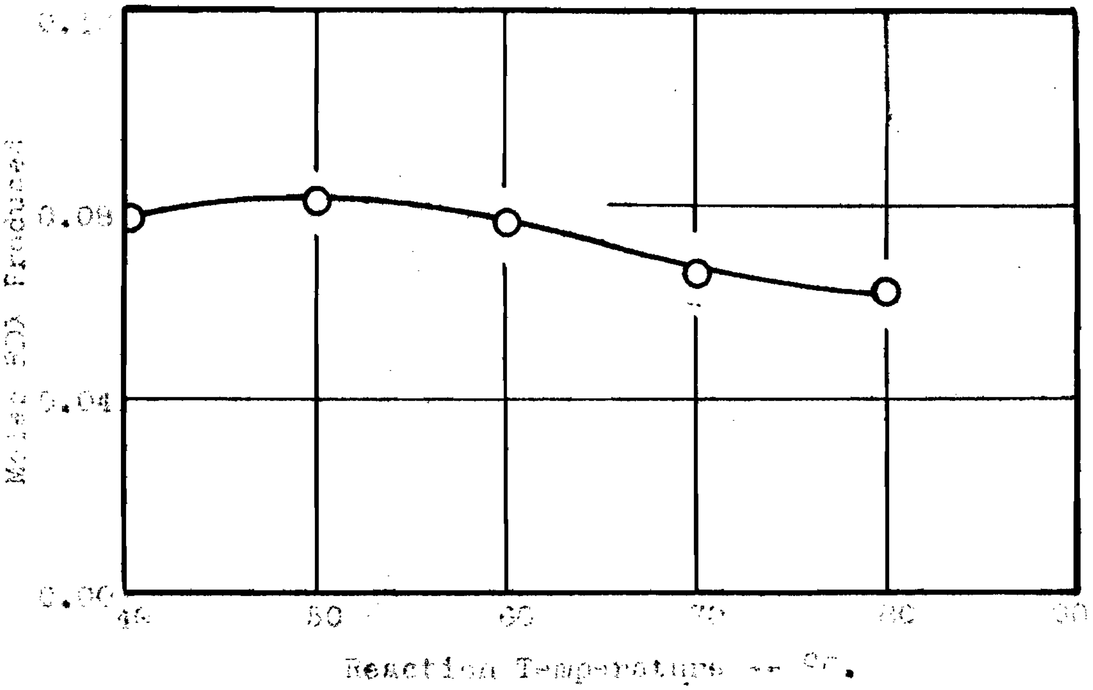
TABLE IX

BACHMANN REACTION:-EFFECT OF TEMPERATURE ON YIELDS AND MATERIAL BALANCES.

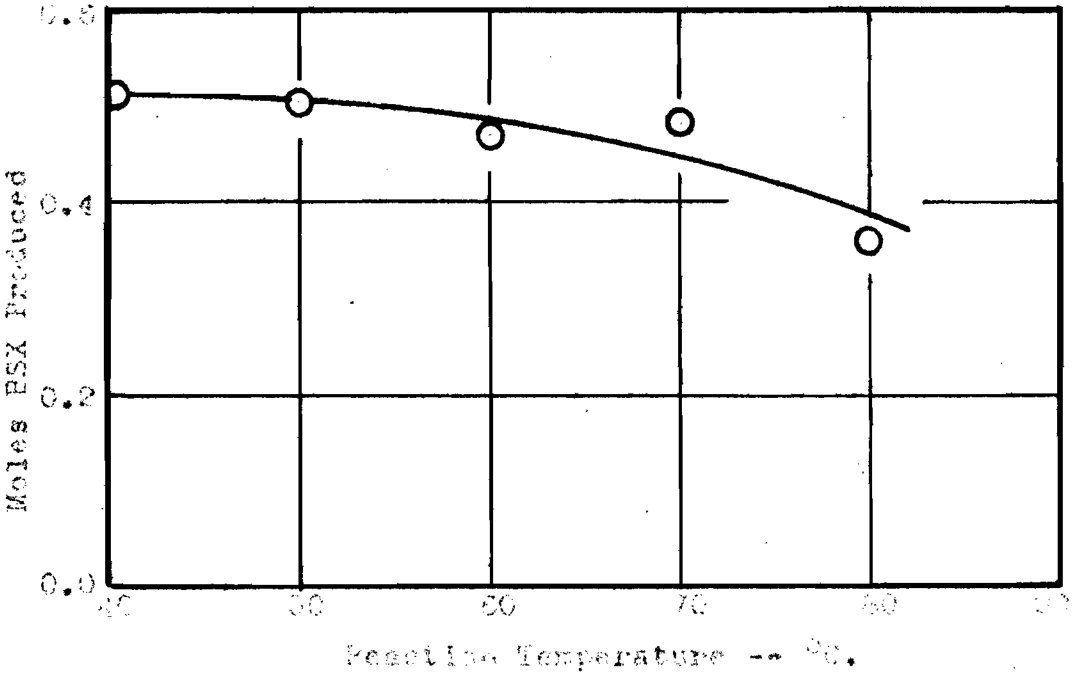
(0.00 MOLES AMMONIUM NITRATE)

(CALCULATED TO ONE MOLE OF HEXAMINE)

RUN NUMBER	TEMPERATURE	AVERAGE OF	RDX(B)	HMX IN RDX(B)	HMX	BSX	FORMALDEHYDE (6 MOLES)			AMMONIA (4 MOLES)			NITRIC ACID (4.44 MOLES)					ACETIC ANHYDRIDE (6.70 MOLES)			$\frac{\text{MOLES } NH_3 \text{ IN MOTHER LIQUOR}}{\text{MOLES HCHO IN MOTHER LIQUOR}}$	$\frac{\text{MOLES } NH_3 \text{ IN MOTHER LIQUOR}}{\text{MOLES [illegible] } HNO_3 \text{ IN MOTHER LIQUOR}}$	$\frac{\text{MOLES } NH_3 \text{ NOT RECOVERED}}{\text{MOLES } HNO_3 \text{ NOT RECOVERED}}$	MOLES HNO_3 CONSUMED × 0.25
							IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR			ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR					
													FREE	COMBINED	TOTAL									
	°C.		MOLES	%	MOLES	MOLES	MOLES	MOLES	%	MOLES	MOLES	%	MOLES	MOLES	MOLES	MOLES	%	MOLES	MOLES	%				
1	40	2	0.077	1.0	0.001	0.51	3.79	6.04	101	0.63	2.39	60	0.45	0.56	1.02	2.77	62	6.86	7.39	110	0.166	1.13	0.97	1.00
2	50	2	0.081	0.0	0.000	0.50	3.88	6.12	102	0.61	2.35	59	0.49	0.45	0.95	2.69	62	6.81	7.31	109	0.157	1.36	0.94	0.99
3	60	2	0.076	1.1	0.001	0.47	3.90	6.00	100	0.62	2.25	56	0.55	0.43	0.98	2.62	59	6.81	7.28	109	0.159	1.44	0.96	0.99
4	70	4	0.066	1.3	0.001	0.48	3.71	5.80	97	0.62	2.23	56	0.56	0.40	0.97	2.59	58	6.61	7.09	106	0.167	1.55	0.96	0.97
5	80	3	0.062	1.0	0.001	0.36	3.90	5.53	92	0.69	1.96	49	0.61	0.43	1.05	2.32	52	6.87	7.23	108	0.177	1.60	0.96	0.96



<u>Figure No. 51</u>



<u>Figure No. 52</u>

Since the yield of RDX(B) is small, HMX values cannot be accurately determined. While small values are reported in Table IX for the HMX content of the RDX(B), it may be that these are in error and that, since the concentration is small, HMX may fail to crystallize out of the diluted mother liquor at all.

As the reaction temperature is increased, the yield of BSX decreases (Figure No. 52). This decrease is more pronounced at high temperatures.

2. Recovery of Reagents from the Mother Liquor

Formaldehyde:- As the reaction temperature is increased (for runs to which no ammonium nitrate is added), the amount of recoverable formaldehyde in the mother liquor remains relatively constant (Figure No. 53).

Ammonia:- As the reaction temperature is increased, the quantity of recoverable ammonia in the mother liquor remains constant (Figure No. 53).

Carmack (92,93,94,94,96) has stated that the presence of distillable amino nitrogen in the diluted mother liquor of a run into which no ammonium nitrate is introduced is due to the fact that hexamine is incompletely nitrated. An alternate explanation has been advanced in this thesis: the amino nitrogen is a product of the hydrolytic decomposition of inisolable nitramines. The fact that the quantity of ammonia recovered from the diluted mother liquor does not vary with temperature would seem to constitute some measure of support for the latter alternative. It seems unlikely that hexamine would be nitrated to the same extent over the whole range of temperatures studied. On the other hand, the quantity

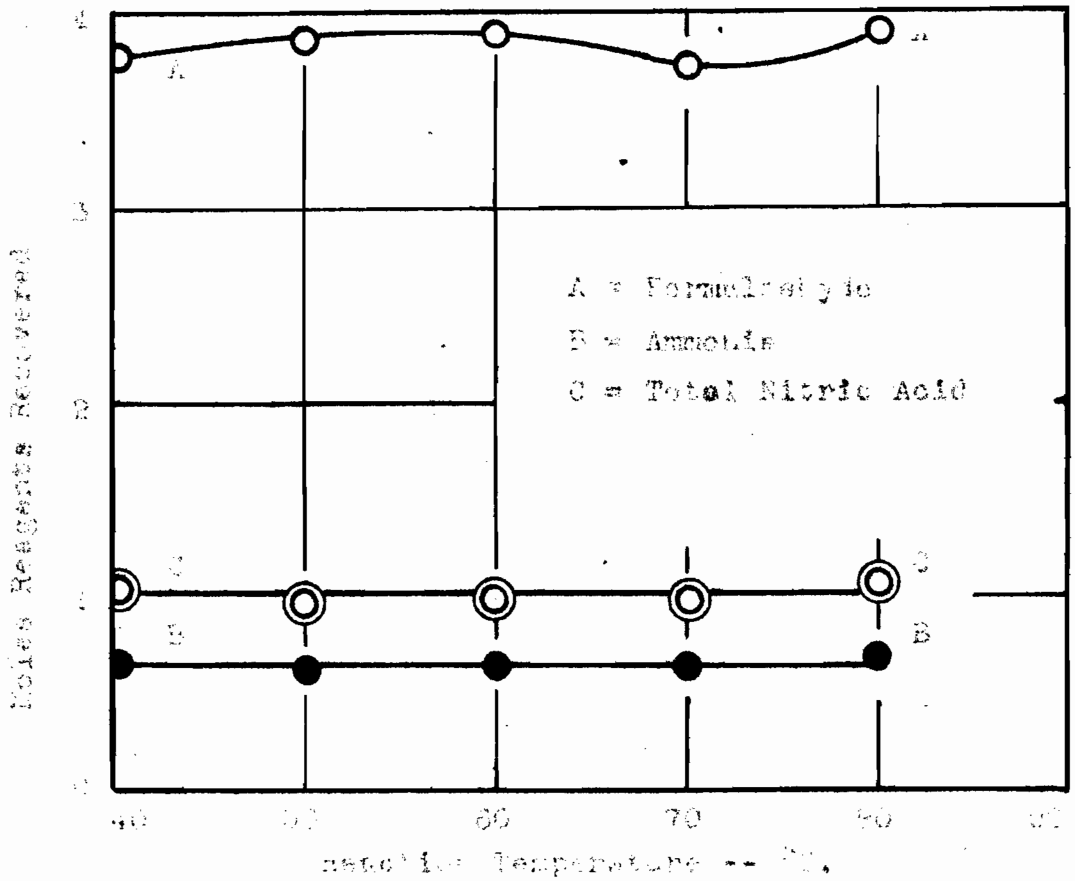


Figure No. 33

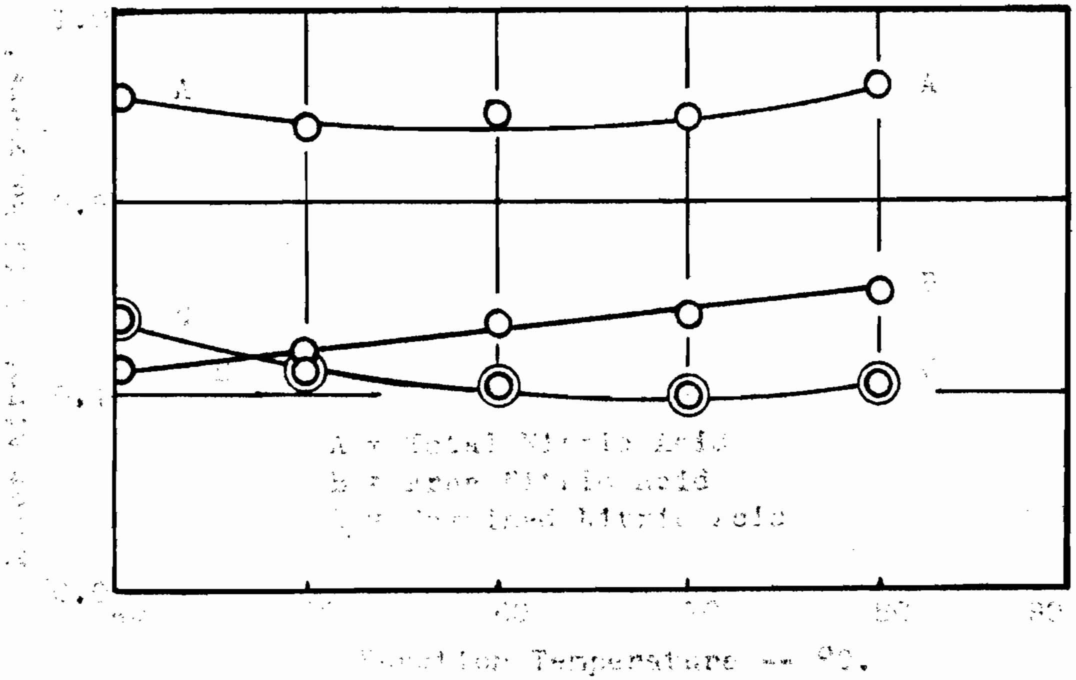


Figure No. 34

of inisolable nitramines produced (assuming the hexamine to have been completely nitrated) would be expected to remain constant since the yields of RDX and BSX are relatively constant. The quantity of amino nitrogen produced on hydrolytic decomposition of these inisolable nitramines would, then, be fairly constant also.

On the basis of experimental results previously reported (p. 195), it was stated that the ratio of hexamine amino nitrogen* to formaldehyde in the diluted mother liquor is a constant for all concentrations of ammonium nitrate. The values for the ratio obtained in this series of experiments, too, are relatively constant (Table IX). The average value for the seven runs reported is 0.167. This compares with a value of 0.165 calculated from Table V.

Nitric Acid:- As the reaction temperature is increased from 40°C. to 80°C. (for runs to which no ammonium nitrate is added), the amount of free (i.e. titratable) nitric acid in the mother liquor increases slightly (Figure No. 54). This corresponds to a slight decrease in the amount of nitric acid consumed (Figure No. 55).

As the reaction temperature is increased, the quantity of combined nitric acid in the mother liquor decreases (Figure No. 55). Since the quantity of ammonia in the mother liquor is constant, and, since it was previously postulated (p.199) that the ammonia and the combined nitric acid existed in the diluted mother liquor as ammonium nitrate, this fact

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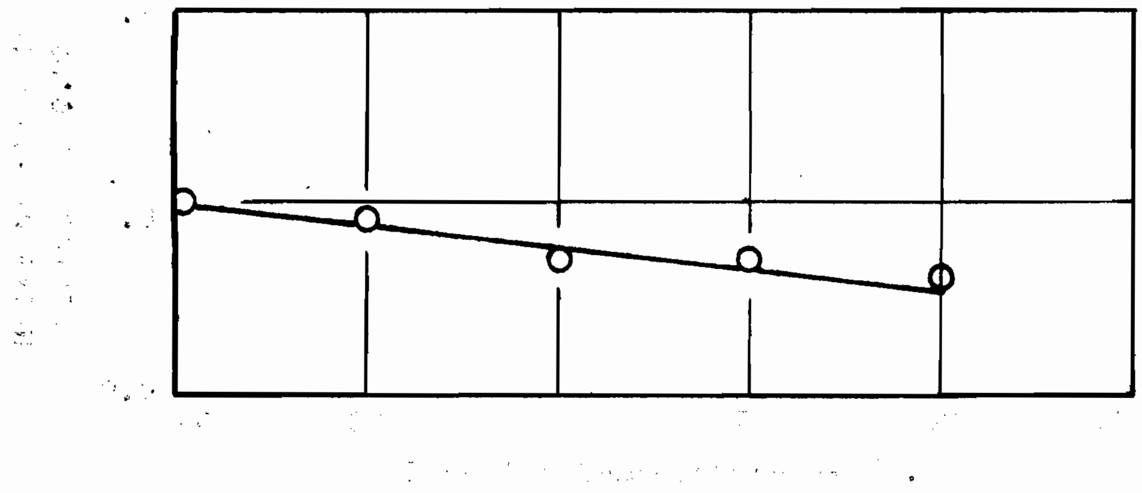
* Amino nitrogen which originated in the hexamine rather than in ammonium nitrate.



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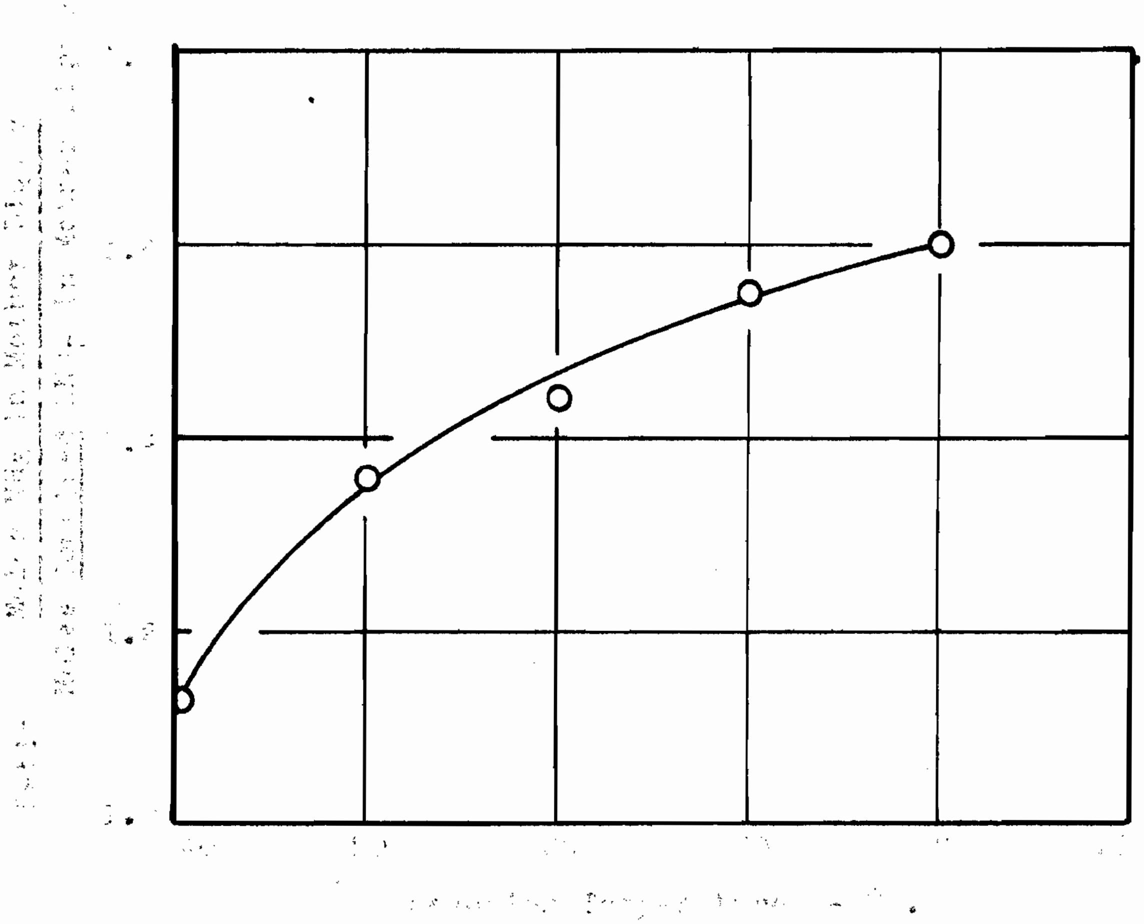

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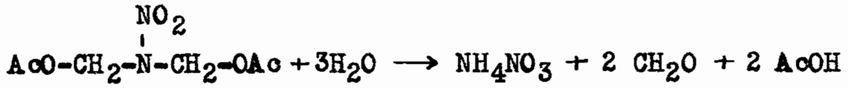
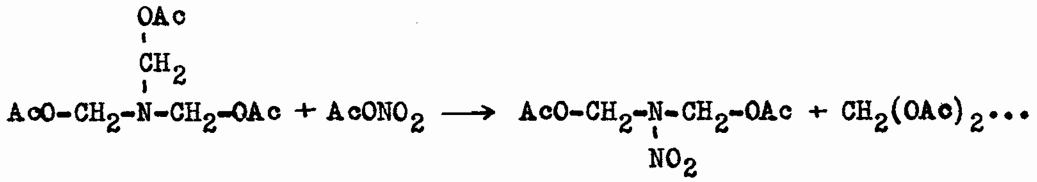
is rather startling. It was suggested that, if the ratio of ammonia to combined nitric acid were greater than unity, hexamine dinitrate might be present in the mother liquor; this would indicate that hexamine had survived treatment with nitric acid and acetic anhydride. Since, in this series of experiments, the ratio of ammonia to combined nitric acid (Figure No. 56) increases with temperature, this explanation would appear to be invalid. An alternate explanation is based on a reconsideration of the proposed mechanism of formation of the ammonium nitrate.

The distillable amino nitrogen in the mother liquor of runs into which no ammonium nitrate is introduced is not present in the undiluted reaction liquor in the form of ammonium nitrate since it would have generated RDX. It has been postulated (p. 213) that it arises after dilution by the hydrolytic decomposition of inisolable nitramines such as the diacetate of dimethylol nitramine:



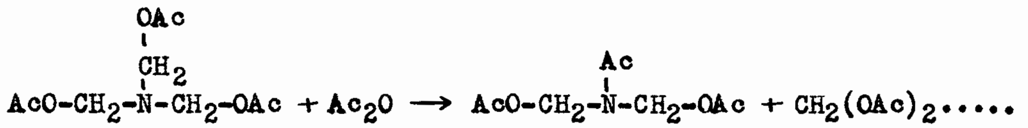
$$\mathrm{AcO{-}CH_2{-}\overset{\overset{NO_2}{|}}{N}{-}CH_2{-}OAc + 3H_2O \longrightarrow NH_4NO_3 + 2\ CH_2O + 2\ AcOH} \quad \ldots\ldots\ldots\ 208$$

It may be supposed that these nitramine linkages result from the attack of acetyl nitrate upon methyleneamine linkages:



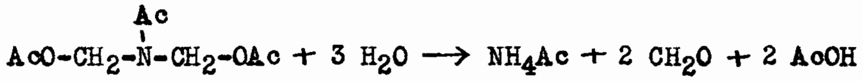
$$\mathrm{AcO{-}CH_2{-}\overset{\substack{OAc\\|\\CH_2\\|}}{N}{-}CH_2{-}OAc + AcONO_2 \longrightarrow AcO{-}CH_2{-}\underset{\substack{|\\NO_2}}{N}{-}CH_2{-}OAc + CH_2(OAc)_2} \ldots\ 209$$

Now, by analogy, if it be supposed that acetic anhydride rather than acetyl nitrate is the active agent, an acetamine rather than a nitramine will be produced:



$$\mathrm{AcO{-}CH_2{-}\overset{\substack{OAc\\ |\\ CH_2\\ |}}{N}{-}CH_2{-}OAc} + \mathrm{Ac_2O} \longrightarrow \mathrm{AcO{-}CH_2{-}\overset{\substack{Ac\\ |}}{N}{-}CH_2{-}OAc} + \mathrm{CH_2(OAc)_2} \;\ldots\ldots\; 210$$

It may be assumed that the acetamine will undergo an analogous hydrolytic decomposition to that of the nitramine:

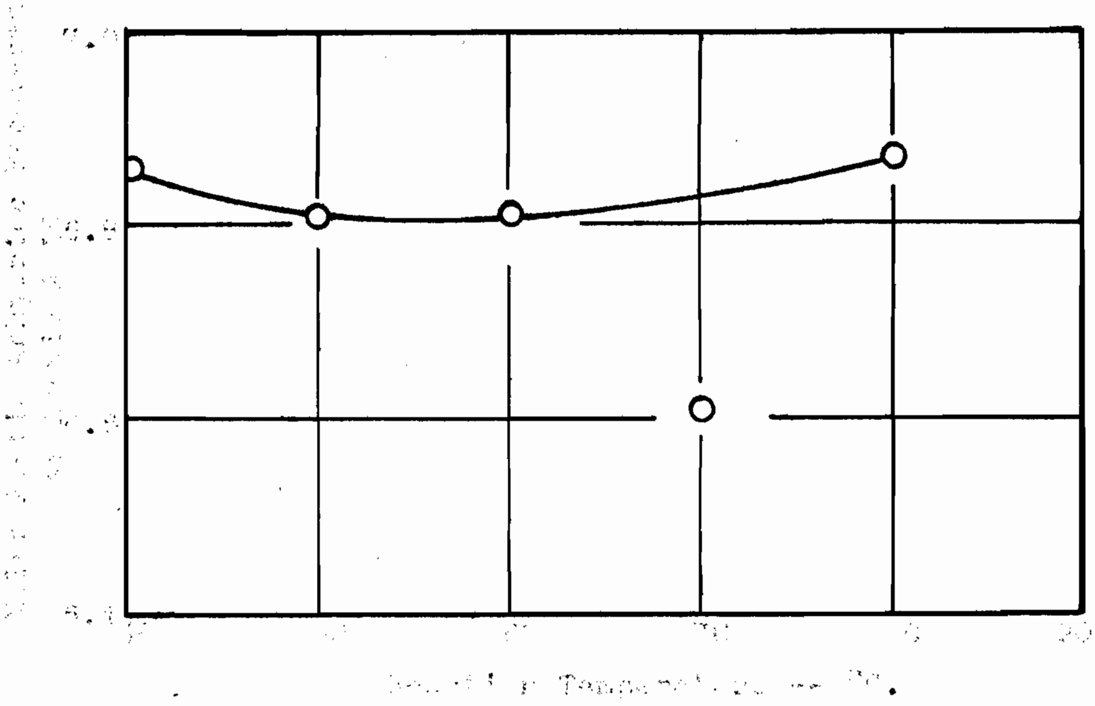


$$\mathrm{AcO{-}CH_2{-}\overset{\substack{Ac\\ |}}{N}{-}CH_2{-}OAc} + 3\,\mathrm{H_2O} \longrightarrow \mathrm{NH_4Ac} + 2\,\mathrm{CH_2O} + 2\,\mathrm{AcOH} \qquad \ldots\ldots\; 211$$

On the basis of these considerations it may be seen that amino nitrogen will be produced on hydrolysis of both nitramines and acetamines, while nitric acid will be produced on hydrolysis of nitramines only. Thus there need be no equivalence between the ammonia and combined nitric acid. It will be seen that the value of the ammonia - combined nitric acid ratio will be a semi-quantitative measure of the number of methyleneamine linkages split by acetic anhydride rather than by acetyl nitrate. Since, in this series of runs, the value of the ratio increases with increasing temperature (Figure No. 56), relatively more methyleneamine linkages are broken by acetic anhydride at high temperatures.

While they have never advanced the view that nitramines can decompose in accordance with equation 208, the above discussion is in general agreement with the views of the researchers at the University of Michigan(60):

> " It is probable that, in the simmer, both O - acetyl and N-acetyl compounds are hydrolysed. When O - acetyl compounds hydrolyse, the quantity of acetic acid is increased but the nitric acid remains unchanged. The hydrolysis of N-acetyl compounds, however, not only increases the amount of acetic acid but liberates basic nitrogens capable of neutralizing free nitric acid. This increases the consumption of free nitric acid. "



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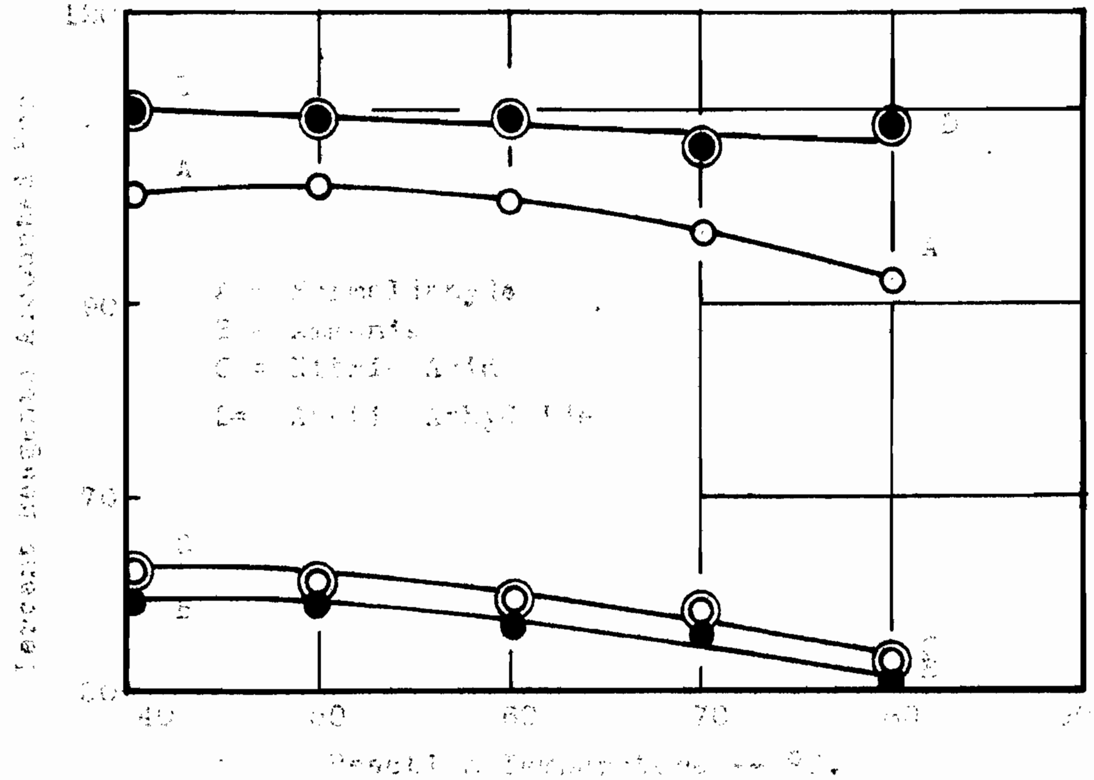

D
A
C = Citric Acid
70
C
B
40
70

[illegible]

peratures. This has not been observed. Nor does the ratio of unrecovered amino nitrogen to unrecovered nitric acid decrease.

Acetic Anhydride:- The total recovery and the percent recovery of acetic anhydride were calculated as previously described (p. 225) and the percent recovery is plotted as a function of the reaction temperature in Figure No. 58.

The recovery of anhydride as herein described gives values in excess of 100 percent. This behaviour has been observed in other series of experiments and reasons for this condition have been suggested on p. 177.

D. Effect of Temperature on Yields and Material Balances (4.74 Moles Ammonium Nitrate)

In this section, the variation in yields and material balances is investigated with respect to temperature for Bachmann runs into which excess ammonium nitrate is introduced.

Experimental

1. Experimental and Analytical Procedures

In general, the same experimental and analytical procedures were used as were reported in section III A (p.160). The Bachmann procedure used was modified somewhat, however, and the reagents introduced into the system were carefully analysed whereas previously they were merely weighed in bulk. Chronologically, this series of runs was the last to be carried out. For this reason and in view of the careful analyses performed, these experiments are probably somewhat more accurate than others reported herein.

Analysis of Reagents:- Acetic anhydride was analysed by the differential alkali titration of two weighed samples after solution in aniline and water. The strength of the acetic anhydride was found to be 99.2 percent.

Acetic acid was titrated with alkali and the total acidity (calculated as acetic acid) was found to be 99.3 percent.

The acetic acid - hexamine solution was analysed for (1) total acid (61.3 percent as acetic acid), (2) formaldehyde (37.3 percent as hexamine) and (3) amino nitrogen (37.3 percent as hexamine). By difference it was estimated that there was 1.1 percent water in the solution.

The ammonium nitrate - nitric acid solution was analysed for (1) total acid (44.2 percent calculated as nitric acid) and (2) ammonia (55.3 percent calculated as ammonium nitrate). By difference it was estimated that there was 0.5 percent water in the solution.

Bachmann Procedure:- The procedure used was similar to that continuous, three-feed addition technique previously described (pp. 121 & 161). The procedure was modified with respect to the quantities of reagents used. The pot was charged with 25 ml. glacial acetic acid, 5 ml. acetic anhydride and 2.5 g. ammonium nitrate. To this charge were added 73 g. acetic anhydride, a solution of 14 gm.hexamine dissolved in 23.5 g. acetic acid, and a solution of 35.5 g. ammonium nitrate dissolved in 28.6 g. strong nitric acid. On the basis of these quantities and the analyses reported above, the exact mole ratios of reagents used were as follows:

Hexamine	1.00
Ammonium Nitrate	4.74
Nitric Acid	4.50
Acetic Anhydride	7.62
Acetic Acid	8.32
Water	0.51

The experimental procedure used was further modified with respect to the holding time after dilution: at least three days were allowed to elapse before filtering off the crude solid product. The reason for this will be apparent after examination of the results of section III F.

Analytical Procedures:- The analytical procedures used were identical with those previously reported (section III A). New calibration curves were drawn up for the RDX(B) and HMX analyses, however, and more advantageous use of blank determinations was made in the analysis of the mother liquor.

2. Experimental Results

The results of the above-described series of runs are presented in Table X and are discussed in the succeeding paragraphs. No attempt has been made to obtain an acetic anhydride balance in view of the unsatisfactory results obtained in other series.

TABLE X

BACHMANN REACTION:-EFFECT OF TEMPERATURE ON YIELDS AND MATERIAL BALANCES (4.74 MOLES AMMONIUM NITRATE)

(CALCULATED TO ONE MOLE HEXAMINE)

RUN NUMBER	TEMPERATURE	AVERAGE OF	RDX + HMX	HMX IN RDX(B)	RDX	HMX	BSX	FORMALDEHYDE (6 MOLES)			AMMONIA (8.74 MOLES)			NITRIC ACID (4.50 MOLES)					NH₄NO₃ CONSUMED			MOLES RDX(B) PRODUCED / MOLES NH₄NO₃ CONSUMED			MOLES RDX PRODUCED / MOLES NH₄NO₃ CONSUMED			MOLES NH₄ IN MOTHER LIQUOR / MOLES COMB. HNO₃ IN MOTHER LIQUOR	MOLES NH₃ NOT RECOVERED / MOLES HNO₃ NOT RECOVERED	MOLES NITRIC ACID CONSUMED × 0.25	HEXAMINE CONVERSION		
								IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR FREE	IN MOTHER LIQUOR COMBINED	IN MOTHER LIQUOR TOTAL	ACCOUNTED FOR		APPARENT	CORRECTED											TO LINEAR NITRAMINES	TO CYCLIC NITRAMINES	TOTAL
	°C.		MOLES	%	MOLES	MOLES	MOLES	MOLES	MOLES	%	MOLES	MOLES	%	MOLES	MOLES	MOLES	MOLES	%	MOLES	MOLES	%	UNCORR.	CORR. I	CORR. II	UNCORR.	CORR. I	CORR. II				%	%	%
1	40	2	0.28	5.1	0.27	0.011	0.38	3.59	5.96	99	5.22	7.21	83	0.50	5.10	5.60	7.59	82	−0.48	+0.11	2	−0.58	+2.55	+1.82	−0.56	+2.45	+1.73	1.01	0.93	1.04	67	15	82
2	50	1	1.04	4.8	1.00	0.038	0.34	1.61	6.12	102	3.69	7.86	90	0.49	3.71	4.20	8.37	90	+1.05	1.32	28	+0.99	+0.79	0.73	+0.95	0.76	0.69	0.99	1.01	1.03	48	54	102
3	60	1	1.58	4.9	1.52	0.059	0.11	0.81	6.05	101	3.12	8.25	94	0.53	3.07	3.60	8.73	95	1.62	1.75	37	0.97	0.90	0.86	0.94	0.87	0.82	1.01	0.97	1.03	21	77	98
4	70	2	1.66	5.2	1.59	0.065	0.05	0.83	6.16	103	3.04	8.22	94	0.54	3.01	3.55	8.73	95	1.70	1.84	39	0.98	0.90	0.86	0.94	0.86	0.82	1.00	1.01	1.03	17	86	103

Discussion

1. Variation in Yields of Solid Products

As the reaction temperature is increased from 40°C. to 70°C. (for runs into which an excess of ammonium nitrate is introduced), the yields of RDX, RDX(B) and HMX increase and the yield of BSX decreases. The percent HMX in the RDX(B) remains relatively constant. (See Figures Nos. 59, 60, 61, 62).

The most significant features of these curves are the great increase in the yield of RDX(B) and the slight decrease in the yield of BSX in the region 40°C. - 50°C. This indicates that the rate of the postulated synthesis process (supposing a two-stage mechanism) is increasing more rapidly than is the efficiency of the catalysed nitrolysis process. This is in accord with other experimental data presented in this section.

2. Recovery of Reagents from the Mother Liquor

Formaldehyde:- The recovery of formaldehyde from the diluted mother liquor decreases rapidly to a constant value as the reaction temperature is increased (Figure No. 63). This observation is in accord with the above deduction that the rate of the synthesis process increases very rapidly between 40°C. and 50°C.

Ammonia:- As the reaction temperature increases, the quantity of amino nitrogen in the diluted mother liquor decreases (Figure No. 63).

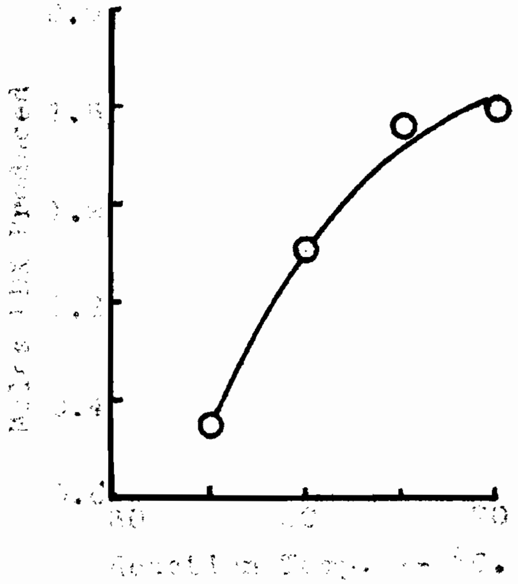


Figure No. 59

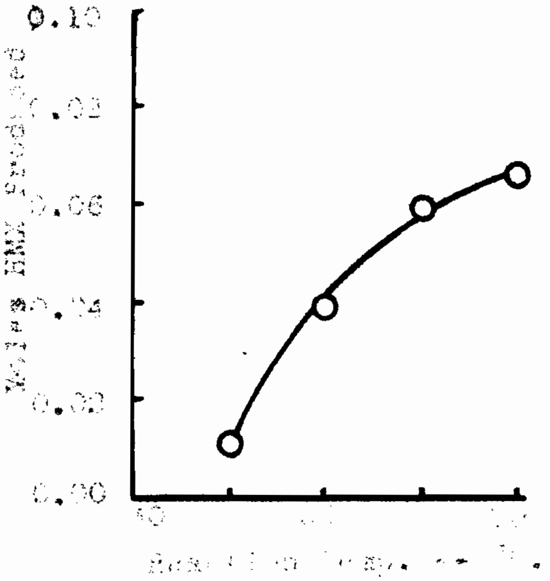


Figure No. 60

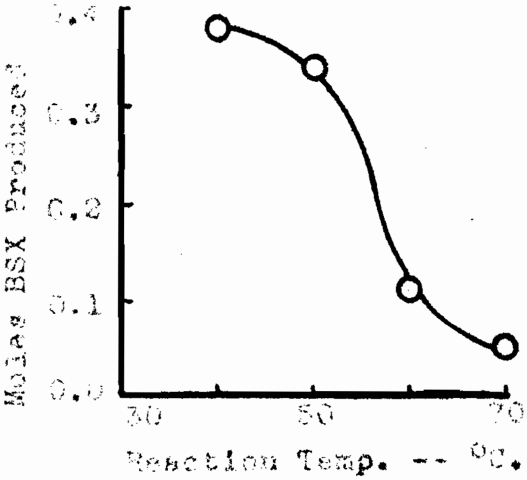


Figure No. 61

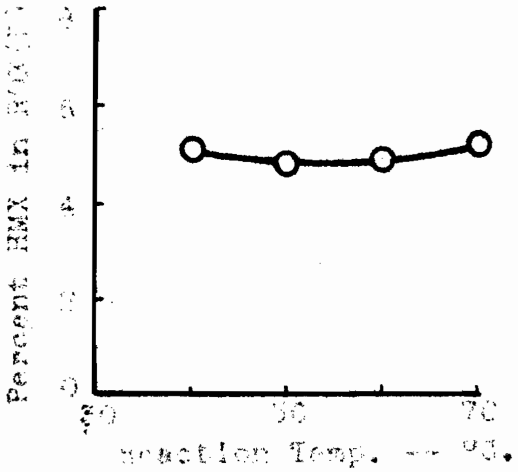


Figure No. 62

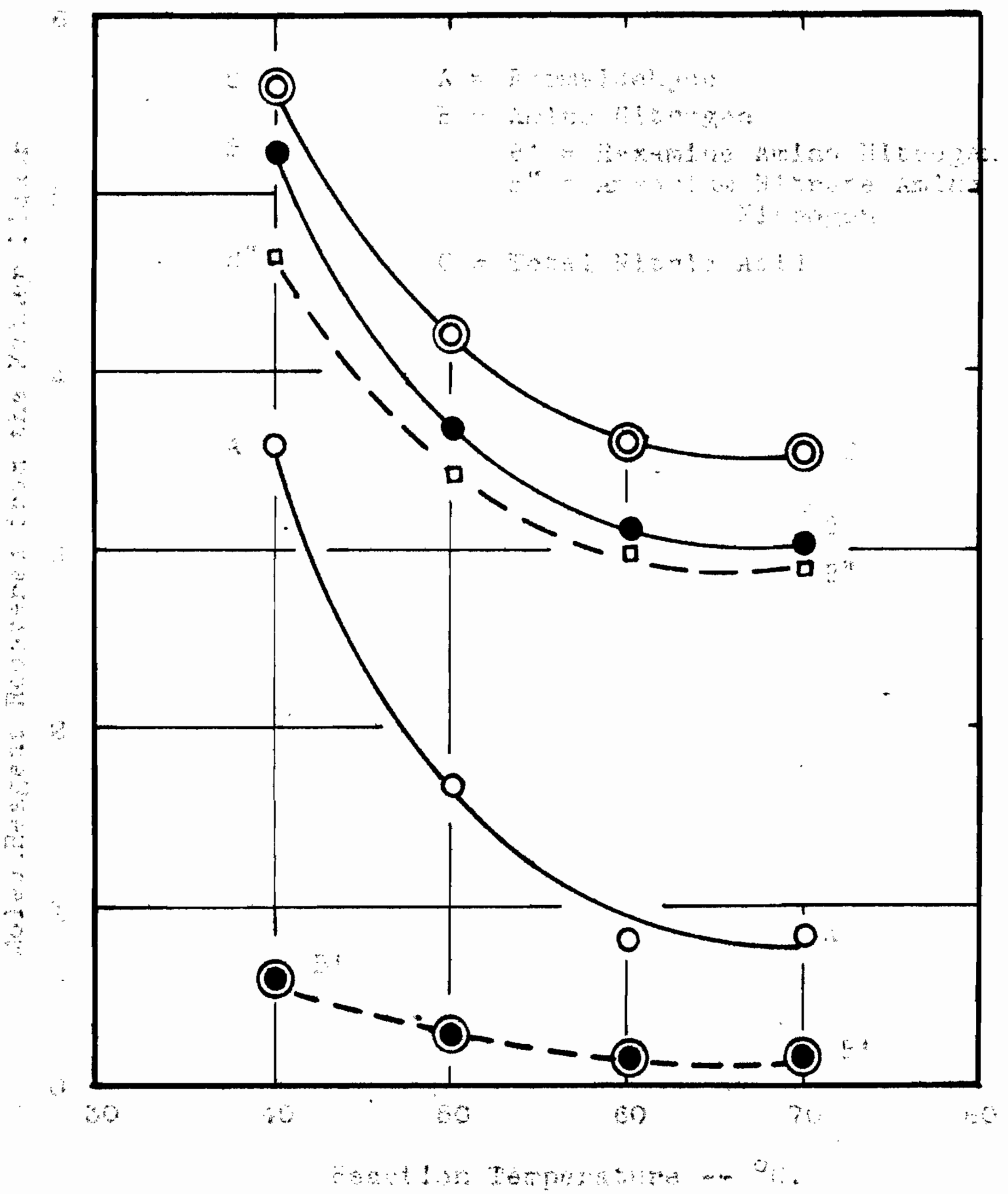

A = Formaldehyde
B = Amino Nitrogen
B' = Hexamine Amino Nitrogen
B" = [illegible] Nitrate Amino Nitrogen
C = Total Nitric Acid
Moles Reagent Remaining in the Filter Liquor
0
1
2
3
4
5
6
30
40
50
60
70
80
Reaction Temperature -- °C.
A
B
B'
B"
C

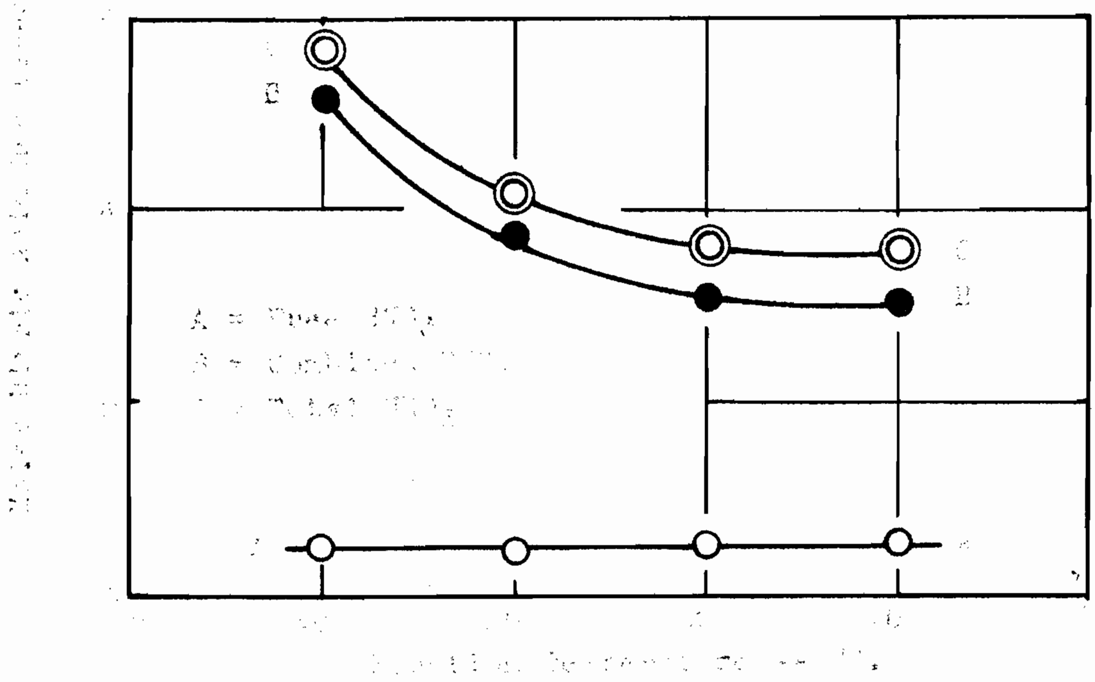
Figure No. 63

This is in accord with the increased efficiency of the whole reaction.

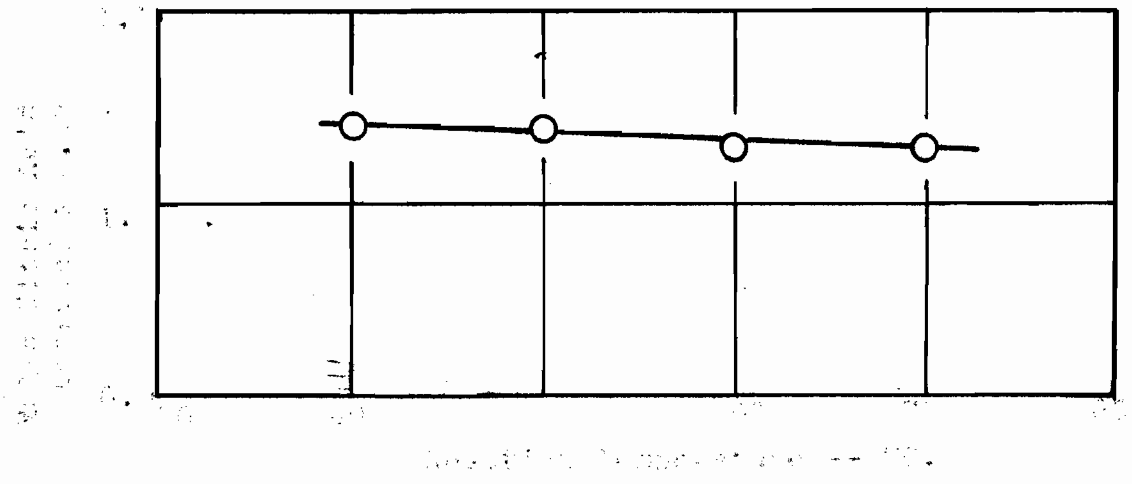
In Figure No. 63, the curve representing amino nitrogen in the mother liquor is broken down into two components representing ammonium nitrate amino nitrogen and hexamine amino nitrogen. This resolution has been carried out on the basis of previous theoretical discussions. (See pp. 195 and 213.)

Nitric Acid:- As the reaction temperature is increased, the quantities of total nitric and combined nitric acids in the mother liquor decrease (Figures Nos. 63 and 64). These observations are in accord with the general increase in the efficiency of the reaction. It is observed that, for all reaction temperatures, the ratio of amino nitrogen to combined nitric acid in the mother liquor equals unity. This is not very significant from a theoretical point of view since such an equivalence seemed almost certain in view of the large excess of ammonium nitrate introduced into the reaction.

As the reaction temperature is increased, the amount of free nitric acid in the mother liquor apparently decreases slightly (Figure No. 64). This corresponds to a slight increase in the amount of nitric acid consumed (Figure No. 65). Some doubt is cast on the validity of this observation when it is realized that the analyses represent the consumption as being somewhat greater than four moles per mole of hexamine. This does not agree with the results formerly obtained (Tables V, VIII and IX). Nor does it agree with the observations of Bachmann (61).


B
C
D

[illegible]


1.
0.

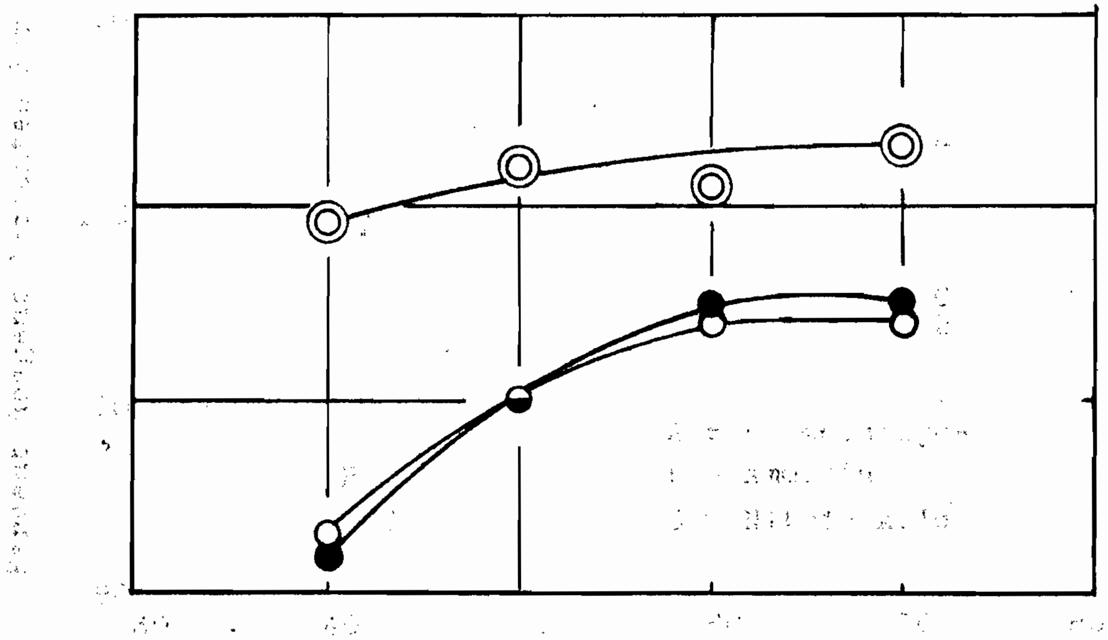
[illegible]

3. Material Balances

Formaldehyde:- The formaldehyde balance apparently increases slightly as the reaction temperature is increased (Figure No. 66). At higher temperatures positive balances are obtained.

Ammonia:- As the reaction temperature is increased, the quantity of amino nitrogen that can be accounted for in terms of solid reaction products and distillable amino nitrogen increases (Figure No. 66). This is in general agreement with the increased efficiency of the process as a whole.

When the material balance is made according to the method of Carmack(92) (p.217), it is found that the percent hexamine converted to linear nitramines decreases and that the percent hexamine converted to cyclic nitramines increases (Figure No. 67). While the calculated total conversion of hexamine generally increases with increasing temperature, the values of the individual results support the viewpoint advanced in this thesis (p. 223) that, while these calculated conversions are a measure of the "extent of the nitrolysis of the hexamine" and of the relative efficiency of the catalysed nitrolysis and synthesis processes (supposing a two-stage mechanism), they are not a measure of the accuracy of the analysis of of the reaction products. As was previously pointed out, calculated conversions of greater than 100 percent are indicative of an efficient synthesis process as compared with the catalysed nitrolysis process. The experimental results indicate that at 50°C. the synthesis process



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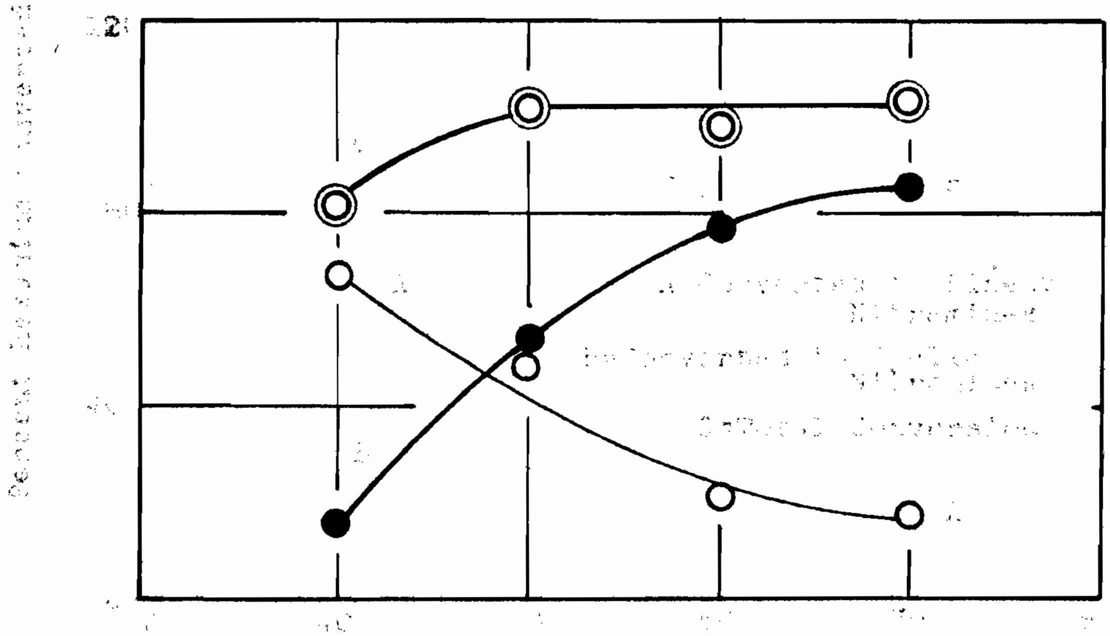
[illegible]



[illegible]

[illegible]

is very much more efficient than is the catalysed nitrolysis process - - the calculated total conversion of hexamine being high even though it is likely that the hexamine is not "completely nitrated". At higher temperatures, the two processes apparently proceed to approximately the same extent.

Nitric Acid:- As the reaction temperature is increased, the quantity of nitric acid accounted for in terms of solid reaction products and nitrate ion in the mother liquor decreases (Figure No. 66). This is in agreement with the increased efficiency of the reaction.

Once again it is found that the ratio of amino nitrogen not accounted for to nitrate ion not accounted for is unity. This constitutes support for the postulation (p. 213) that the loss of these two substances is due to the evolution of nitrous oxide on hydrolytic decomposition of the by-product, inisolable nitramines.

4. Miscellaneous Considerations Concerning the Reaction Mechanism

As the reaction temperature is increased, the apparent consumption of ammonium nitrate increases from a negative value (minus one-half mole) to a positive value of about 1.7 moles per mole of hexamine; the corrected* value for the ammonium nitrate consumption, however, increases from a small positive value (Figure No. 68). The fact that,

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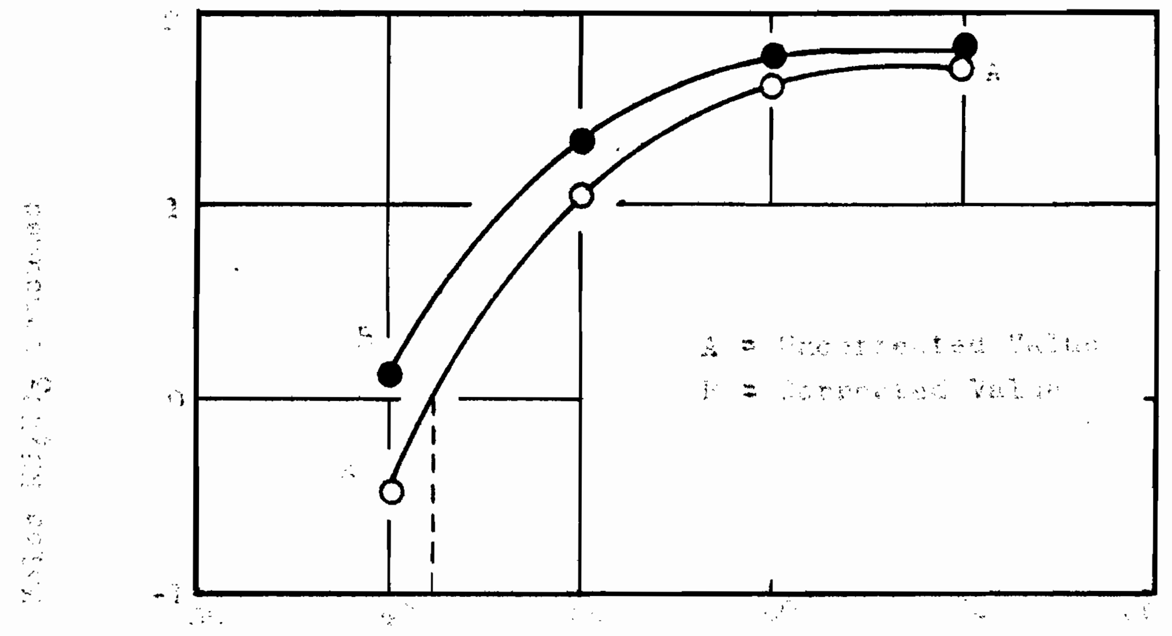
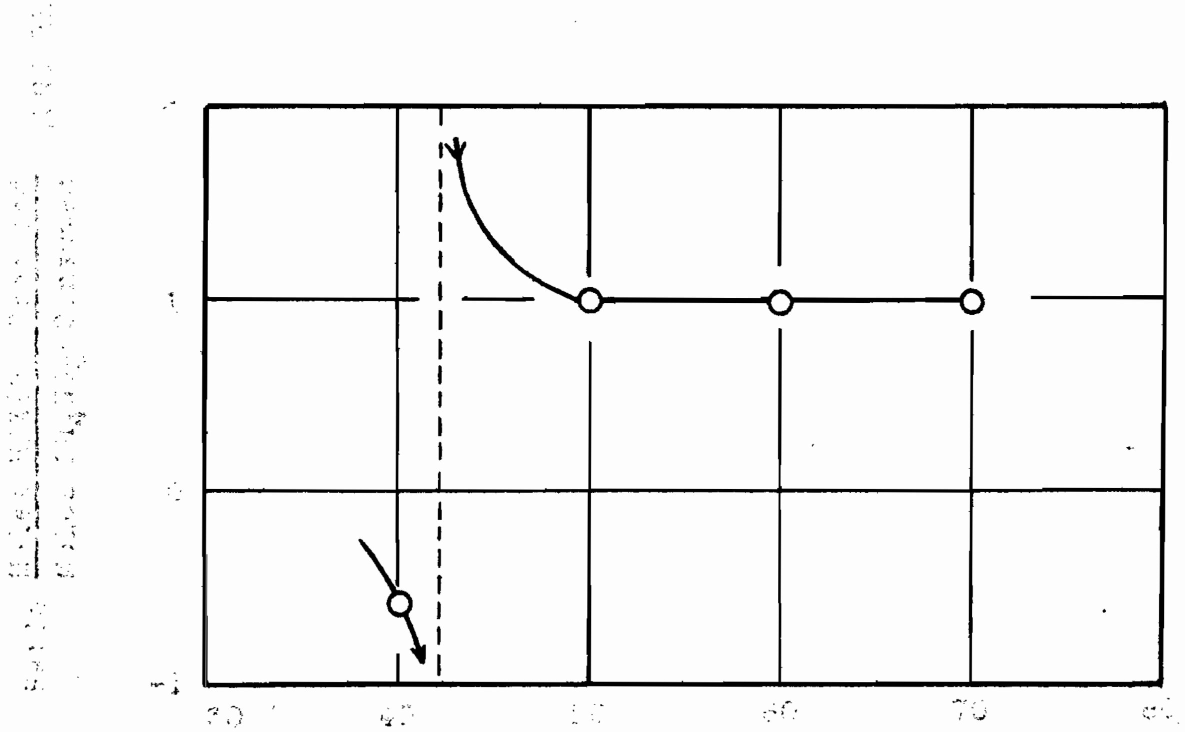
* See p. 198 for the method of correcting the apparent consumption of ammonium nitrate.



Reaction Temperature -- °C.

Figure No. [illegible]



Reaction Temperature -- °C.

Figure No. [illegible]

on applying the emperical correction suggested in this thesis, significant values for the ammonium nitrate consumption are obtained over the whole range of temperatures studied provides strong support for the theoretical considerations advanced with regard to the recovery, consumption and material balance of amino nitrogen in the reaction (pp. 191, 207 and 225).

In Table X, six different values for the ratio of RDX (and RDX(B)) production to ammonium nitrate consumption are given for each reaction temperature investigated. The first set of three values is based on the RDX(B) yield while the second set of three values is based on the yield of RDX.*

The first ratio ("UNCORR.") in each set of three values is uncorrected in any way and is based on the RDX(B) (or RDX) yield and the apparent consumption of ammonium nitrate. It will be seen (Figure No. 69) that, as the reaction temperature is increased, the value of the ratio increases numerically from a small negative value to minus infinity, decreases numerically from plus infinity to a fairly constant value representing (approximately) an equivalence between the two factors.

The second ratio in each set of three ("CORR.I") is obtained by using the corrected value for the ammonium nitrate consumption. In this case, as the reaction temperature is increased, the ratio falls

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* Since the two sets of values do not differ to any great extent, only those ratios based on RDX(B) are plotted in Figures Nos. 69 and 70.

rapidly from a large positive value to a minimum (at approximately 50°C.) and then rises to a constant value (Figure No. 70).

The third ratio in each set of three ("CORR.II") is obtained by using the corrected value for the ammonium nitrate consumption as before and, in addition, subtracting from the yields of RDX and RDX(B) the base value representing the yield of RDX obtained at a given temperature when no ammonium nitrate was present in the reaction (see Table IX). The reason for this correction has already been pointed out (p. 232). In this case, the graph showing the variation in the value of the ratio with changing temperature is similar to the above ratio ("CORR.I") but is displaced downwards somewhat over the whole range of temperatures investigated. (Figure No. 70).

The unusual shape of the curves shown in Figure No. 70 is very significant. The initial high values in the curves show that, at low temperatures, the catalysed nitrolysis process (even though very inefficient) proceeds to a much greater extent than does the synthesis process. The rate of the synthesis process, however, increases very rapidly until, in the region of 50°C - 55°C., it proceeds almost quantitatively in the short reaction times used and certainly to a greater extent than does the catalysed nitrolysis process at these temperatures: this is shown by the minimum in the curves in Figure No. 70. The efficiency of the catalysed nitrolysis process, however, increases steadily until in the region of 60°C. - 70°C. it approaches maximum efficiency; the value of the ratio thus increases again until

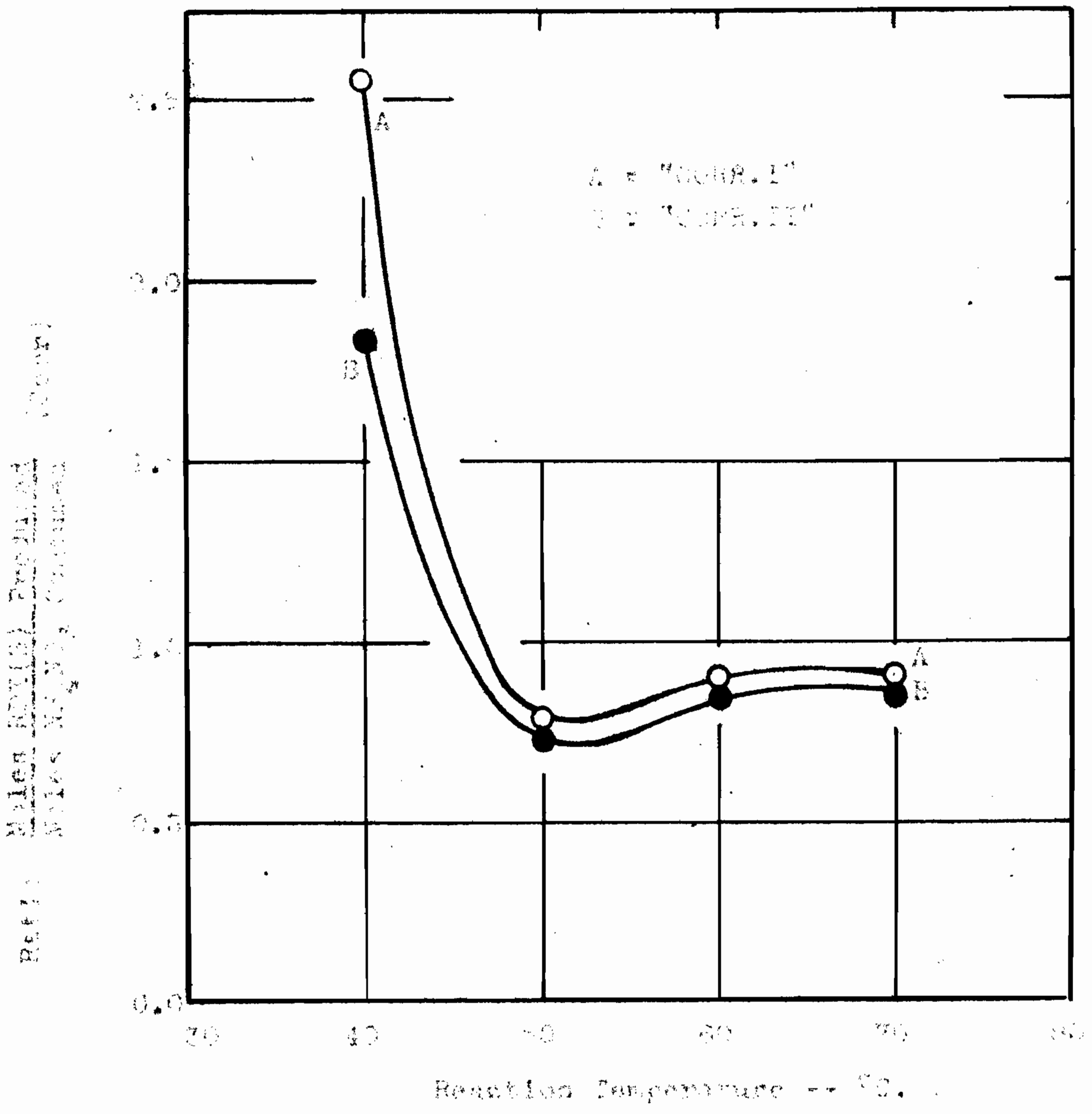


Figure No. [illegible]

a region is reached where the two processes are relatively insensitive to temperature and the value of the ratio remains constant. The final value for the corrected ratio indicates that the synthesis process produces slightly more RDX than does the catalysed nitrolysis process under optimum conditions.

The variation in the corrected ratio of RDX production to ammonium nitrate consumption with changing temperature was not unexpected. The initial high values of this ratio were predicted as early as a year before these experiments were carried out in the recognition (on the basis of independent experimental evidence) that RDX produced in low-temperature runs of short holding time is largely the product of a catalysed nitrolysis rather than a synthesis reaction (p. 145). Again, with reference to the rapid increase in the rate of the proposed synthesis process in the region of 40°C. - 50°C., the exceptionally high temperature coefficient of both the McGill and Bachmann reactions at these temperatures has long been recognized.

The rapid increase in the rate of the synthesis process in the region 40°C. - 50°C. is also evidenced in an examination of the curves representing RDX production, BSX production and formaldehyde recovery and was independently predicted on the basis of the calculated percent conversion of hexamine (p.264).

An examination of all these data shows that the ratio of RDX (or RDX(B)) production is not necessarily equivalent to the ammonium nitrate consumption. The fact that at high temperatures the value of the uncorrected ratio approximates unity constitutes some support for the views of Davy and Carmack. The successful interpretation of the values of the ratio over the whole range of temperatures studied in terms of the proposed "catalysed nitrolysis - synthesis" mechanism, however, constitutes support for the opposing views advanced in this thesis. The conclusion that may be reached, then, with regard to the mechanism of the reaction is that the values of the ratio obtained at different temperatures do not exclude mechanisms which assume that the two moles of RDX are formed by different processes.

E. Effect of Holding Time before Dilution on Yields and Material Balances (2.86 Moles Ammonium Nitrate, Temp. 40°C.) (CARMACK)

Carmack (93, 94, 95, 96) has investigated the effect of varying the holding time before dilution for low-temperature Bachmann runs.

Experimental

The experimental and analytical procedures used were essentially the same as those previously described (p. 178).

The Bachmann procedure was modified with respect to temperature in that the runs were carried out at 35°C. - 40°C. The time of addition of the reagents was 25 minutes instead of the 12.5 minutes previously reported. In addition, the holding time between the completion of the addition of the reagents and dilution was varied as indicated in

Table XI. The concentration of ammonium nitrate was 2.86 moles per mole of hexamine.

The results of these experiments are reproduced in Table XI and are discussed in the following paragraphs. All results have been calculated on the basis of one mole of hexamine.

Discussion

1. Yields of Solid Products

The yield of RDX(B) increases slowly with an increase in holding time (Figure No. 71). This result was previously observed in this laboratory (Table III). It is believed that the initial yield of RDX(B) (i.e. the RDX(B) obtained in runs of very short holding time) is produced mainly by a catalysed nitrolysis reaction. The increase in RDX(B) yield with increased holding time is regarded as being due to a synthesis process. This process is slow at low temperatures.

2. Recovery of Reagents from the Mother Liquor

The quantity of ammonia recovered from the diluted mother liquor decreases with increased holding time (Figure No. 72). This is in accord with the concept of a slow synthesis continuing over a period of some hours.

3. Material Balances

The quantity of amino nitrogen accounted for in terms of solid

TABLE XI

BACHMANN REACTION:-EFFECT OF HOLDING TIME BEFORE DILUTION ON YIELDS AND MATERIAL BALANCES (2.86 MOLES AMMONIUM NITRATE TEMPERATURE 40°C.) - CARMACK

(CALCULATED TO ONE MOLE HEXAMINE)

RUN NUMBER	HOLDING TIME	RDX(B)	AMMONIA (6.86 MOLES)			NH_4NO_3 CONSUMED	MOLES RDX(B) PRODUCED / MOLES NH_4NO_3 CONSUMED	Δ RDX(B) PRODUCED	Δ NH_4NO_3 CONSUMED	Δ NH_4NO_3 CONSUMED / Δ RDX(B) PRODUCED
			IN MOTHER LIQUOR	ACCOUNTED FOR						
	MINS.	MOLES	MOLES	MOLES	%	MOLES	UNICAR.	MOLES	MOLES	
1	0	0.20	3.02	3.62	53	−0.16	−1.25	−0.04	−0.29	+7.3
2	10	0.20	2.90	3.50	51	−0.04	−5.00	−0.04	−0.17	+4.3
3	20	0.24	2.73	3.45	50	+0.13	+1.84	—	—	—
4	30	0.25	2.68	3.43	50	0.18	1.39	0.01	0.05	5.0
5	40	0.28	2.63	3.47	51	0.23	1.21	0.04	0.10	2.5
6	50	0.29	2.55	3.42	50	0.31	0.94	0.05	0.18	3.6
7	60	0.32	2.46	3.42	50	0.40	0.80	0.08	0.27	3.4
8	90	0.37	2.33	3.44	50	0.53	0.70	0.13	0.40	3.1
9	120	0.38	2.35	3.49	51	0.51	0.74	0.14	0.38	2.7
10	150	0.43	2.26	3.55	52	0.60	0.72	0.19	0.47	2.5
11	420	0.40	2.28	3.48	51	0.58	0.69	0.16	0.45	2.8

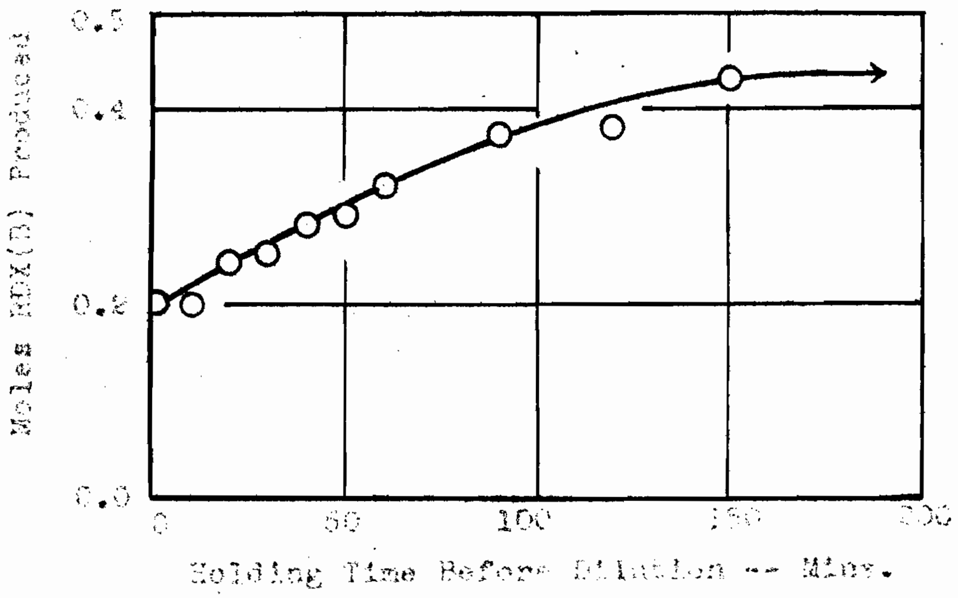


Figure No. 71

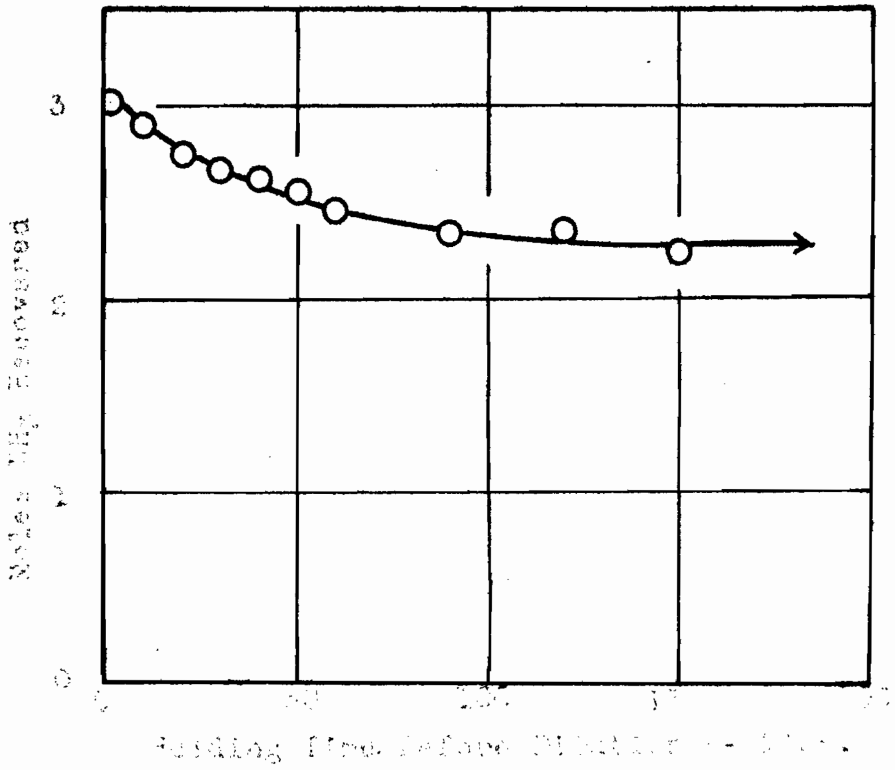


Figure No. 72

reaction products and distillable amino nitrogen remains constant (Table XI) as the holding time is increased. This indicates that, at these low temperatures, ammonium nitrate is not consumed in reactions other than those leading to RDX(B).

No attempt has been made to calculate the percent hexamine converted to linear and cyclic nitramines or the percent total conversion of hexamine. In view of the comparatively large yields of by-product, inisolable nitramines (which generate amino nitrogen on hydrolytic decomposition), the percent total conversion of hexamine would be low and without significance.

4. Miscellaneous Considerations Concerning the Reaction Mechanism

As the holding time before dilution is increased, the apparent consumption of ammonium nitrate increases from a small negative value to a positive value of about 0.5 moles per mole of hexamine (Figure No. 73). It is not possible to calculate the corrected values for the ammonium nitrate consumption since no data on the formaldehyde recovery are available for these reaction conditions.

As the holding time is increased, the ratio of RDX(B) produced to ammonium nitrate consumed increases numerically from a small negative value to minus infinity, is discontinuous, and decreases numerically from plus infinity to a relatively constant value of about 0.7 after two hours (Figure No. 74). While it is not possible to calculate the

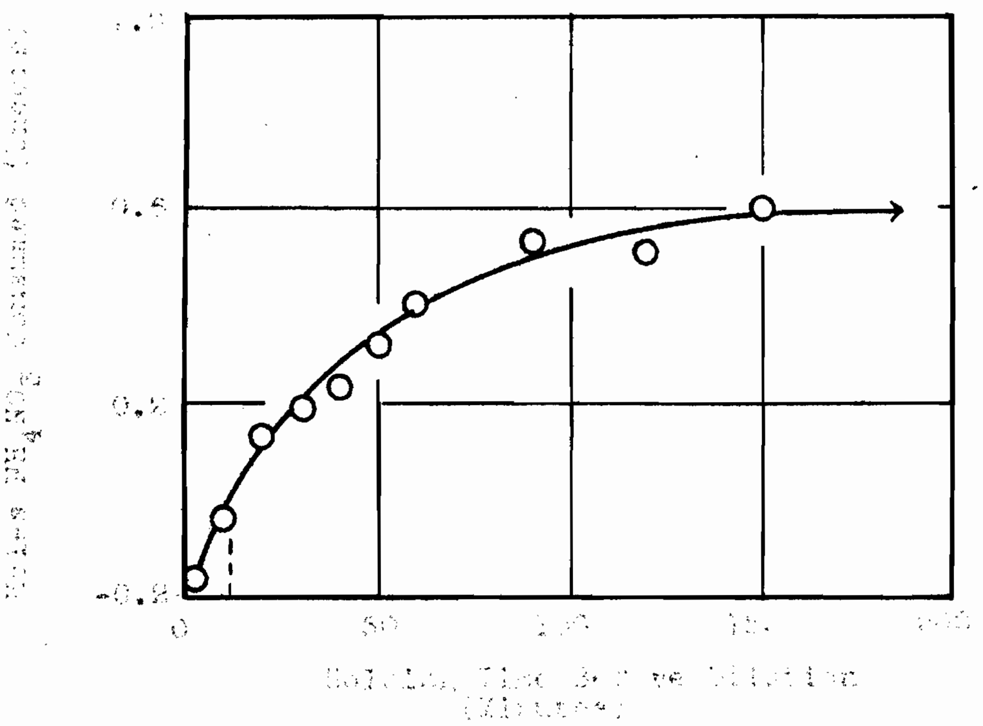


Figure No. 73

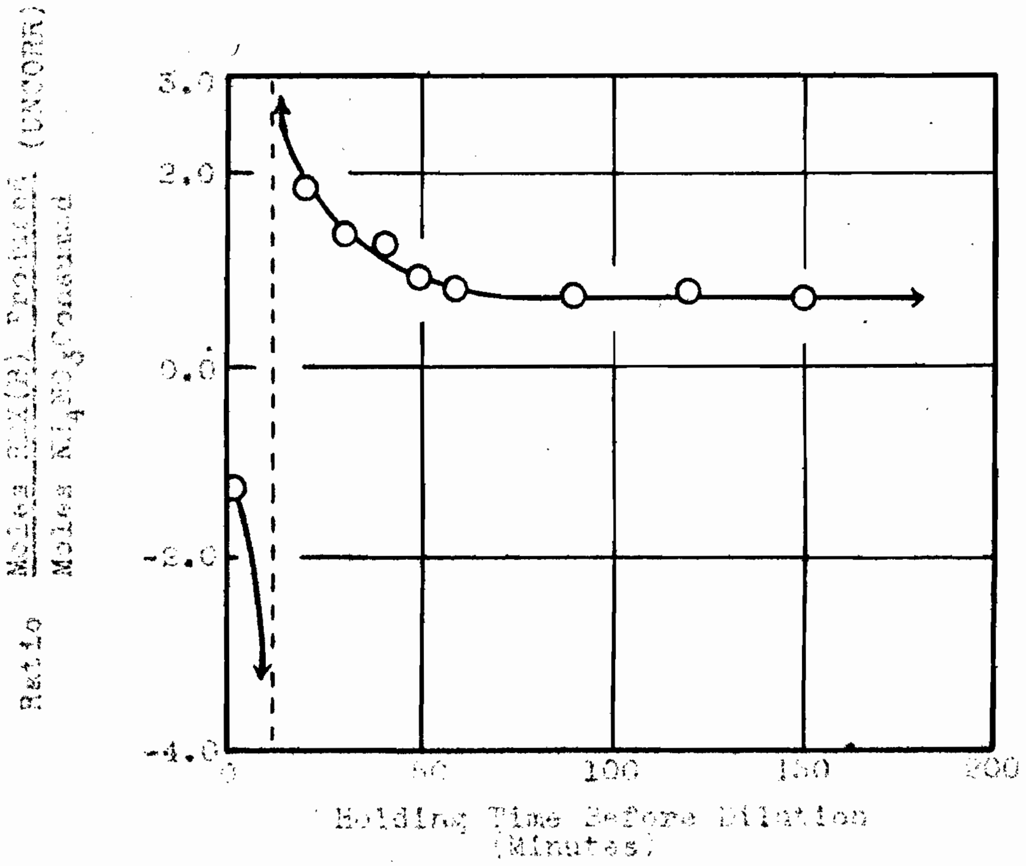


Figure No. 74

corrected ratio as in previous series, experience suggests that this would decrease rapidly from a large positive value to a fairly constant value somewhat below the 0.7 level.

Carmack, in a discussion of these results, has failed to assign them any theoretical significance. He points out that they do not agree with the requirements of the proposed Davy mechanism, but attempts to show that the deviations from unity are due to experimental inaccuracies. He suggests, as a possible source of error, that ammonium nitrate may be lost to the system through reactions other than those leading to RDX(B) formation. The author regards this possibility as an unlikely one since it has been shown that the quantity of amino nitrogen accounted for does not decrease with increased holding time (Figure No. 73). Furthermore, if this were true, it would invalidate many of the ratios at higher temperatures, data which constitute almost the only support for the proposed Davy mechanism. Carmack has shown that the presence of formaldehyde and formaldehyde-producing substances during the simmer interfere with the recovery of ammonia. Even if this is so, however, it is difficult to see why the interference would be greater after long holding times (in the undiluted condition) since the quantities of formaldehyde and formaldehyde-producing substances are almost the same, if not somewhat less, as at short holding times.

Actually it seems that, while the results may not be accurate in an absolute sense, the general trend of the ratio is beyond doubt and is of theoretical significance.

It has been postulated (p. 145) that the RDX(B) produced in low-temperature runs of short holding time is generated mainly by a catalysed nitrolysis process. If this is so, one would expect that the ratio of RDX(B) production to ammonium nitrate consumption would be very high since no ammonium nitrate is consumed in the catalysed nitrolysis reaction. It has been further postulated that, as the holding time is increased in such a run, additional RDX is slowly generated by a synthesis process. If this is so, one would expect the ratio of RDX(B) production to ammonium nitrate consumption to decrease since either two or three moles of ammonium nitrate are consumed in the formation of one mole of RDX. These predictions are in agreement with the experimental results of Carmack.

It may be concluded, then, that for low temperature runs, the ratio of RDX(B) production to ammonium nitrate consumption decreases with increasing holding time and is not equal to unity over any wide range of conditions. This fact cannot be accommodated by the symmetrical fission theory of Davy but is in complete accord with the requirements of the proposed "catalysed nitrolysis - synthesis" mechanism.

It is noteworthy that, if one calculates the increase in RDX(B) yields and the increased quantities of ammonium nitrate consumed in the later stages of the reaction (e.g. beyond the twenty minute holding period), in general, three moles of ammonium nitrate are consumed for each mole of RDX(B) that is formed. When based on Run 3, for example, the average consumption for Runs 5 - 11 is found to be 2.96 moles ammonium nitrate per mole of RDX(B). (See Table XI). This fact, which cannot be explained on the basis of the proposed Davy theory, is one of the principal criteria for the existence of a synthesis process.

F. Effect of Holding Time after Dilution on Yields and Material Balances (Zero Moles Ammonium Nitrate; Temp. 40°C.)

In this series of experiments, the effect of varying the length of time between dilution of the reaction liquor and filtration was investigated. In these experiments no ammonium nitrate was introduced into the reaction liquor. The reaction temperature was 40°C.

One of the principle objectives of this series of runs was to gain some insight into the mechanism of generation of the amino nitrogen which can be shown to be present in the diluted mother liquor of a run into which no ammonium nitrate is introduced.

Experimental

The experimental and analytical procedures used were the same as those described in connection with the experiments of section III A. The results of these experiments are presented in Table XII and are discussed in the following paragraphs.

Discussion

1. Variation in Yields of Solid Products

TABLE XI

BACHMANN REACTION:-EFFECT OF HOLDING TIME AFTER DILUTION ON YIELDS AND MATERIAL BALANCES (0.00 MOLES AMMONIUM NITRATE - TEMP. 40°C.)

(CALCULATED TO ONE MOLE HEXAMINE)

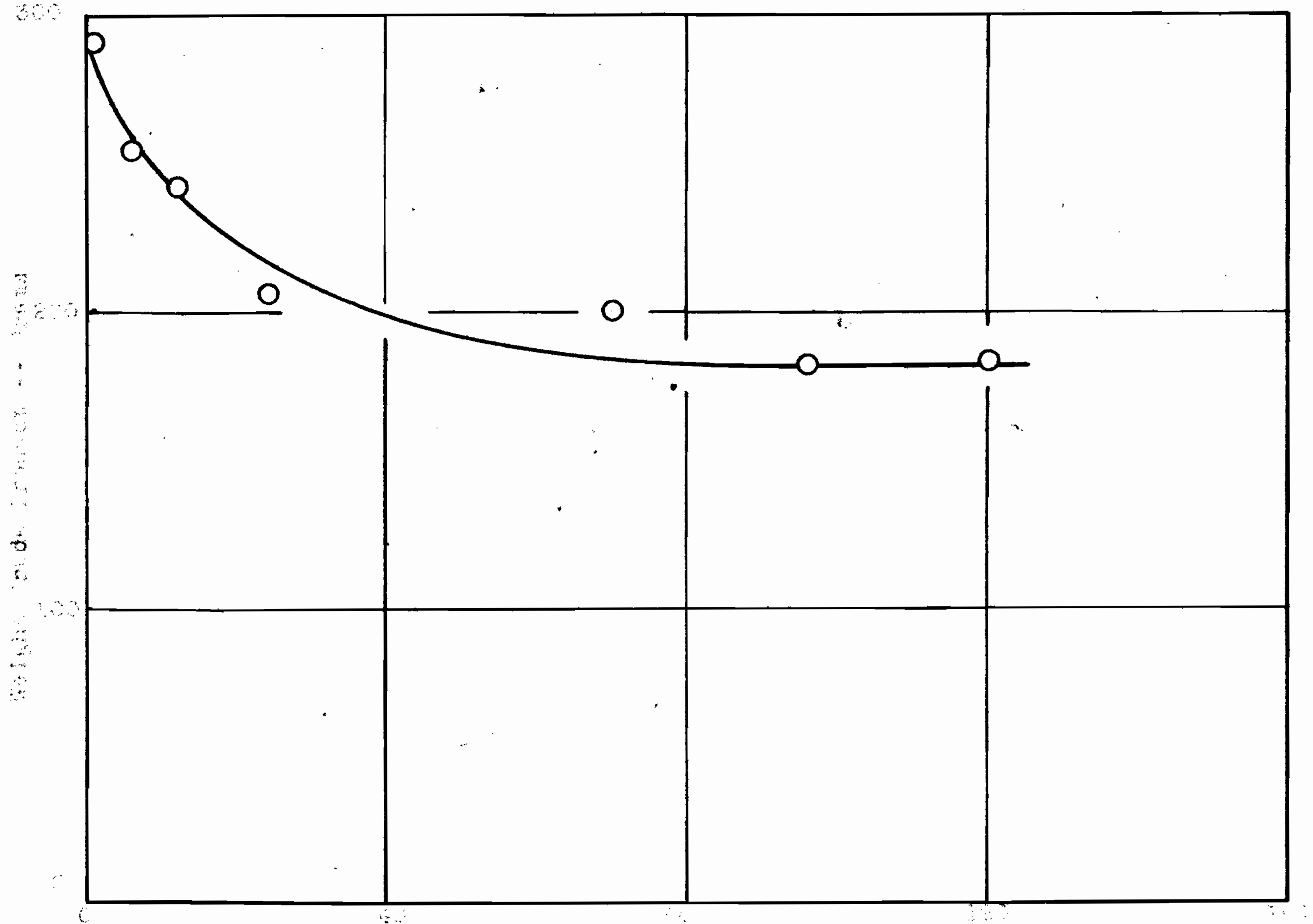
RUN NUMBER	HOLDING TIME	AVERAGE OF	RDX (B)	TOTAL SOLIDS	BSX	BAMN *	FORMALDEHYDE (6 MOLES)			AMMONIA (4 MOLES)			NITRIC ACID (4.44 MOLES)					ACETIC ANHYDRIDE (6.70 MOLES)			$\frac{\text{MOLES } NH_3 \text{ IN MOTHER LIQUOR}}{\text{MOLES } HCHO \text{ IN MOTHER LIQUOR}}$	$\frac{\text{MOLES } NH_3 \text{ IN MOTHER LIQUOR}}{\text{MOLES COMB. } HNO_3 \text{ IN MOTHER LIQUOR}}$	$\frac{\text{MOLES } NH_3 \text{ NOT RECOVERED}}{\text{MOLES } HNO_3 \text{ NOT RECOVERED}}$	MOLES NITRIC ACID CONSUMED x 0.25
							IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR FREE	IN MOTHER LIQUOR COMBINED	IN MOTHER LIQUOR TOTAL	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR					
	HRS.		MOLES	GRAMS	MOLES	MOLES	MOLES	MOLES	%	MOLES	MOLES	%	MOLES	MOLES	MOLES	MOLES	%	MOLES	MOLES	%				
1	1	1	0.055	2.91	0.51	0.56	2.12 (2.7)	5.46 (6.0)	91 (100)	0.51	2.77	69	0.48	0.39	0.88	3.14	71	5.75 (6.2)	6.82 (7.3)	102 (108)	0.238 (0.189)	1.31	0.95	0.99
2	6	1	0.073	2.54	0.51	0.36	3.02	6.00	100	0.53	2.64	66	0.51	0.42	0.93	3.04	68	6.40	7.27	108	0.176	1.26	0.97	0.98
3	12	1	0.073	2.41	0.51	0.29	3.21	6.05	101	0.59	2.63	66	0.54	0.41	0.94	2.98	67	6.57	7.39	110	0.184	1.44	0.94	0.98
4	24	1	0.073	2.06	0.51	0.12	3.51	6.01	100	0.65	2.52	63	0.50	0.50	1.01	2.88	65	6.94	7.57	113	0.185	1.30	0.95	0.99
5	70	1	0.073	2.00	0.51	0.10	3.73	6.19	103	0.62	2.47	62	—	—	0.97	2.82	64	—	—	—	0.166	—	0.95	—
6	96	1	0.073	1.81	0.51	0.00	3.81	6.07	101	0.65	2.40	60	0.51	0.48	1.01	2.76	62	6.93	7.44	111	0.190	1.35	0.95	0.98
7	120	1	0.073	1.23	0.51	0.01	3.73	6.01	100	0.63	2.39	60	0.56	0.47	1.03	2.79	63	6.68	7.20	107	0.169	1.34	0.98	0.97

* BIS-(ACETOXYMETHYL)-NITRAMINE

Total Solids:- The variation in yield of total solids is a very interesting factor. It will be seen from Table XII and from an examination of Figure No. 75 that the weight of solid products obtained when the mother liquor is filtered immediately after dilution is about 50 percent greater than is the case when the mother liquor is filtered 100 hours after dilution. It may be further observed that (1) after 100 hours no further decomposition takes place and (2) the decrease in yield of solid product in excess of this minimum indicates a simple mass law relationship.

From these facts it may be concluded that some compound is precipitated on dilution of a crude Bachmann reaction liquor (into which no ammonium nitrate was introduced) which is not RDX, HMX or BSX and that this compound is unstable and will slowly decompose in the diluted mother liquor. That the decomposition products of this compound are formaldehyde, acetic acid, nitric acid, ammonia and nitrous oxide may be seen from a more extensive examination of the material balance data.

On the basis of the theoretical considerations of many workers in this field, it was postulated that this compound is bis-acetoxymethylnitramine (or, the diacetate of dimethylol nitramine), hereinafter designated as BAMN. At the time that this viewpoint was first reported, BAMN was unknown. Evidence for its existence in the crude reaction product (other than that reported in this section) was obtained and is presented in an appendix to this thesis. Subsequently Wright (53) was able to isolate BAMN in 39 percent yield from this source; the proper-


300
200
100
0
0
40
80
120
160

[illegible]

ties of this compound corresponded to those properties predicted on the basis of the earlier experiments reported herein.

RDX(B):- As the holding time after dilution is increased, the yield of RDX(B) remains constant (Table XI). This would be expected since RDX(B) is stable towards dilute acids. It will be observed that, for the run of one hour holding time, a somewhat smaller yield of RDX was obtained. This is believed to be due to a secondary effect such as incomplete precipitation. No data are available concerning the composition of the RDX(B).

BSX:- In this series of experiments it is assumed that the yield of BSX is constant as the holding time after dilution is varied. This assumption seems justified in that after 100 hours no further loss in yield of solid product is observed even though BSX is present.

The value of the BSX yield is taken as being the difference between the weight of the crude product for runs of long holding time (when all the BAMN has been destroyed) and the weight of RDX(B) (as determined by a fume-off). For a run in which the holding time after dilution is 96 hours, it is calculated that the yield of BSX is 0.512 moles, and after 120 hours, 0.517 moles. These values show good agreement with the calculated yield of BSX of 0.51 moles obtained under similar conditions in another series of runs (Table IX).

BAMN*:- If the difference between the weight of the crude product and the sum of the weights of RDX and BSX is calculated and is

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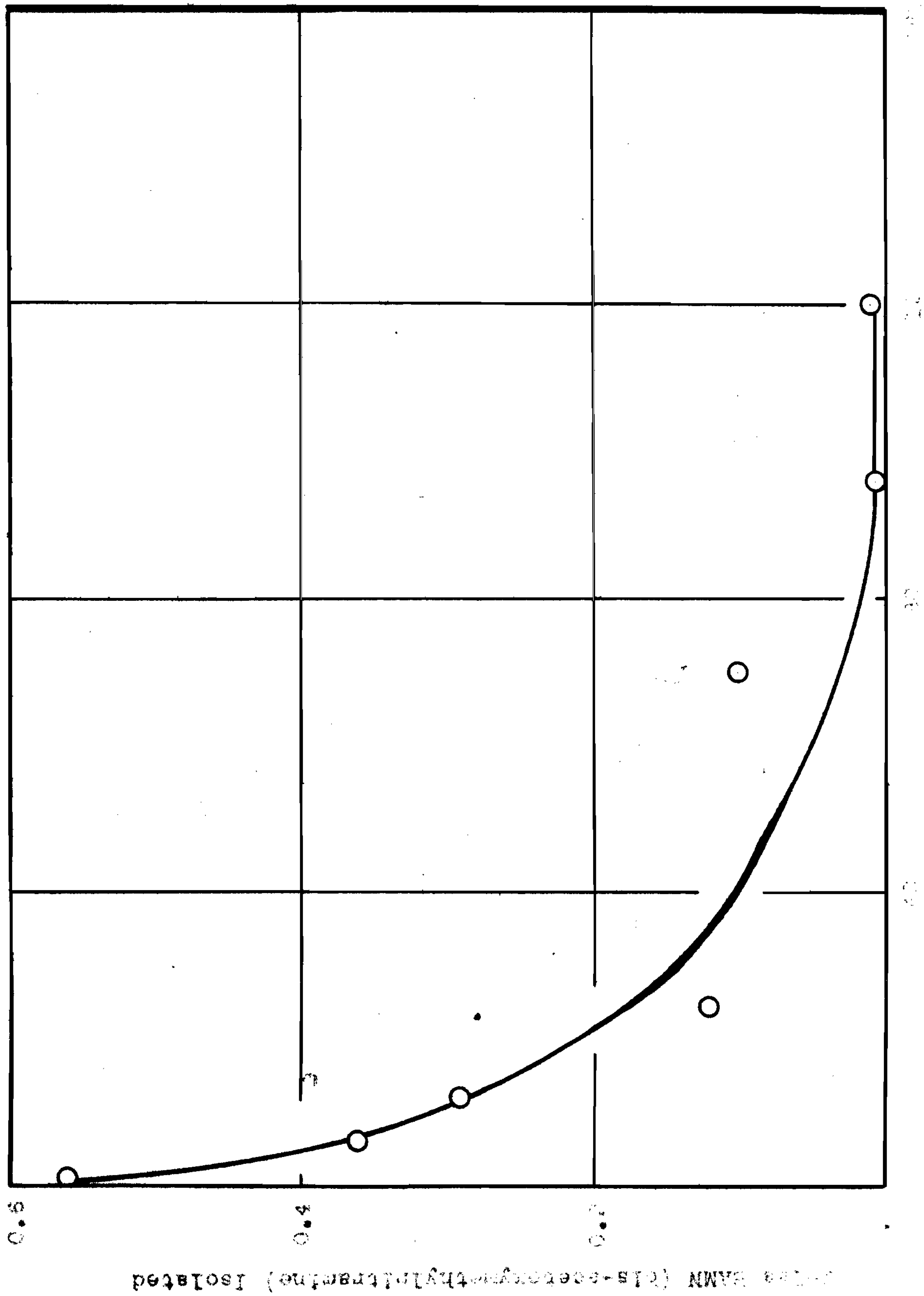
* Bis-acetoxymethylnitramine.

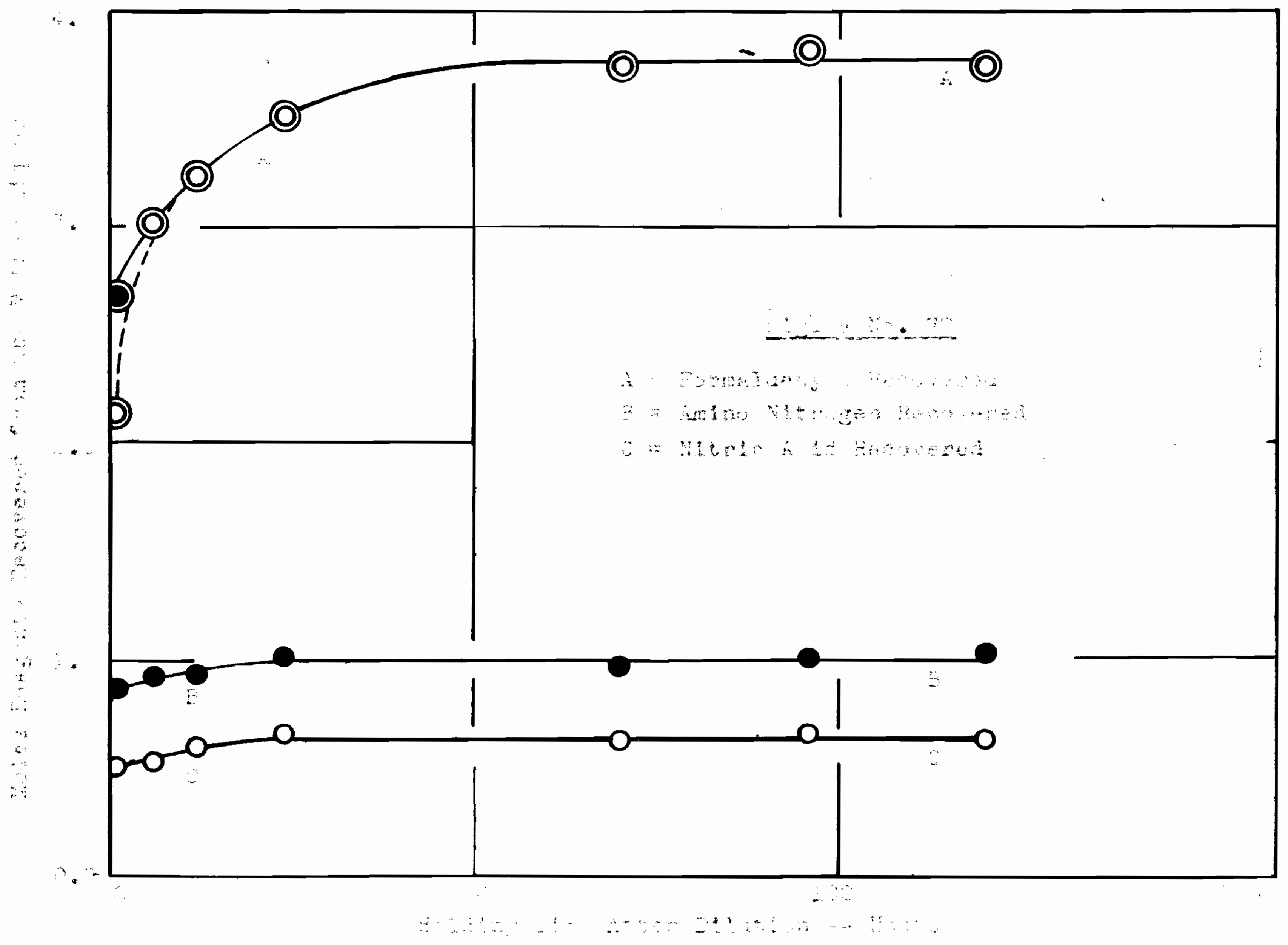
divided by a factor of 206, a value for the molar yield of BAMN is obtained. These values are shown in Table XII and are plotted as a function of the holding time after dilution in Figure No. 76. It will be seen that the yields approximate 0.5 moles for short holding times and that these fall off very rapidly and approximate zero moles after 90 hours. The value of 0.5 moles corresponds closely to the yield of BSX in the reaction. This might be significant since BAMN has been postulated as a by-product of BSX formation. On the other hand, the correspondence between the two values might be fortuitous and the initial yield of BAMN might be considerably higher. Such a condition could be explained on the basis that BAMN is the logical end-product for any degradation process of hexamine, whether or not BSX is produced.

2. Recovery of Reagents from the Mother Liquor.

Formaldehyde:- As the holding time after dilution is increased, the quantity of formaldehyde in the mother liquor increases to a constant value (Figure No. 77). The final value is attained after about 70 hours standing of the diluted mother liquor. The increase in the quantity of formaldehyde (provided that the corrected initial value is used - - see below) corresponds to about 30 percent of the final value. Furthermore, this increase is estimated to be of the order of one mole. This is significant in that the calculated yield of BAMN is of the order of one-half mole.

Reference has been made to the "corrected" initial value of the


0.6
0.4
0.2
BAMN (bis-acetoxymethylnitramine) Isolated


A = Formaldehyde Recovered
B = Amino Nitrogen Recovered
C = Nitric Acid Recovered
A
B
C
After Dilution -- Hours

recovered formaldehyde and it will be observed that in Table XII run 1 alternate values are suggested for this factor, for the moles total recovery of formaldehyde, for the percent formaldehyde accounted for and for the ratio of amino nitrogen in the mother liquor to formaldehyde in the mother liquor. These "corrected" values are suggested in the believe that the quantity of formaldehyde in the mother liquor would be higher were it not for some secondary effect. This belief, in turn, is based on extrapolation of the curves of the four, above-mentioned variables. The values for these factors (which are included parenthetically in Table XI), then, are the values obtained by extrapolation of the other experimental data.

It should be emphasized (1) that these "corrections" have only been applied to one run and (2) that it is not implied that the deviations are due to experimental error. The secondary effect causing the deviation in the formaldehyde balance is thought to be adsorption of formaldehyde diacetate by the crude solid product. It has been predicted that this compound will be formed to a greater or less extent in the modified Bachmann reaction into which no ammonium nitrate is introduced. If this compound has any real existence in the Bachmann reaction liquor, it will undoubtedly be hydrolysed very rapidly on dilution. It is possible, however, that one hour is not sufficiently long to allow complete hydrolysis. In this case the methylene bisacetate would appear in the crude solid product (either due to precipitation or adsorption). On standing in air (in a moist or dry condition), this product would lose formaldehyde and acetic acid to the atmosphere. Thus, formaldehyde which would normally appear in the mother liquor is lost to the system.

Support for these theoretical considerations is to be found in the fact that a "corrected" value for the acetic acid recovery is obtained on extrapolation and in the fact that the anhydride balance is much lower than usual if no account is taken of the postulated existence of the formaldehyde diacetate.

Ammonia:- As the holding time after dilution is increased, the quantity of ammonia in the diluted mother liquor increases to a constant value (Figure No. 77). The final value is attained after about 25 hours standing of the diluted mother liquor. This increase is of such a magnitude as to represent about 30 percent of the final ammonia value. This behaviour is in accord with previous theoretical considerations (p. 213) which supposed that BAMN decomposes slowly in the diluted mother liquor to give off the greater part of its nitrogen as nitrous oxide but yielding, in addition, some ammonium nitrate.

It has been shown that the ratio of amino nitrogen in the mother liquor to formaldehyde in the mother liquor is a constant (1) as the ammonium nitrate concentration is varied (provided that an excess of ammonium nitrate is not present) and (2) as the reaction temperature is varied when no ammonium nitrate is introduced. It will be seen that, as the holding time after dilution is increased, this ratio decreases very slightly in magnitude. The value of the ratio for long holding times is 0.168; this agrees with the values of 0.165

and 0.167 as determined in Table V and Table IX respectively. The value of the ratio is plotted as a function of the holding time after dilution in Figure No. 78.

Nitric Acid:- As the holding time after dilution is increased, the quantity of nitrate ion in the mother liquor increases (Figures Nos. 77 and 79). The quantity of combined nitric acid also increases (Figure No. 79). The behaviour of both of these factors is in accord with the postulated decomposition of BAMN in the diluted mother liquor. It will also be observed that, as the holding time is increased, the ratio of amino nitrogen to combined nitric acid in the mother liquor remains relatively constant (Table XII). The fact that this ratio has a value greater than unity shows that acetylation of amino nitrogen has taken place during the reaction (see p. 250).

The behavior of the free nitric acid in this series of experiments is somewhat less certain. It seems as if there might be an increase in the amount of free nitric acid present in the diluted mother liquor as the holding time is increased (Table XI) but this is uncertain and cannot be accounted for in terms of the theoretical considerations thus far advanced. If this behaviour is valid, it corresponds to the generation of free nitric acid on standing in the diluted mother liquor.

Acetic Anhydride:- As the holding time after dilution is increased, the quantity of acetic anhydride recovered from the diluted mother liquor as acetic acid increases (Figure No. 80). The final value seems to have been attained after 24 hours standing. Using the extrapolated value

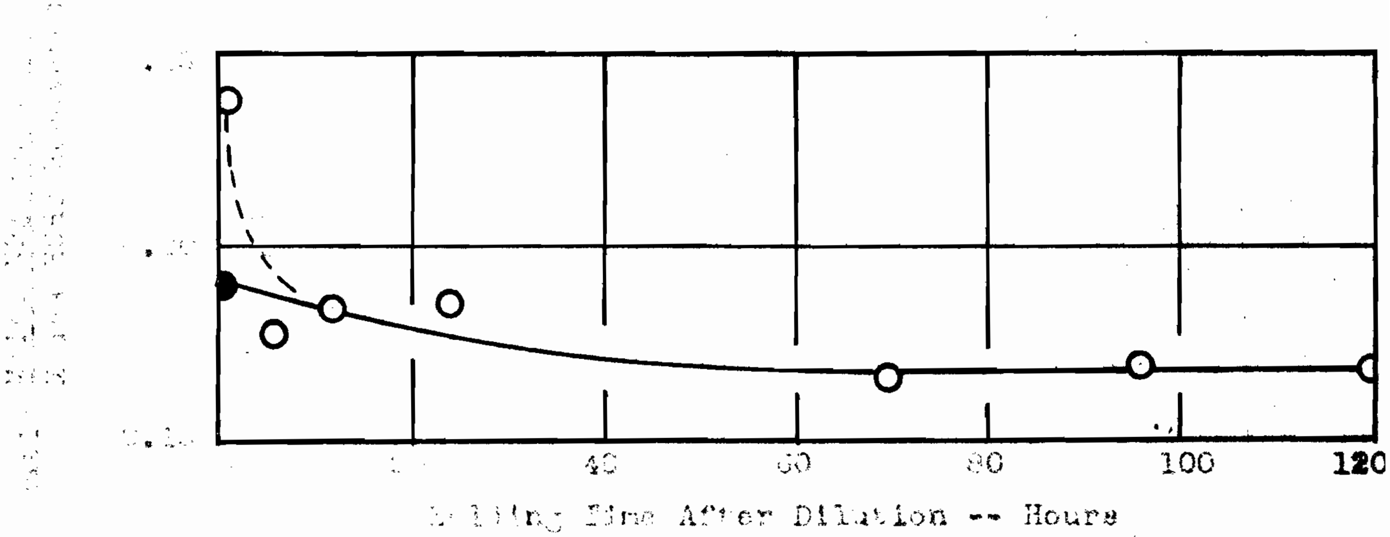


Figure No. 78

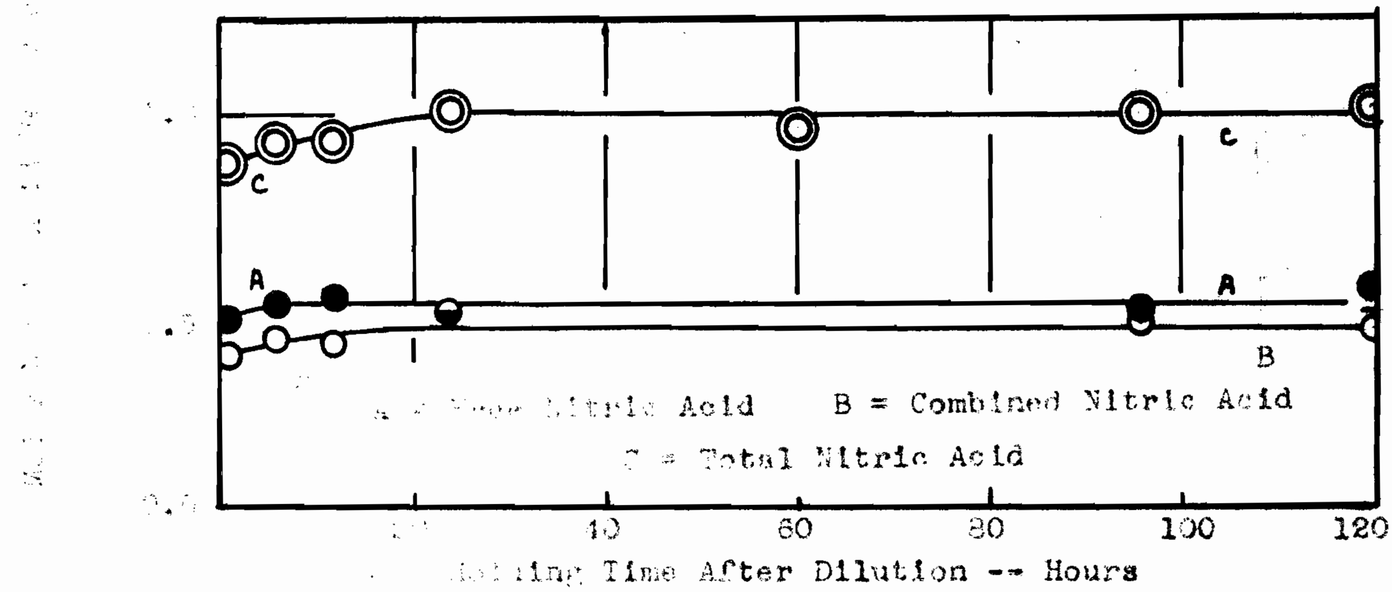


Figure No. 79

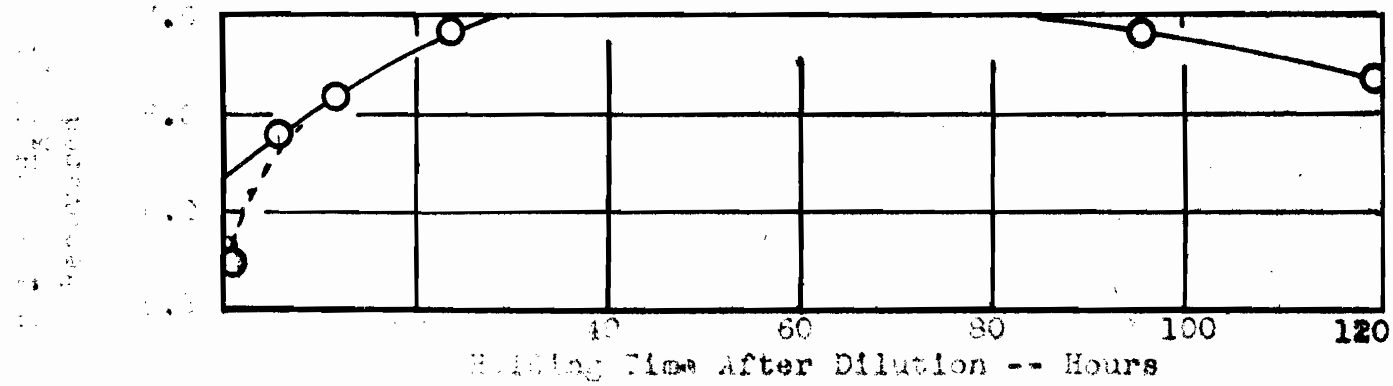


Figure No. 80

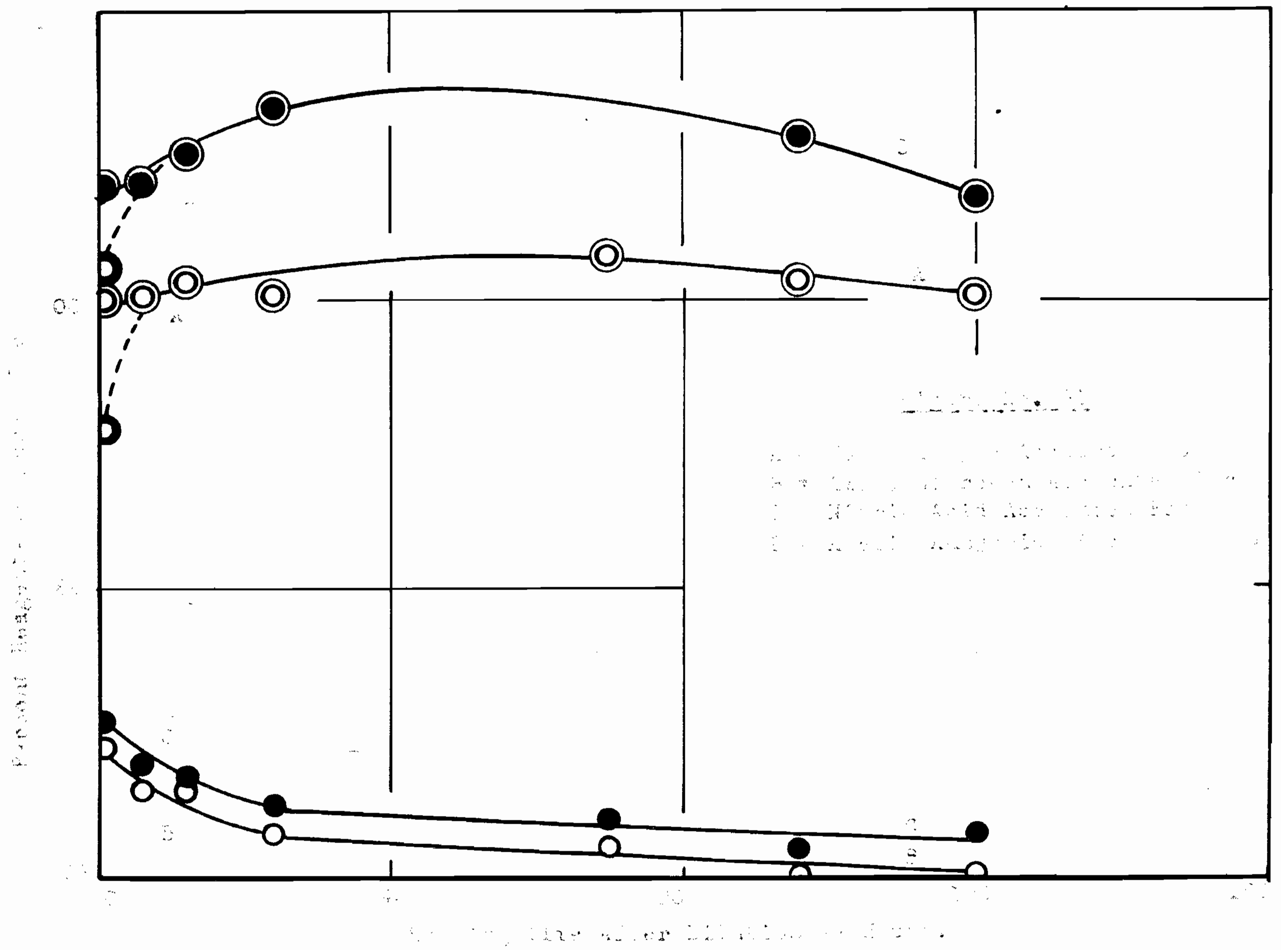
for the one hour holding time, the increase in the quantity of anhydride approximates 0.8 moles. This agrees reasonably well with the decrease in BAMN yield of about 0.5 moles. The behaviour, in general, is in accord with the other experimental data.

As has already been pointed out, the value for the quantity of acetic anhydride in the mother liquor of the one hour holding time run as obtained by analysis differs considerably with the value obtained by extrapolation of the other points in the curve. The extrapolated value is included parenthetically in Table XII. The deviation between the two values is thought to be due to the precipitation of methylene bisacetate in runs of short holding time after dilution.

3. Material Balances

Formaldehyde:- The number of moles of formaldehyde accounted for and percent total recovery of formaldehyde were calculated from the yields of RDX(B), BSX and BAMN and the quantity of formaldehyde present in the diluted mother liquor. The results of these calculations are presented in Table XII and the percent total recovery is plotted as a function of the holding time in Figure No. 81.

In six out of the seven cases, a formaldehyde balance of about 100 percent is indicated. This fact strongly supports the postulation of the precipitation and decomposition of bis-acetoxymethylnitramine in these runs since, if the BAMN is not taken into account or if the non-RDX(B) fraction of the crude product is calculated as BSX, a formalde-


Percent Weight
10
A
B
C
D

hyde balance cannot be made. This is important since, in the past, the formaldehyde balance has been found to be a dependable criterion of the accuracy of the experimental methods used.

In the run of one hour holding time after dilution, however, even with the difference between the total solids and weight of RDX plus BSX being calculated as BAMN, only 90 percent of the formaldehyde introduced can be accounted for. This fact seems to indicate that the crude solid product probably contains, in addition to BAMN, some compound with a higher formaldehyde equivalent than BAMN. It has been suggested that this compound is methylene-bis-acetate and that it decomposes very rapidly on dilution to give formaldehyde and acetic acid. This compound would probably decompose even after filtration and the formaldehyde evolved would be lost to the system. In view of this situation, an alternate value has been obtained for the amount of formaldehyde in the diluted mother liquor by extrapolating the curve passing through the other experimental points. If this value is used, 100 percent of the formaldehyde can be accounted for in this run, too.

Ammonia:- The number of moles of ammonia accounted for and the percent total recovery of ammonia were calculated from the yields of RDX, BSX and BAMN and the quantity of amino nitrogen present in the diluted mother liquor. The results are presented in Table XII and the percent amino nitrogen accounted for is plotted as a function of the holding time after dilution in Figure No. 81.

As the holding time after dilution is increased, the quantity of amino nitrogen accounted for in terms of solid reaction products and distillable amino nitrogen decreases. This behaviour is in agreement with the postulated decomposition of BAMN with the evolution of nitrous oxide.

Nitric Acid:- The number of moles of nitric acid accounted for and the percent total recovery of nitric acid were calculated from the yields of RDX, BSX and BAMN and the quantity of (total) nitric acid present in the diluted mother liquor. These results are presented in Table XIi and the percent nitric acid accounted for is plotted as a function of the holding time after dilution in Figure No. 81.

As the holding time after dilution is increased, the total recovery of nitric acid decreases. This corresponds to loss of nitrous oxide during the decomposition of BAMN. This postulate is further supported by the fact that the ratio of amino nitrogen not recovered to nitric acid not recovered approximates unity.

Acetic Anhydride:- The number of moles of acetic anhydride accounted for and the percent total recovery of acetic anhydride were calculated from the yields of BSX and BAMN and from the quantity of acetic acid present in the diluted mother liquor. These results are presented in Table Xii and the percent acetic acid accounted for is shown as a function of the holding time after dilution in Figure No. 81.

The percent total recovery of acetic anhydride is calculated to be greater than 100 percent. Possible explanations for this condition have been advanced (p. 177). In spite of the obvious inaccuracies in the determinations, it is evident that the consistency of the results is improved (1) by allowing for the presence of the postulated BAMN in the crude solid product and (2) by recognizing that the acetic acid value for run 1 as determined by analysis does not coincide with the value obtained by extrapolation of the other experimental points and using this latter value. These facts support the postulated generation and decomposition of BAMN and methylene-bis-acetate.

A survey of the data presented in this section of the thesis indicates that at least one, and possibly two, compounds are produced in addition to RDX, HMX and BSX in Bachmann runs into which no ammonium nitrate is introduced. These compounds are precipitated on dilution. One of these appears to be hydrolysed very rapidly in the diluted mother liquor (i.e. one to six hours) and it is suggested that it is methylene-bis-acetate. The other appears to be hydrolysed more slowly in the diluted mother liquor (i.e. 24 - 48 hours) and it is suggested that it is bis-acetoxymethylnitramine. At least one of these compounds appears to generate ammonia and nitric acid on hydrolysis, although not in any simple stoichiometric quantities. Both of these compounds liberate formaldehyde and acetic acid on hydrolysis, apparently in near-quantitative amounts.

These indications constitute strong support for the theoretical considerations which postulated that the amino nitrogen recovered from the mother liquor of a run into which little or no ammonium nitrate was introduced is generated during the hydrolytic decomposition of low molecular weight, inisolable nitramines (P. 213). The strengthening of this postulate, in turn, adds weight to the stand that there is no equivalence between RDX production and ammonium nitrate consumption over any wide range of conditions.

G. Effect of Withholding Ammonium and Monomethylammonium Nitrates on Yields and Material Balances

In these series of experiments, the effect of belatedly adding various quantities of ammonium and amine nitrates to Bachmann runs carried out in the absence of ammonium nitrate is investigated. The effect of the temperature of the preliminary reaction involving acetic anhydride, nitric acid and hexamine is also studied. Specifically, the following series were carried out:

(1) Preliminary reaction at 40°C., subsequent addition of various quantities of ammonium nitrate with heating at 70°C. (<u>NH_4NO_3- - 40°C.</u>),

(2) Preliminary reaction at 70°C., subsequent addition of various quantities of ammonium nitrate (maintained at 70°C.) (<u>NH_4NO_3- - 70°C.</u>)

(3) Preliminary reaction at 40°C., subsequent addition of various quantities of monomethylammonium nitrate with heating at 70°C. (<u>$CH_3NH_3NO_3$- - 40°C.</u>)

As the variations of the original Bachmann procedure increase in complexity, the difficulty of interpreting the material balances in terms of the various proposed mechanisms for the reaction increases rapidly. Furthermore, as the original reaction is modified more and more, the experimental results derived from these modified procedures are less and less significant from a point of view of the original reaction mechanism. For these reasons, the three series of experiments are considered together rather than separately and not discussed as exhaustively as has been the case in the other material balance studies.

Experimental

1. Experimental and Analytical Procedures

In general, the experimental and analytical procedures used were the same as those described previously (Section III A). Certain modifications of the original Bachmann procedure were instituted, however, in view of the nature of the runs, and a new analytical procedure was introduced in order that separate values could be obtained for the ammonia and monomethylamine salts in the diluted mother liquor. Furthermore, in anticipation of an extended study involving the use of other amine nitrates, values were obtained for total ammonia and primary amines (as distinct from secondary and tertiary amines) by the method of van Slyke. Since the other series of experiments did not materialize, these results are not reported and the analytical procedure is not detailed here.

Bachmann Procedure:- The preliminary part of the run was carried out in the usual manner: nitric acid, acetic anhydride and a solution of hexamine in acetic acid were added slowly, proportionately and continuously to an initial charge of acetic acid, acetic anhydride and nitric acid. The "reaction temperature" was either 38-40°C. or 68-71°C. (as indicated in the tables of results). After the completion of the addition of these reagents, the reaction mixture was held on temperature for an additional 20 minutes. At the conclusion of this time, a weighed amount of ammonium nitrate or monomethylammonium nitrate was added to the reaction mixture and the whole was heated as rapidly as possible to 68-71°C. ("holding temperature") if it was not already at this temperature. The mixture was held for 20 minutes and was then diluted with water and worked up in the uusual manner.

Ammonia:- In the runs where ammonium nitrate was added in the second stage of the reaction, ammonia was determined in the diluted mother liquor in the usual manner (i.e. by distilling the ammonia from the alkaline solution after previous acid distillation). In runs where monomethylammonium nitrate was added, however, the above procedure was considered to be a measure of the "total base", and ammonia was determined separately by a modification of the widely-used nesslerization procedure.

The Nessler reagent used was made up as follows: Five grams potassium iodide was dissolved in 3.5 ml. distilled water, and saturated aqueous mercuric chloride was added to the point of incipient precipitation. Forty millilitres of 50 percent KOH was then added and, after 24 hours standing, the supernatent liquid was decanted and stored in a brown-glass bottle.

The ammonia was estimated as follows. A one millilitre sample of the diluted mother liquor contained in a test tube was treated with 0.10 ml. of the Nessler reagent. If a precipitate (cloudiness) appeared after 30 seconds, the mother liquor was greater than 0.005 N. with respect to ammonia. In this case 0.5 ml. distilled water was added to 1 ml. of diluted mother liquor in another test tube and 0.15 ml. Nessler reagent was introduced. If the solution turned cloudy, this operation was continued, the dilution of the mother liquor being increased 0.5 ml. per ml. and the quantity of Nessler reagent by0.05 ml. The solution which just gave a positive test for ammonia (i.e. precipitate) was considered to be approximately 0.005 N. with respect to ammonia. Then,

$$\text{Moles } NH_3 \text{ in Mother Liquor} = \frac{0.005\ (1 + x)\ V}{1000}$$

where x = number of millilitres water added per millilitre of mother liquor, and

V = volume of diluted mother liquor.

This procedure* was not tested on synthetic samples and the results must be accepted with reserve.

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* Suggested by W.E. Scheer, Technical Service Division, Commercial Solvents Corporation.

One further comment is necessary in connection with the analytical results obtained in this section of the thesis. The formaldehyde and ammonia (total base) analyses were not carried out by the author personally but by a technician. A survey of the results will show that some of these values do not fit into series. While it may be that, due to the complexity of the experimental procedure, these variations are genuine, there is a distinct possibility that they may be due to experimental error. Outstanding cases, then, are regarded with suspicion.

2. Experimental Results

The results of the above-described series of experiments are presented in Tables XIII, XIV and XV and are discussed in the following paragraphs. In general, it is found advantageous to compare the data in both Tables XIV and XV to the data in Table XIII.

Discussion

1. Variation in Yields of Solid Products

RDX (RDX(B)):- For the belated addition of ammonium nitrate, the yield of RDX(B) increases to a maximum as the mole ratio of ammonium nitrate is increased at both 40°C. and 70°C.* (Figure No. 82.) The maximum yield is approximately twice as great for the 40°C. run

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* The temperatures refer to the preliminary reaction.

TABLE XIII

BACHMANN REACTION:- EFFECT OF WITHHOLDING THE AMMONIUM NITRATE ON YIELDS AND MATERIAL BALANCES (VARIOUS MOLE RATIOS OF AMMONIUM NITRATE; REACTION TEMP. 40°C. HOLDING TEMP. 70°C.)
(CALCULATED TO ONE MOLE OF HEXAMINE)

RUN NUMBER	NH_4NO_3 INTRODUCED	AVERAGE OF	RDX(B)	BSX	HMX IN RDX(B)	FORMALDEHYDE (6 MOLES)			AMMONIA (4+X MOLES)			NITRIC ACID (4·44+X MOLES)					ACETIC ANHYDRIDE (6·70 MOLES)			NH_4NO_3 CONSUMED			MOLES RDX(B) PRODUCED / MOLES NH_4NO_3 CONSUMED			MOLES NH_3 IN MOTHER LIQUOR / MOLES HNO_3 IN MOTHER LIQUOR	MOLES NH_3 NOT RECOVERED / MOLES HNO_3 NOT RECOVERED	MOLES NITRIC ACID UNCONSUMED x 0·25
						IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR: FREE	IN MOTHER LIQUOR: COMBINED	IN MOTHER LIQUOR: TOTAL	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR		APPARENT	CORRECTED							
	MOLES		MOLES	MOLES	%	MOLES	MOLES	%	MOLES	MOLES	%	MOLES	MOLES	MOLES	MOLES	%	MOLES	MOLES	%	MOLES	MOLES	%	UNCORR.	CORR. I	CORR. II			
1	0·00	2	0·07	0·68	—	3·14	6·18	103	0·48	2·72	68·0	0·53	0·33	0·85	3·09	69·5	6·19	6·87	102	-0·48	—	—	-0·15	—	—	1·45	0·95	0·98
2	0·24	1	0·11	0·71	—	2·96	6·24	104	0·34	2·80	66·0	0·55	0·21	0·76	3·22	69·0	6·33	7·04	105	-0·10	0·36	150	-1·10	0·31	0·11	1·62	0·98	0·97
3	0·48	1	0·16	0·75	2·0	2·08	5·54	92	0·37	2·99	66·5	0·45	0·21	0·66	3·38	69·0	5·96	6·71	100	+0·11	0·43	90	+1·46	0·37	0·21	1·76	0·97	1·00
4	0·96	1	0·40	0·77	7·7	1·87	6·23	104	0·17	3·74	75·0	0·49	0·06	0·56	4·13	76·5	5·68	6·47	97	0·79	1·08	113	0·51	0·37	0·30	2·84	0·96	0·99
5	1·44	1	0·51	0·69	6·0	1·86	6·15	103	0·47	4·07	75·0	0·48	0·39	0·87	4·47	76·0	6·01	6·70	100	0·97	1·26	87	0·53	0·41	0·35	1·21	0·97	0·99
6	1·92	1	0·49	0·71	5·2	1·47	6·28	105	1·03	4·63	78·2	0·50	0·81	1·32	4·92	77·5	6·55	7·26	108	0·89	1·19	62	0·55	0·41	0·35	1·27	0·90	0·99
7	2·40	2	0·49	0·71	4·2	1·99	6·29	105	1·62	5·21	81·5	0·55	1·36	1·97	5·57	81·5	6·25	6·96	104	0·78	1·08	45	0·63	0·45	0·39	1·19	0·94	0·97

X = MOLES AMMONIUM NITRATE INTRODUCED

TABLE XIV

BACHMANN REACTION:-EFFECT OF WITHHOLDING THE AMMONIUM NITRATE ON YIELDS AND MATERIAL BALANCES (VARIOUS MOLE RATIOS OF AMMONIUM NITRATE; REACTION TEMP. 70°C. HOLDING TEMP. 70°C.)
(CALCULATED TO ONE MOLE OF HEXAMINE)

RUN NUMBER	NH_4NO_3 INTRODUCED	AVERAGE OF	RDX(B)	BSX	HMX IN RDX(B)	FORMALDEHYDE (6 MOLES)			AMMONIA (4+X MOLES)			NITRIC ACID (4·44+X MOLES)					ACETIC ANHYDRIDE (6·70 MOLES)			NH_4NO_3 CONSUMED			$\frac{\text{MOLES RDX(B) PRODUCED}}{\text{MOLES } NH_4NO_3 \text{ CONSUMED}}$			$\frac{\text{MOLES } NH_3 \text{ IN MOTHER LIQUOR}}{\text{MOLES COMB. } HNO_3 \text{ IN MOTHER LIQUOR}}$	$\frac{\text{MOLES } NH_3 \text{ NOT RECOVERED}}{\text{MOLES } HNO_3 \text{ NOT RECOVERED}}$	MOLES NITRIC ACID CONSUMED x 0·25
						IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR			ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR		APPARENT	CORRECTED							
												FREE	COMBINED	TOTAL														
	MOLES		MOLES	MOLES	%	MOLES	MOLES	%	MOLES	MOLES	%	MOLES	MOLES	MOLES	MOLES	%	MOLES	MOLES	%	MOLES	MOLES	%	UNCORR.	CORR.I	CORR.II			
1	0·00	1	0·07	0·69	—	3·42	6·39	106	0·48	2·76	69	0·67	0·35	1·01	3·29	74	6·19	6·88	103	-0·48	—	—	-0·15	—	—	1·37	1·08	0·94
2	0·24	1	0·11	0·50	—	3·28	5·61	94	0·42	2·25	53	0·72	0·27	0·98	2·81	60	6·31	6·81	102	-0·18	0·28	116	-0·61	0·39	0·14	1·56	1·06	0·93
3	0·48	1	0·19	0·56	11·2	3·02	5·83	97	0·43	2·68	60	0·65	0·22	0·88	3·13	63	6·32	6·88	103	+0·05	0·47	98	3·80	0·40	0·26	1·95	1·00	0·95
4	0·96	1	0·22	0·51	9·4	2·66	5·36	89	0·92	3·11	63	0·60	0·71	1·31	3·50	65	6·18	6·69	100	0·04	0·41	43	5·50	0·51	0·37	1·29	0·97	0·96
5	1·44	1	0·27	0·50	9·6	2·93	5·74	96	1·18	3·49	64	0·56	1·07	1·63	3·94	67	6·09	6·59	98	0·26	0·67	47	1·02	0·40	0·30	1·10	1·00	0·97
6	1·92	1	0·29	0·51	10·9	2·88	5·79	97	1·64	4·04	68	0·57	1·47	2·04	4·44	70	6·08	6·58	98	0·28	0·69	36	1·02	0·42	0·32	1·12	0·98	0·97
7	2·40	1	0·27	0·52	7·3	2·92	5·81	97	2·17	4·54	71	0·65	2·07	2·72	5·09	75	6·26	6·78	101	0·23	0·64	27	1·17	0·42	0·31	1·05	1·06	0·95

X = MOLES AMMONIUM NITRATE INTRODUCED

TABLE XV

BACHMANN REACTION:-EFFECT OF "WITHHOLDING" MONOMETHYLAMMONIUM NITRATE ON YIELDS AND MATERIAL BALANCES (VARIOUS MOLE RATIOS OF MONOMETHYLAMMONIUM NITRATE; REACTION TEMP. 40°C. HOLDING TEMP. 70°C.
(CALCULATED TO ONE MOLE OF HEXAMINE)

RUN NUMBER	$CH_3NH_3NO_3$ ADDED	AVERAGE OF	RDX(B)	BSX	FORMALDEHYDE (6 MOLES)			AMMONIA (4 MOLES)			METHYLAMINE (x MOLES)			TOTAL BASE (4+X MOLES)			NITRIC ACID (4.44 + X MOLES)					ACETIC ANHYDRIDE (6.7 MOLES)			$CH_3NH_3NO_3$ CONSUMED	MOLES $CH_3NH_3NO_3$ CONSUMED / MOLES RDX(B) PRODUCED		MOLES NH_3 IN MOTHER LIQUOR / MOLES COMB. HNO_3 IN MOTHER LIQUOR	MOLES NH_3 NOT RECOVERED / MOLES HNO_3 NOT RECOVERED	MOLES NITRIC ACID CONSUMED × 0.25
					IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR		IN MOTHER LIQUOR FREE	IN MOTHER LIQUOR COMBINED	IN MOTHER LIQUOR TOTAL	ACCOUNTED FOR		IN MOTHER LIQUOR	ACCOUNTED FOR							
	MOLES		MOLES	MOLES	MOLES	MOLES	PERCENT	MOLES	MOLES	PERCENT	MOLES	MOLES	PERCENT	MOLES	MOLES	PERCENT	MOLES	MOLES	MOLES	MOLES	PERCENT	MOLES	MOLES	PERCENT	MOLES	UNCORR.	CORR.			
1	0.00	2	0.07	0.68	3.14	6.18	103	0.43	2.68	67	0.05	0.05	—	0.48	2.72	68	0.53	0.33	0.86	3.10	70	6.19	6.87	102	−0.05	− 1.46	—	1.45	0.96	0.98
2	0.24	2	0.10	0.74	2.42	6.18	103	0.26	2.78	70	0.09	0.09	37	0.35	2.87	68	0.56	0.24	0.80	3.32	71	6.19	6.93	103	+0.15	+ 0.67	0.20	1.46	1.01	0.97
3	0.48	1	0.14	0.77	2.47	5.96	99	0.16	2.89	72	0.27	0.27	56	0.43	3.15	70	0.75	0.20	0.95	3.67	75	5.68	6.45	96	0.21	0.67	0.33	2.15	1.06	0.92
4	0.96	2	0.15	0.78	2.50	6.08	101	0.22	3.01	75	0.45	0.45	47	0.67	3.45	70	0.85	0.47	1.31	4.09	76	5.94	6.72	100	0.51	0.29	0.16	1.43	1.15	0.90
5	1.44	1	0.16	0.70	2.76	6.05	101	0.22	2.80	70	0.89	0.89	62	1.11	3.70	68	0.79	0.85	1.63	4.22	72	5.99	6.69	100	0.55	0.29	0.16	1.31	1.05	0.91
6	1.92	1	0.16	0.66	3.01	6.14	102	0.31	2.77	69	1.40	1.40	73	1.71	4.18	71	0.73	1.34	2.07	4.54	73	6.22	6.88	103	0.52	0.31	0.17	1.28	0.96	0.93
7	2.40	1	0.16	0.66	3.09	6.21	104	0.22	2.68	67	1.74	1.74	73	1.96	4.22	69	0.71	1.75	2.55	5.01	73	6.54	7.20	107	0.66	0.24	0.14	1.12	1.19	0.93

X = MOLES $CH_3NH_3NO_3$ INTRODUCED

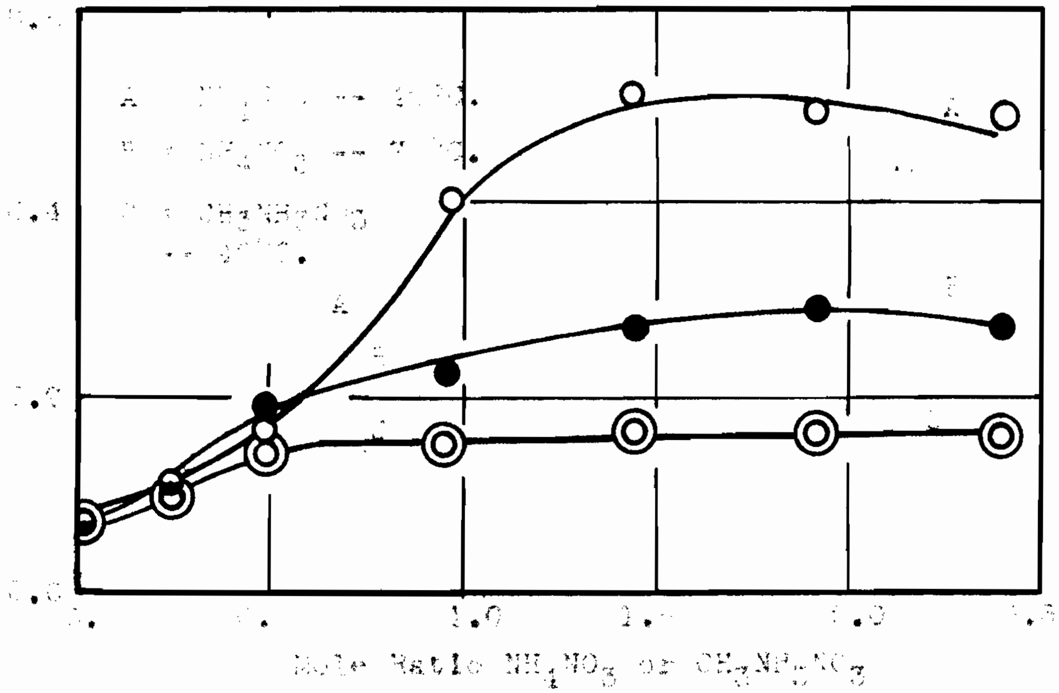


Figure No. [illegible]

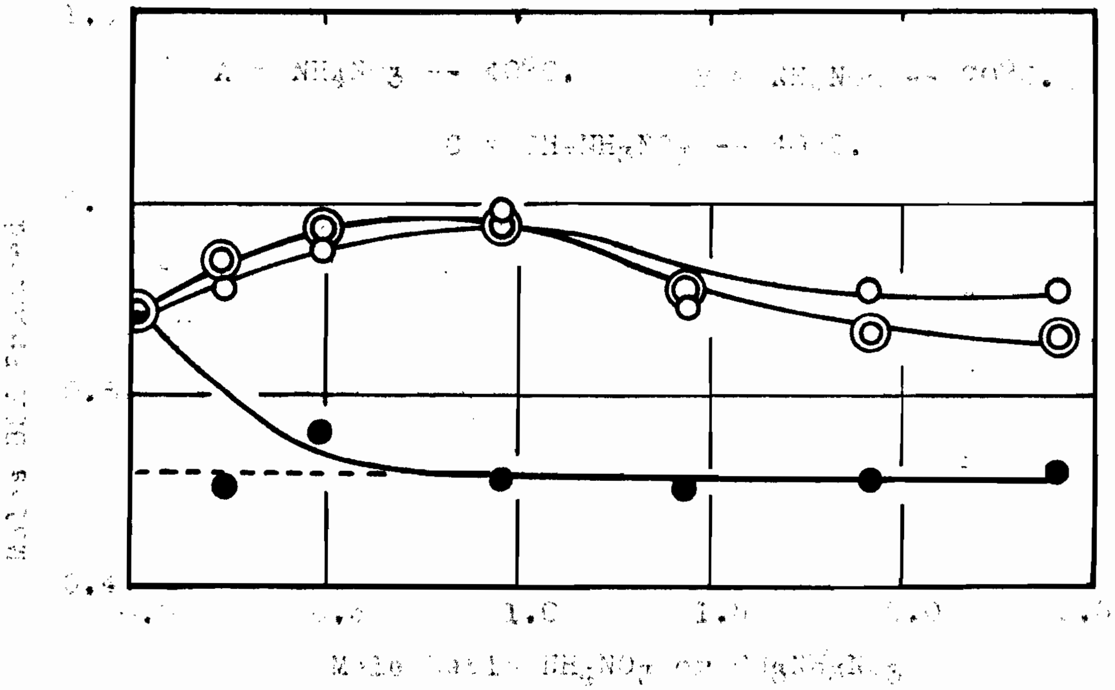


Figure No. [illegible]

as for the 70°C. run. It is interesting to observe that the maximum yield of RDX(B) in these runs bears no relationship to the quantity of amino nitrogen which would have been obtained on dilution of the mother liquor just before the time of addition of the ammonium nitrate (Table IX). Run 1, Table IX, shows that after holding the undiluted liquor for 20 minutes at 40°C., the diluted liquor has an amino nitrogen content of 0.63 moles; Run 4 Table IX shows that in the corresponding 70°C. run, 0.69 moles will be present. In the belated addition runs, the maximum yield for the 40°C. procedure approximates 0.5 moles while the 70°C. procedure approximates 0.3 moles RDX(B). It is thus evident that the production of RDX(B) does not depend on the quantity of amino nitrogen in the mother liquor (i.e. upon the "hexamine incompletely nitrated"). In view of these facts, there can be no reasonable doubt concerning the validity of the proposed "synthesis" process under these reaction conditions and it seems highly likely that, in Bachmann runs into which no ammonium nitrate is introduced, the amino nitrogen in the diluted mother liquor is produced during the hydrolytic decomposition of inisolable, by-product nitramines, and is not due to the survival of unnitrated amino nitrogen in the reaction liquor.

For the belated addition of monomethylammonium nitrate, the yield of RDX (RDX(B)(?)) increases relatively rapidly at the beginning and then more slowly as the mole ratio of monomethylammonium nitrate is increased. It seems that the two portions of the curve represent different mechanisms. The slow increase at high salt concentrations is probably due to the presence of ammonium nitrate in the monomethylammonium nitrate. (See p. 147). The rapid initial rise (comparable in magnitude to that when ammonium nitrate is used) cannot be attributed to this cause, however. It may be supposed, then, that there survives a little precursor (corresponding to 0.07 moles RDX) which can give rise to RDX through a catalysed nitrolysis process. One other possibility also exists. The initial rise in RDX yield corresponds to, roughly, about 0.2 moles of ammonium nitrate (by synthesis). It will be observed that the nitric acid excess introduced into these runs was of the order of 0.4 moles. In view of these quantities, the possibility of ammonium nitrate being generated by interaction of nitric acid and monomethylammonium nitrate cannot be discounted. This point may be tested experimentally, however.

BSX:- It has been stated previously that the fate of the hexamine is decided in a very few minutes after the start of the reaction in the absence of ammonium nitrate (p. 151). This is not strictly true. For the 40°C. run, the belated addition of a small quantity of ammonium nitrate increases the yield of BSX while the addition of larger quantities reduces it to its original level. (Figure No. 83). Monomethylammonium nitrate has exactly the same effect. This phenomenon is very interesting, particularly from a point of view of Linstead's mechanism which assigns to the ammonium nitrate the role of modifying the reaction liquor in the nitrolysis stage of the Bachmann reaction.

For the 70°C. run, the belated addition of ammonium nitrate decreases the yield of BSX. This was unexpected. What is even more startling is the fact that this decrease is equivalent to the increase in RDX(B) yield. This is in direct contradiction to previous evidence (p. 151). No* explanation is volunteered for the very different behaviour of the BSX yield for the two ammonium nitrate series.

2. Recovery of Reagents from the Mother Liquor

Formaldehyde:- Data for the recovery of formaldehyde from the diluted mother liquor are shown in Figure No. 84. These are not discussed further.

Ammonia (Total Base):- Data concerning the recovery of ammonia (total base) are presented in Figure No. 85. For the belated addition of ammonium nitrate, the quantity of ammonia in the diluted mother liquor decreases at first and then increases as the mole ratio of ammonium nitrate is increased. This is true of both the 40°C. and 70°C. runs. The initial decrease in ammonia recovery is probably due to the decreased yield of by-product, inisolable nitramines (see p. 213) resulting from increased synthesis of RDX(B). The later increase is due directly to the presence of excess ammonium nitrate and represents almost

---

* The initial value of the BSX yield in Table XIV (Run 1) seems to be extraordinarily high. This statement is based on an examination of results formerly obtained (Table II) and seems to be borne out by the fact that the corresponding values for the total recovery of formaldehyde, amino nitrogen, nitric acid and acetic anhydride are all high. (These depend, in part, on the BSX yield). If this is so, the BSX yield decrease would only be "apparent" and the results would coincide more closely with those predicted on the basis of previous experiments.

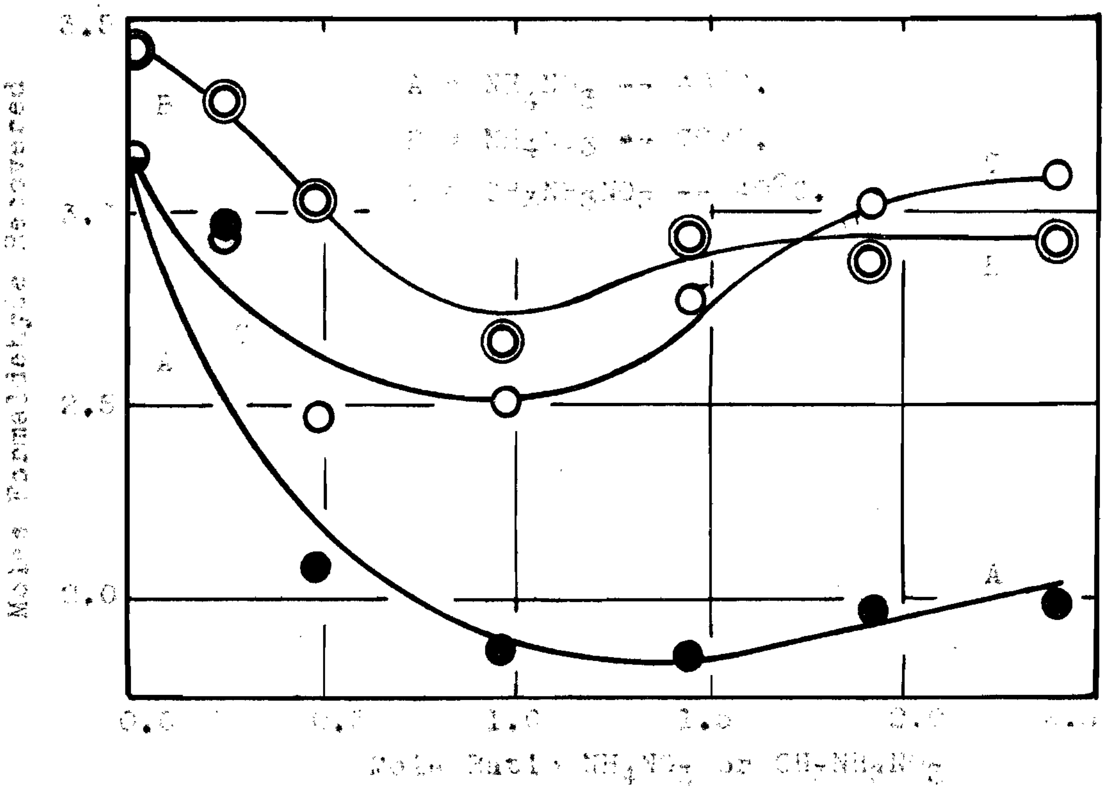
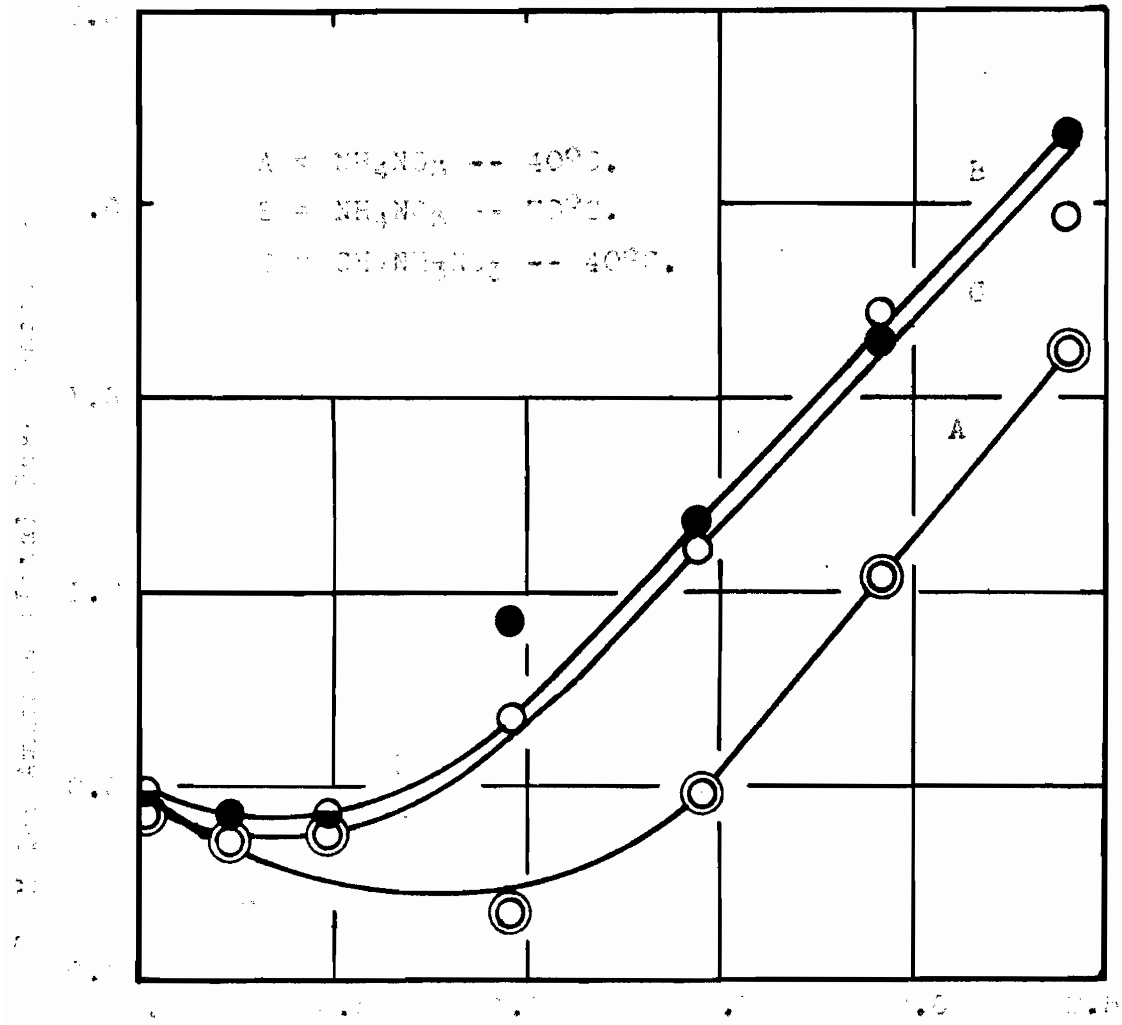

A = NH_4NO_3 --
B = NH_4NO_3 --
C = $CH_3NH_3NO_3$ --
3.5
3.0
2.5
2.0
Moles Formaldehyde Recovered
0.0
0.5
1.0
1.5
2.0
2.5
Mole Ratio NH_4NO_3 or $CH_3NH_3NO_3$
A
B
C

Figure No. 11


A = NH$_4$NO$_3$ -- 40°C.
B = NH$_4$NO$_3$ -- [illegible]°C.
C = CH$_3$NH$_3$NO$_3$ -- 40°C.
B
C
A

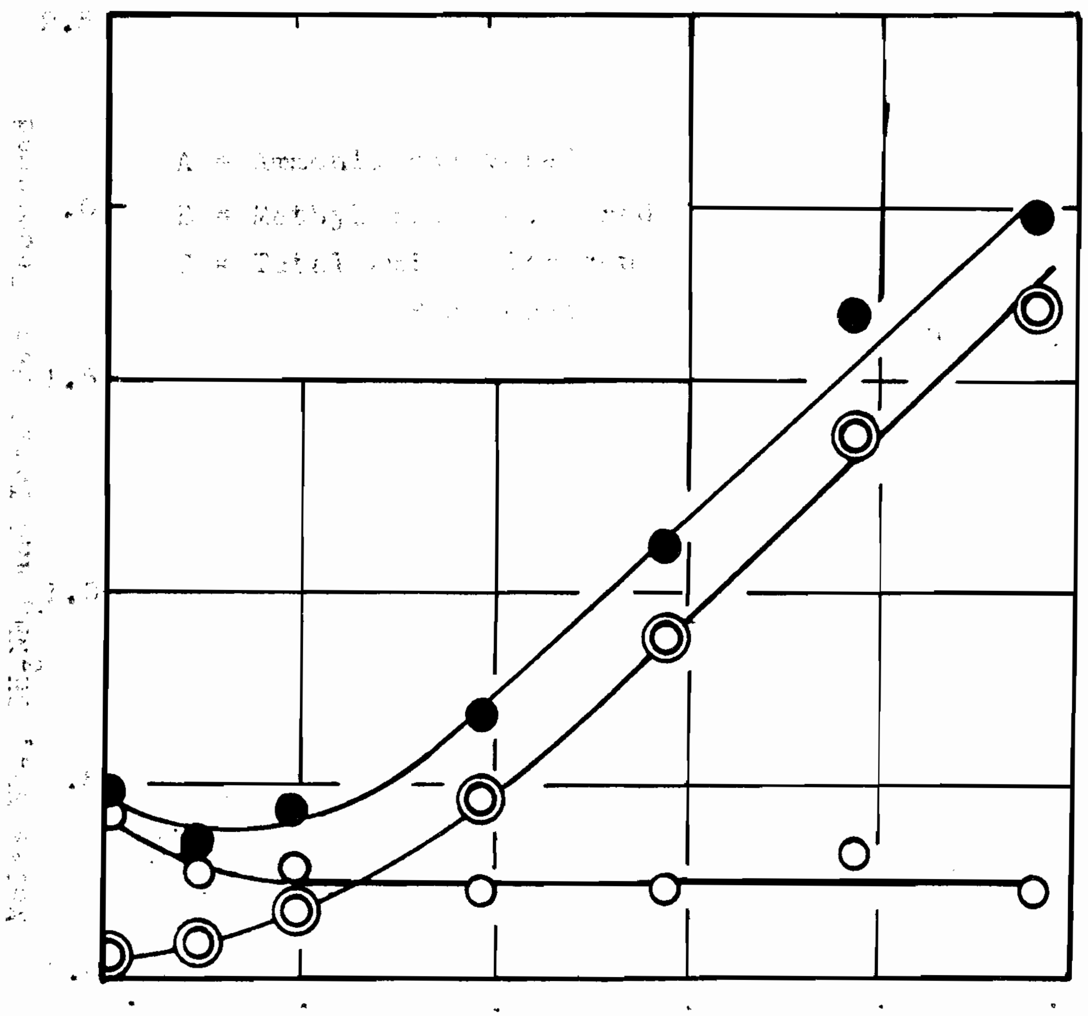
[illegible]

[illegible]

quantitative recovery of this excess. It is also interesting to observe that the difference in level of the two curves (they are parallel at high concentrations of ammonium nitrate) represents a consumption of 0.6 moles ammonium nitrate while the difference in level in RDX(B) yields is 0.2 moles (Figure No. 82). The consumption of three moles of ammonium nitrate per mole of RDX(B) formed is a criterion of a synthesis reaction.

For the belated addition of monomethylammonium nitrate, the behaviour of the total base recovered from the mother liquor is essentially the same as that for corresponding runs involving the use of ammonium nitrate if allowance is made for the greater RDX yields in the latter series. The initial decrease in recovery seems to be due to the slightly decreased yield of inisolable nitramines. The subsequent increase represents a near-quantitative recovery of excess monomethylammonium nitrate. It is rather startling to observe, however, that extrapolation of the curve to zero recovery of amino nitrogen shows that at least 0.4 moles of monomethylammonium nitrate is consumed during the reaction. It is not known whether this monomethylammonium nitrate unaccounted for is destroyed by the action of nitric acid or acetic anhydride, or whether it is consumed during the formation of RDX, BSX, MSX or inisolable nitramines.

The resolution (Figure No. 86) of the total base into ammonia and methylamines by the nesslerization tests shows that there is an initial



Mole Ratio

drop in ammonia concentration (possibly due to decreased formation of inisolable nitramines although this decrease seems to be too great to be accounted for in this manner alone) but that at high concentrations of monomethylammonium nitrate about one-half of the ammonia expected (on the basis of comparison with Table IX) is still present. The recovery of monomethylamine (calculated by difference) increases slowly at first but more rapidly at higher mole ratios. These results show that there is a considerable loss of the amine nitrate; this loss is greater than 0.5 moles at high mole ratios of monomethylammonium nitrate. It is of considerable interest to note that the van Slyke determinations* indicate that all of the "total base" may not be present as ammonia and primary amine salts in the diluted mother liquors of the monomethylammonium nitrate runs.

Nitric Acid:- Data concerning the recovery of combined nitric acid, free nitric acid and total nitric acid are plotted as a function of the ammonium or monomethylammonium nitrate concentration in Figures Nos. 88, 89 and 87 respectively. The only significant feature of these data is that the recovery of free nitric acid is appreciably higher for runs in which monomethylammonium nitrate is used. This corresponds to decreased nitric acid consumption.

The calculated consumptions of nitric acid (moles per mole of hexamine x 0.25) are given in the tables.

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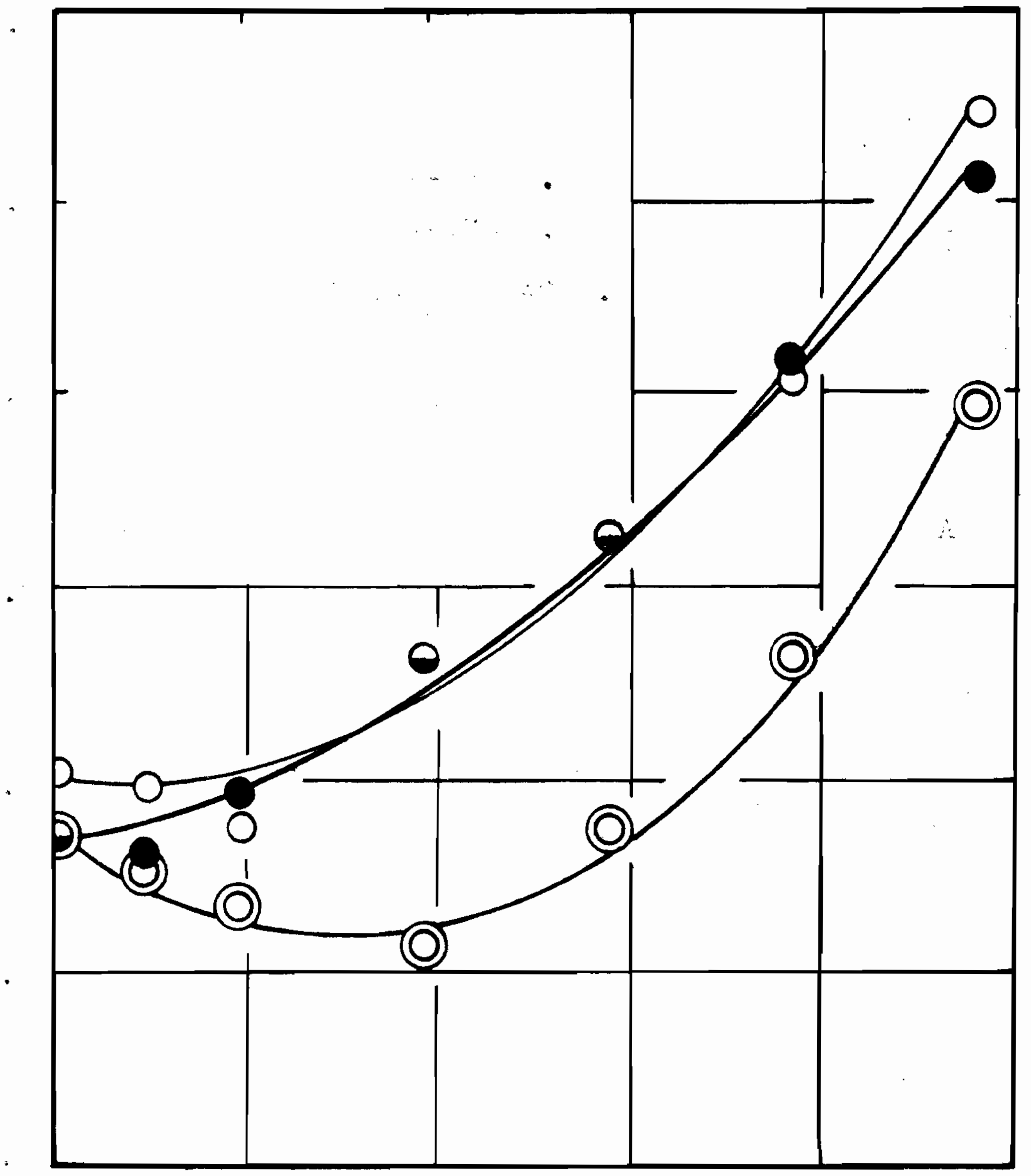
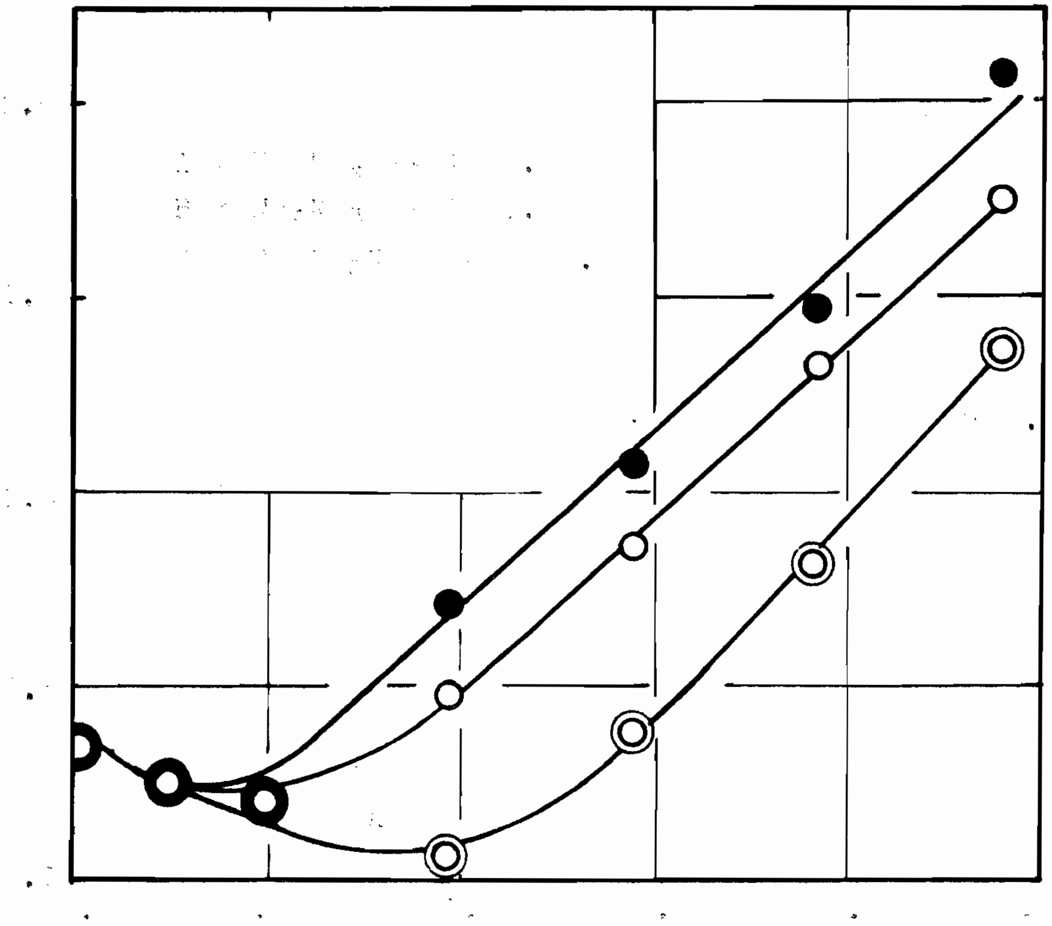
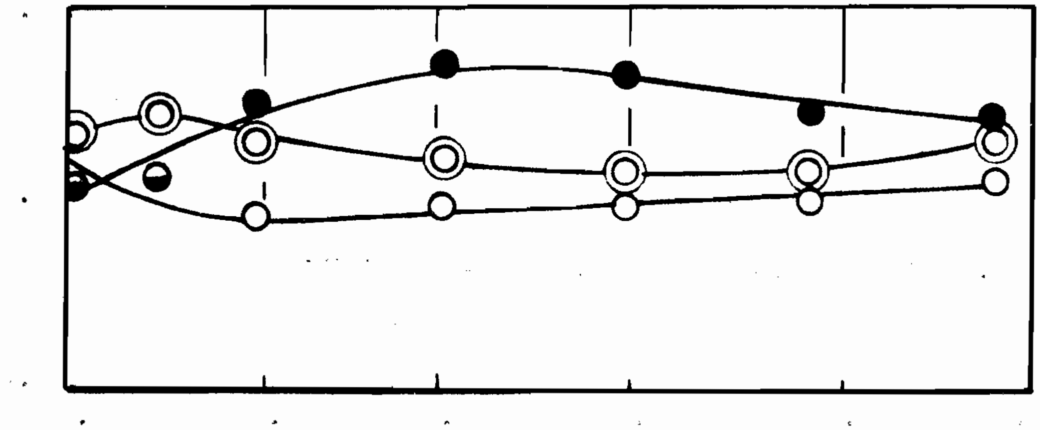
* Results not presented here.







The ratio of ammonia (total base) in the mother liquor to combined nitric acid in the mother liquor has been calculated for each run. The values of this ratio are all greater than unity and all show an initial rise and subsequent decrease as the mole ratio of ammonium or monomethylammonium nitrate is increased. The decrease is undoubtedly due to the establishment of amine or ammonium nitrate excesses. The initial increase indicates increased N-acetylation (rather than nitration) as the mole ratio of ammonium or monomethylammonium nitrate is increased (p. 250). The reason for this is not clear.

Acetic Anhydride:- Data concerning the recovery of acetic anhydride in the diluted mother liquor (as acetic acid) are presented in the tables but are not believed to be significant.

3. Material Balances

Formaldehyde:- The number of moles of formaldehyde accounted for and the percent total recovery of formaldehyde were calculated as previously described (p. 204) and the results are presented in Tables XIII, XIV and XV.

The calculated values are somewhat more irregular than were obtained in other series. It will be observed that, for the 70°C. runs involving the belated addition of ammonium nitrate, the quantity of formaldehyde recovered is somewhat less than for the 40°C. runs. This phenomenon has been previously observed (p. 252). In Table XIV, the initial value of the total recovery is unusually high: this could have been due to an error in the BSX determination for this run (see above).

Ammonia (Total Base):- The number of moles of amino nitrogen accounted for and the percent total recovery of total base were calculated as previously described (p. 207) and the results are plotted as functions of the mole ratio of ammonium or monomethylammonium nitrate in Figure No. 90.

The only significant result obtained seems to be that, whereas in the runs involving belated addition of ammonium nitrate the percent total recovery of amino nitrogen increases, the percent total recovery (of total base) remains constant in runs involving the belated addition of monomethylammonium nitrate. The meaning of this is not clear. It will be further observed that the initial value for the 70°C. runs involving the belated addition of ammonium nitrate is high. As has been pointed out in the case of the formaldehyde material balance, this deviation could have been caused by an error in the BSX determination.

In Figure No. 91, the calculated recoveries of ammonia, methylamine and total amino nitrogen are plotted as a function of the mole ratio of the monomethylammonium nitrate introduced. The percent recoveries of ammonia and total amino nitrogen are fairly constant while the percent recovery of methylamine increases. The loss of methylamine in these runs has already been mentioned and, at present, its fate is unknown. It may be represented in the diluted mother liquor by methyl acetate.

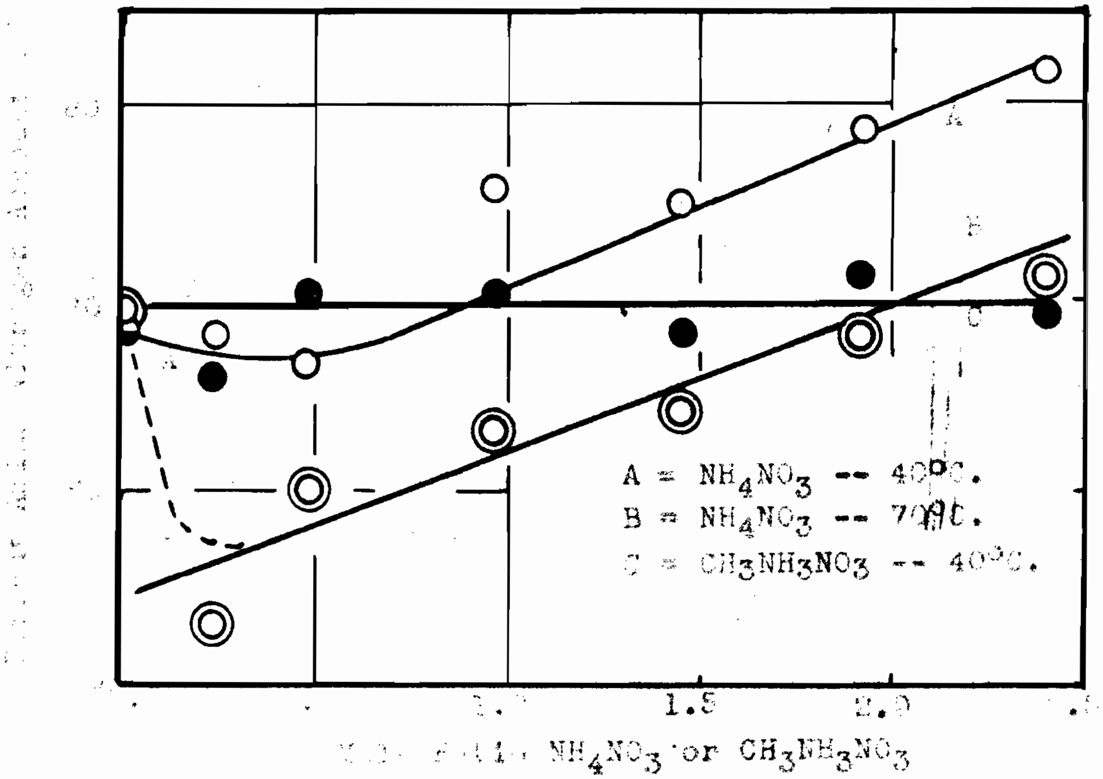


Figure No. 90

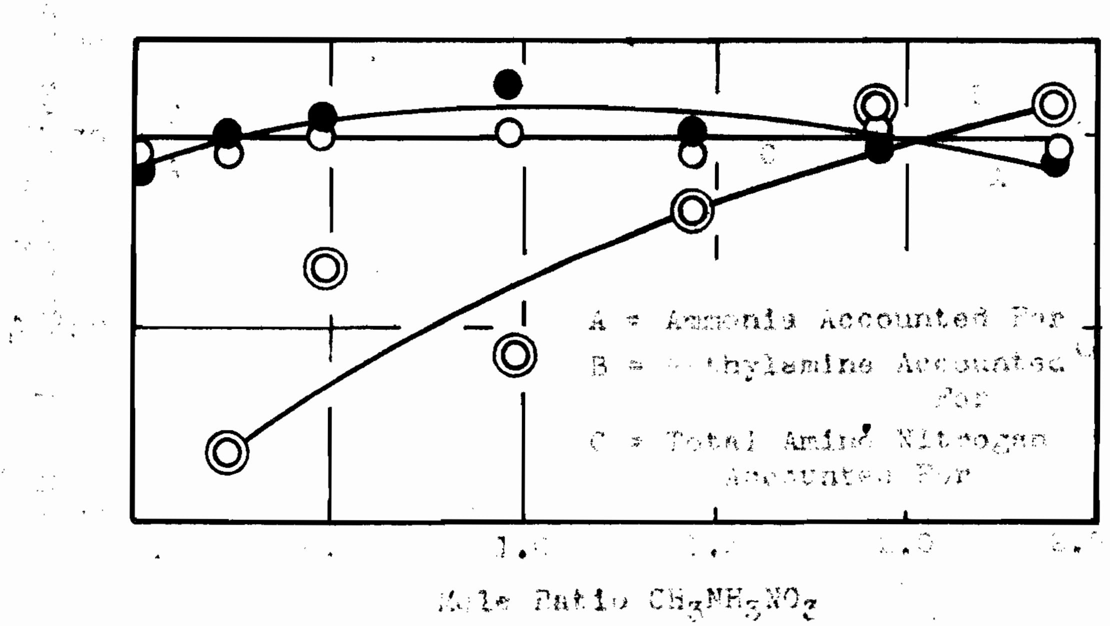


Figure No. [illegible]

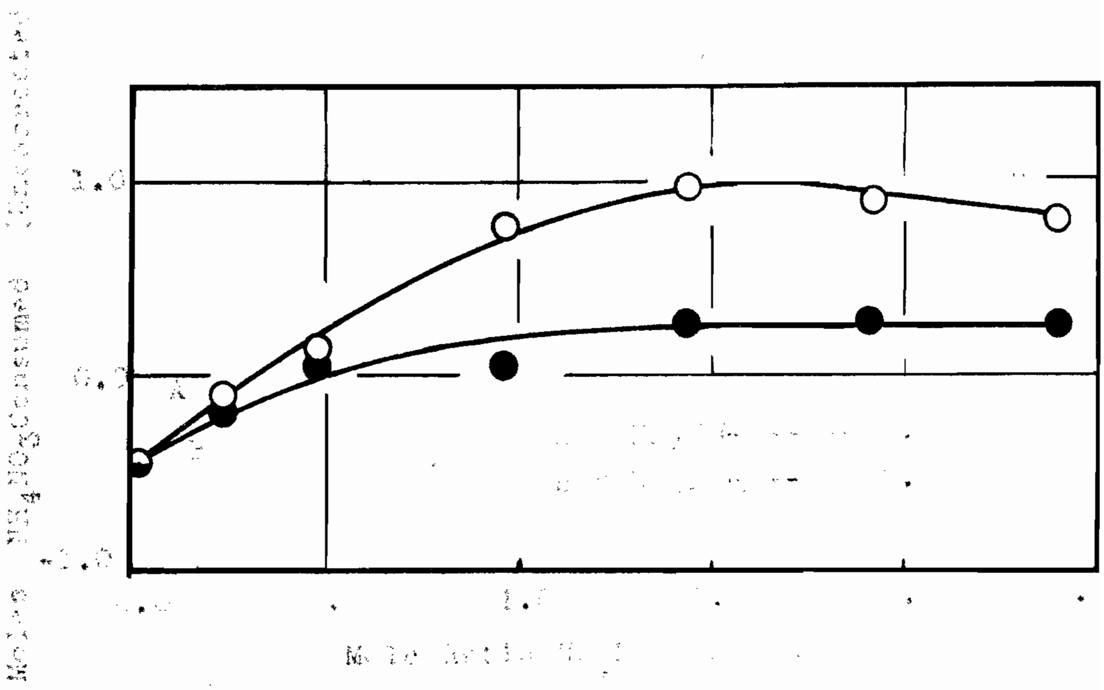
Nitric Acid:- The total recovery of nitric acid and the percent nitric acid accounted for were calculated as previously described (p. 224) and the results are presented in Tables XIII, XIV and XV. The total recovery of nitric acid closely parallels that of the amino nitrogen. Furthermore, the ratio of the number of moles of amino nitrogen not accounted for to the number of moles of nitric acid not accounted for approximates unity. This indicates that the two losses are related and that nitrous oxide is produced.

Acetic Anhydride:- The total recovery and the percent acetic anhydride accounted for were calculated as previously described (p. 225). The results are not believed to be significant.

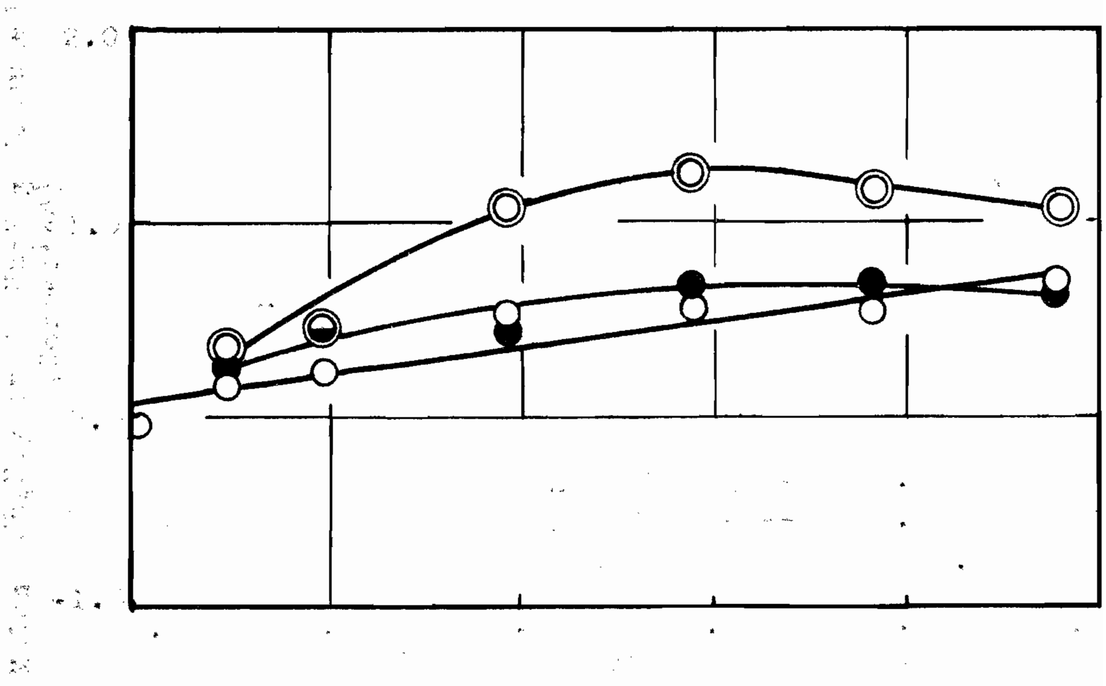
4. Miscellaneous Considerations Concerning the Reaction Mechanism

The values for the apparent consumption of ammonium nitrate, in runs characterized by the belated addition of ammonium nitrate, increase from about - 0.5 moles to a constant positive value (Figure No. 92). The corrected values for the consumption (see p. 198) increase from approximately zero moles to a constant value (Figure No. 93).

The uncorrected values for the ratio of RDX production to ammonium nitrate consumption (Figure No. 94) show characteristic discontinuity in the region of low ammonium nitrate mole ratios but attain fairly constant positive values at higher mole ratios. The value for the 40°C. run approximates 0.5. This indicates that almost all of the


Moles NH_4NO_3 Consumed
1.0
0.2
A
1.0

[illegible]


2.0

[illegible]

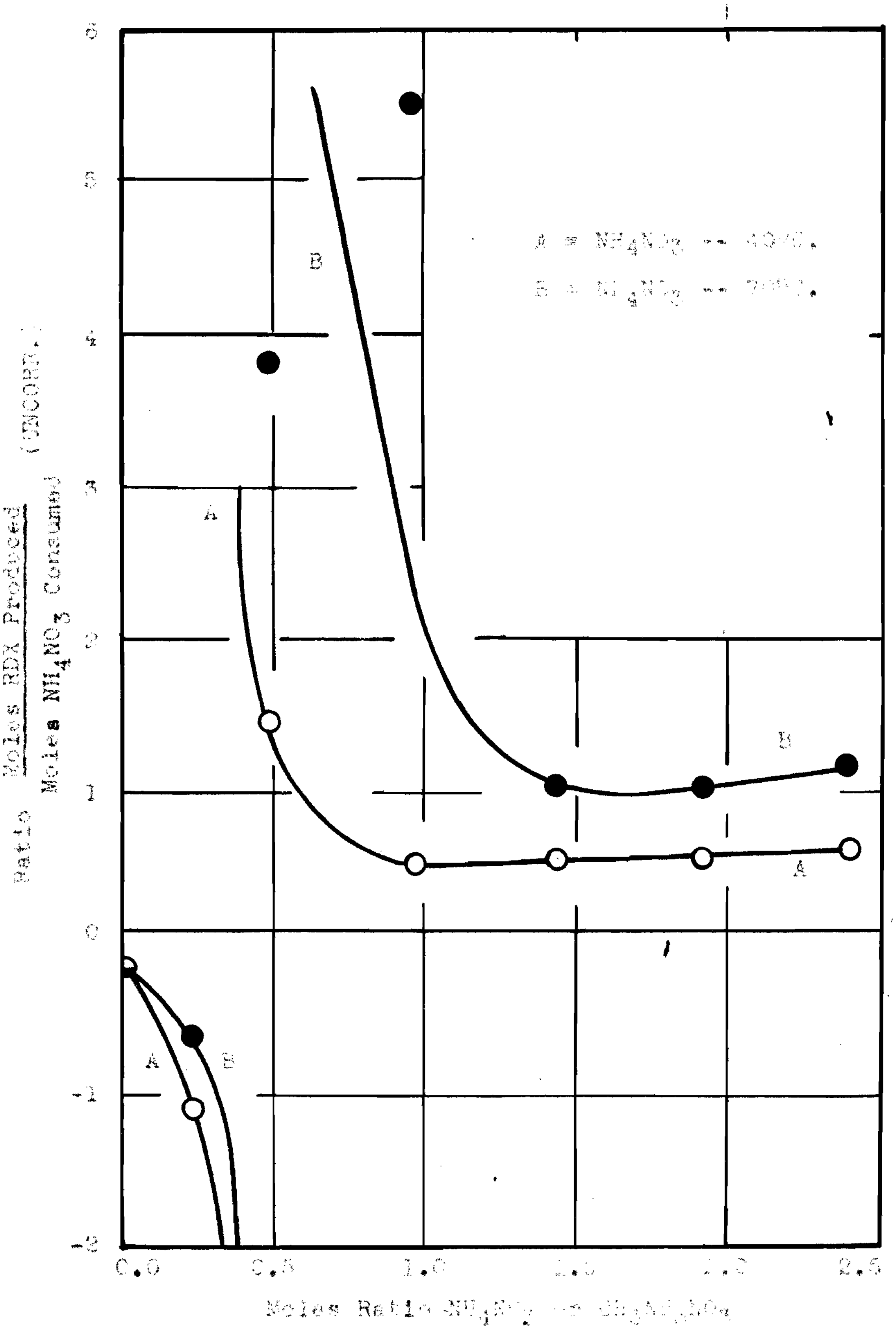

Ratio $\frac{\text{Moles RDX Produced}}{\text{Moles } NH_4NO_3 \text{ Consumed}}$ (UNCORR.)
6
5
4
3
2
1
0
-1
-2
0.0
0.5
1.0
1.5
2.0
2.5
Moles Ratio NH_4NO_3 -- [illegible]
A = NH_4NO_3 -- 40°C.
B = NH_4NO_3 -- 70°C.
A
B
A
B
A
B

Figure No. [illegible]

RDX formed is the product of a synthesis process. The value for the 70°C. run approximates unity. This fact is rather disturbing in that it indicates that the RDX is formed, at least in part, by a nitrolysis process. While the relationship may be fortuitous, it seems the values for the uncorrected ratio for the belated addition experiments are approximately the same as those for the normal addition experiments at corresponding temperatures. In both types of runs, the values for the 40°C. runs support the "catalysed nitrolysis - synthesis" mechanism while the values for the 70°C. runs lend at least some support to the Davy mechanism.

The corrected values for the ratio (Figures Nos. 95 and 96) are all very much less than unity and many of these lie between 0.3 and 0.4. This is in complete agreement with the requirements of the "catalysed nitrolysis - synthesis" mechanism.

The calculated consumptions of monomethylammonium nitrate* and ratios of RDX produced to monomethylammonium nitrate consumed are of somewhat doubtful value and are difficult to interpret theoretically. It had been anticipated that no amine salt would be consumed. It is apparent, however, that monomethylammonium nitrate is consumed during the reaction (Figure No. 93) and that, at high mole ratios, it is consumed to the approximate extent of four to five moles per mole of RDX produced (Figures Nos. 95 and 96). Thus, it may be that the consumption

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* It should be pointed out that the value for the consumption of monomethylammonium nitrate corresponds to the <u>corrected</u> value for the ammonium nitrate consumption.

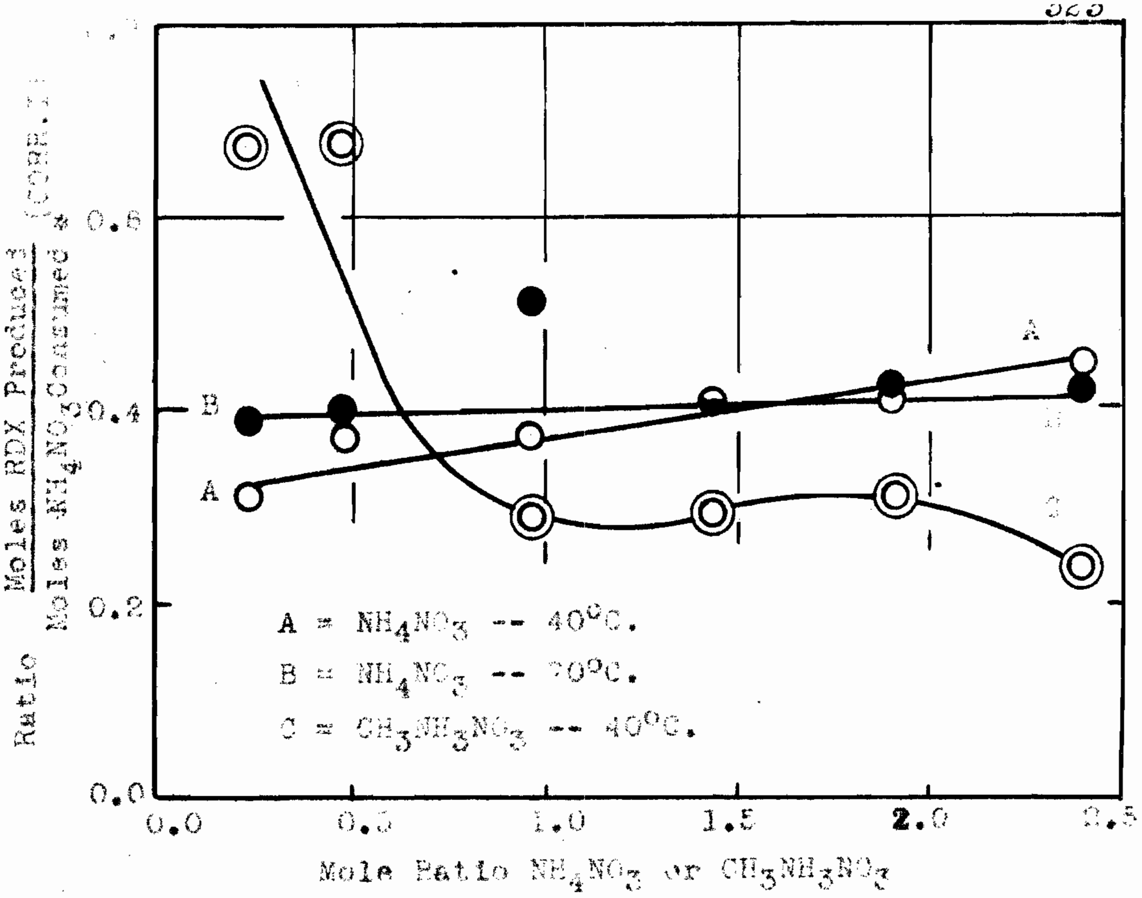


Figure No. 95

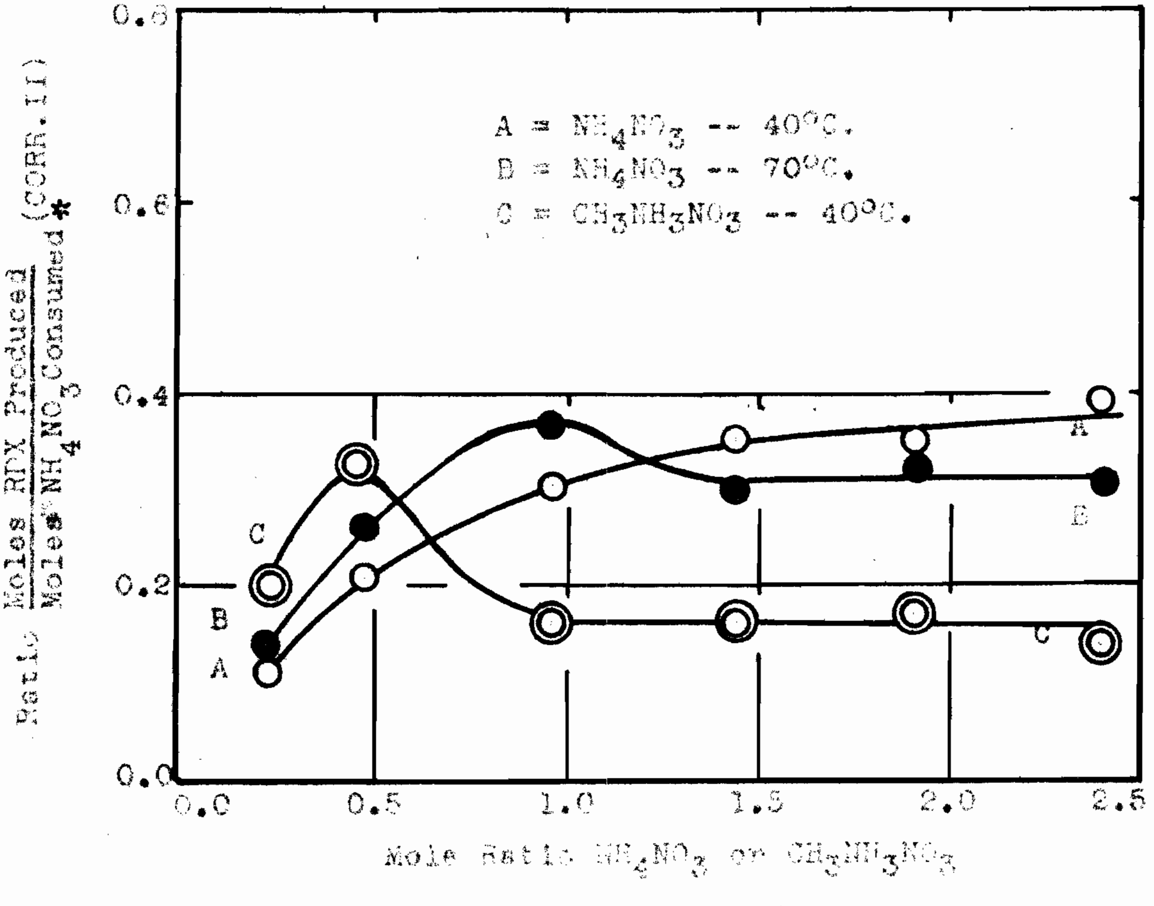


Figure No. 96

* Footnote: "Or $CH_3NH_3NO_3$"

of the amine nitrate is not theoretically related in any way to the production of RDX. It may be, however, that monomethylammonium nitrate is consumed during the production of RDX, but it is certainly consumed in other reactions as well.

In summary, then, it may be stated that the results of the experiments dealing with the belated addition of ammonium and amine nitrates, in general, support the view that the RDX produced in these reactions arises largely through synthesis. This is in accord with previous predictions.

H. Miscellaneous Material Balance Experiments

(Carmack)

In order to present as complete a picture as possible, several experiments of Carmack (92, 95, 96) are herein reported dealing with variables in the Bachmann reaction which have not, as yet, been considered in this thesis. In Table XVI, results dealing with the effect of a large excess of nitric acid and the effect of varying the holding time before dilution of a 75°C. run (into which only 0.52 moles of ammonium nitrate per mole of hexamine is introduced) are investigated. In Table XVII, a summary of Carmack's study of the gaseous products of the reaction and simmer is presented.

Effect of Excess Nitric Acid on Yields and Material Balances

Duplicating (on large scale) the modified reaction described by Bachmann (83) in connection with his tracer studies,(see p. 98, procedure No. 3), Carmack has investigated the effect of a large excess of nitric acid on the yield of RDX(B), the recovery of distillable amino nitrogen and the ratio of RDX(B) production to ammonium nitrate consumption. The mole ratios of reagents used were as follows:

Hexamine	1.00
Ammonium Nitrate	3.27
Nitric Acid	7.80

Another run of Carmack's was selected from Table VI to form the basis for comparison. The mole ratios of reagents used in this case were:

Hexamine	1.00
Ammonium Nitrate	2.86
Nitric Acid	4.90

It may be seen from an examination of Table XVI that the increased nitric acid concentration reduces the yield of RDX(B) and increases the recovery of amino nitrogen from the diluted mother liquor. The ratio of RDX(B) production to ammonium nitrate consumption approximates unity. When a ratio (corrected) of unity is obtained it may be interpreted as meaning (1) that the two moles of RDX(B) are produced by identical or similar processes, or (2) that, if the two moles of RDX are produced by different processes, these proceed to approximately the same extent. Neither of these two conditions coincide with the assumptions which Young (84) made in his interpretation of Bachmann's tracer experiments. Young was able to

TABLE XVI

BACHMANN REACTION:-EFFECT OF SIMULTANEOUSLY INCREASING THE NITRIC ACID AND AMMONIUM NITRATE CONCENTRATIONS AND OF VARYING THE HOLDING TIME BEFORE DILUTION (TEMP. 75°C.) CARMACK

(CALCULATED TO ONE MOLE HEXAMINE)

RUN NUMBER	NH_4NO_3 INTRODUCED	HNO_3 INTRODUCED	HOLDING TIME	RDX(B)	AMMONIA (4 + x MOLES) IN MOTHER LIQUOR	AMMONIA (4 + x MOLES) ACCOUNTED FOR		NH_4NO_3 CONSUMED	$\frac{RDX(B)\ PRODUCED}{NH_4NO_3\ CONSUMED}$	HEXAMINE CONVERTED TO LINEAR NITRAMINES	HEXAMINE CONVERTED TO CYCLIC NITRAMINES	TOTAL HEXAMINE CONVERTED
	MOLES	MOLES	MINS.	MOLES	MOLES	MOLES	%	MOLES	UNCORR.	%	%	%
1	2·87	4·90	10	1·47	1·29	5·70	83	1·58	0·93	27	74	101
2	3·27	7·80	10	0·82	2·44	4·90	68	0·83	0·99	59	41	100
3	0·52	4·90	10	0·29	0·59	1·46	32	−0·07	−4·15	76	14	90
4	0·52	4·90	30	0·27	0·58	1·39	31	−0·05	−5·40	78	14	92

x = MOLES NH_4NO_3 INTRODUCED

interpret the results of these experiments in terms of a "two-process" mechanism, but in so doing assumed that the catalysed nitrolysis process proceeded to a greater extent than did the synthesis process when a large excess of nitric acid was used. It may be remarked that, since the yield of RDX(B) is relatively small, the yield of inisolable nitramines (generating ammonia on hydrolytic decomposition) will be large and that the correction for the ammonium nitrate consumed factor will be large (p. 213). Taking this fact into account, however, does not improve the situation from a point of view of Young's arguments since it will lower the value of the ratio: this indicates greater efficiency of the synthesis process as compared with the nitrolysis process.

It should be emphasized that these results, while they undermine the arguments of Young, do not prove that the two moles of RDX arise through identical processes. On the contrary, the results still strongly favour a two-process mechanism (see p. 107).

Effect of Varying the Holding Time Before Dilution on Yields and Material Balances (0.50 Moles Ammonium Nitrate, 75° C.)

Carmack observed that analysis of the diluted mother liquor of a Bachmann run (into which little or no ammonium nitrate had been introduced) showed that more amino nitrogen could be recovered than was ammonium nitrate introduced. This amino nitrogen obviously originated in the hexamine molecule and Carmack assumed that the hexamine had been incompletely nitrated. In view of this assumption he supposed that the quantity of amino nitrogen in the diluted liquor would decrease if the holding time before dilution were increased. On experiment, however, it was found that, on increasing the holding time before dilution from ten to thirty minutes, the yield of RDX did not increase and that the quantity of amino nitrogen in the diluted mother liquor did not decrease (Table XVI, runs 3 and 4). The results of these experiments support the viewpoint advanced in this thesis that small quantities of ammonium nitrate introduced are quantitatively converted to RDX and that the amino nitrogen in the diluted mother liquor of these runs is not due to the incomplete nitration of the hexamine but arises during the hydrolytic decomposition of the by-product, inisolable nitramines.

Recovery of the Gaseous Products of the Reaction and of the Subsequent Simmer Process

It has been observed that not all of the amino nitrogen introduced into the reaction can be accounted for in terms of solid reaction products and distillable amino nitrogen in the mother liquor. It was postulated by the author (p. 213) that the amino nitrogen unaccounted for had been lost to the system during the formation and subsequent decomposition of inisolable nitramines, nitrous oxide being produced. This assumption seems to be correct since Carmack (95,96) has been able to collect the gaseous products by the reaction and, calculating the neutral gas obtained as nitrous oxide, was able to account for 94 -98 per cent of all of the amino nitrogen introduced. The results of these experiments are reproduced in Table XVII.

TABLE XVII

BACHMANN REACTION:-AMINO NITROGEN BALANCE (INCLUDING THE RECOVERY OF NITROUS OXIDE) - CARMACK

(CALCULATED TO ONE MOLE HEXAMINE)

RUN NUMBER	TEMPERATURE	HOLDING TIME	AMINO NITROGEN INTRODUCED			AMINO NITROGEN RECOVERED					MOLES RDX(B) PRODUCED / MOLES NH_4NO_3 CONSUMED
			AS $(CH_2)_6N_4$	AS NH_4NO_3	TOTAL	AS RDX(B)	AS NH_3 IN THE MOTHER LIQUOR	AS N_2O EVOLVED	TOTAL	TOTAL	
	°C.	MINS.	MOLES	MOLES	MOLES	MOLES	MOLES	MOLES	MOLES	%	MOLAR.
1	40	60	4·00	2·86	6·86	1·60	2·31	2·80	6·71	98	0·97
2	40	60	4·00	2·86	6·86	1·51	2·41	2·64	6·56	96	1·11
3	40	120	4·00	2·86	6·86	1·13	2·27	3·14	6·44	94	0·72
4	40	120	4·00	2·86	6·86	1·34	2·22	2·93	6·49	94	0·69
5	75	10	4·00	2·86	6·86	4·46	1·30	0·93	6·69	98	0·94
6	75	10	4·00	2·86	6·86	4·34	1·34	0·98	6·66	97	0·94

The Mechanism of RDX Formation

The experimental results presented in this thesis can, in general, be successfully interpreted in terms of a mechanism supposing the two processes of "catalysed nitrolysis" and "synthesis". Many of these results cannot be interpreted in terms of a mechanism postulating that the two moles of RDX are formed by identical or similar processes.

Thus far, reference to the postulated mechanism of catalysed nitrolysis and synthesis has only been made in very general terms. The experiments described in this thesis were not specifically designed to explicitly define the mechanism but were only designed to decide whether the two moles of RDX in the Bachmann reaction are formed by identical or different processes. Nevertheless, during the research, certain concepts were developed which contribute to the knowledge of the stepwise mechanism. In order to enunciate these concepts and to illustrate the two processes, the mechanism is discussed more extensively below.

In general, the mechanism of Linstead (5) (see pp. 72-80) satisfies the requirements of the two-process mechanism necessary to explain the experimental results obtained. There are two important differences, however, between the mechanism of Linstead and the proposed "catalysed nitrolysis - synthesis" mechanism. Both of these differences centre around the definition of the function of the ammonium nitrate.

The first point of difference lies in the postulated function of the ammonium nitrate in the degradation of hexamine. With regard to the mole of RDX produced during the degradation of hexamine, Linstead makes the following statement: "The ammonium nitrate modifies the nature of the reagent, for example, by preventing the formation of the active agent which attacks the ring". While it is not unlikely that the reaction mixture differs somewhat when ammonium nitrate is present, the author does not believe that this factor alone will account for the different results obtained using different amine nitrates and for the fact that salts, other than ammonium and amine nitrates, do not give rise to RDX. It is considered that the ammonium or amine nitrate must alter the nature of the intermediate compounds.

It is suggested that any modification of the reagent is based on simple mass law principles such as the following:

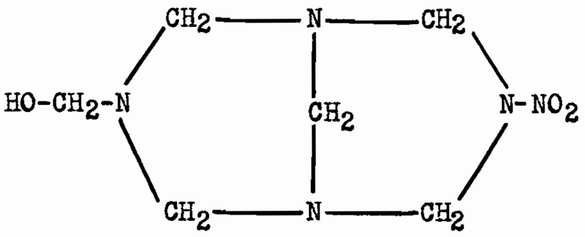
$HNO_3 + Ac_2O \rightleftharpoons AcONO_2 + AcOH$ ----- 212

$2\ HNO_3 + 2\ Ac_2O \rightleftharpoons N_2O_5 + 2\ AcOH$ ----- 213

$2\ HNO_3 + NH_4NO_3 \rightleftharpoons NH_4NO_3 \cdot 2\ HNO_3$ ----- 214

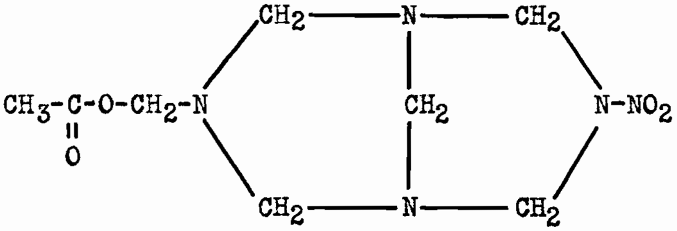
The ammonium (or amine) nitrate, then, may act in such a manner as to increase the active concentration of nitric acid. It is suggested, however, that the true "catalytic" effect is a function of (1) the ability of the ammonium or amine nitrate to condense with methylol groups in the presence of acetic anhydride and (2) the relative electronegativity of the resulting ionic group. This effect is further discussed below.

The first fission of the three-dimensionally symmetrical hexamine is arbitrary and, if nitric acid be supposed to be the active agent, the resulting compound must be



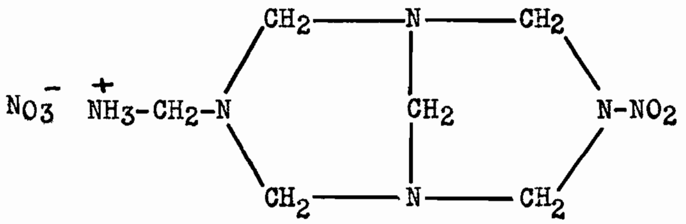
Two possibilities now present themselves.

(1) If there is no ammonium or amine nitrate present, or, if the nitrate introduced does not readily condense with methylol groups in the presence of acetic anhydride, the free hydroxy group will esterify with the acetic anhydride:



The subsequent fissions will be determined by the relative polarization of the various methyleneamine linkages; this will in turn be dictated by the relative electronegativity of the acetyl and nitro groups and by their position in the molecule.

(2) If ammonium or amine nitrate is present, and if this nitrate can readily condense with methylol groups in the presence of acetic anhydride, the free hydroxy group will not esterify but will condense with this nitrate. In the case of ammonium nitrate the resulting compound will be



The subsequent fissions will be determined, once again, by the relative polarization of the various methyleneamine linkages; this will be dictated by the relative electronegativity of the amine and nitro groups.

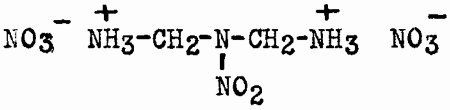
No attempt is made here to predict the order of bond fissions. Simple tests show that there is no reason for not considering them as proceeding in the same sequence as in the mechanisms of Linstead.

The second point of difference between the mechanism of Linstead and the proposed "catalysed nitrolysis - synthesis" mechanism lies in the postulated function of the ammonium nitrate in the synthesis reaction. Linstead points to the experiments of Winkler (64) (who was able to isolate hexamine dinitrate after reacting paraform with ammonium nitrate in the presence of glacial acetic acid) and postulates a resynthesis or partial resynthesis of hexamine in the second stage of the Bachmann reaction. This postulation is very artificial and fails to take into account the function of the acetic anhydride. In the opinion of the author, the synthesis reaction involves the following compounds:

$$\overset{-}{NO_3}\ \overset{+}{NH_3}\text{-}CH_2\text{-}\overset{+}{NH_3}\ \overset{-}{NO_3}$$

(methylenediammonium nitrate)

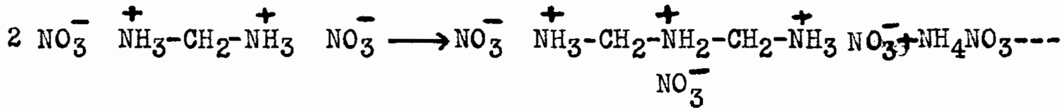
and



$$\overset{-}{NO_3}\ \overset{+}{NH_3}\text{-}CH_2\text{-}\underset{NO_2}{N}\text{-}CH_2\text{-}\overset{+}{NH_3}\ \overset{-}{NO_3}$$

(bis-methylaminonitramine dinitrate)

The corresponding acetates may also be capable of taking part in the synthesis reaction. It seems likely that the condensation reactions are of the following type:



$$2\ NO_3^-\ \overset{+}{N}H_3\text{-}CH_2\text{-}\overset{+}{N}H_3\ NO_3^- \longrightarrow NO_3^-\ \overset{+}{N}H_3\text{-}CH_2\text{-}\underset{NO_3^-}{\overset{+}{N}H_2}\text{-}CH_2\text{-}\overset{+}{N}H_3\ NO_3^- + NH_4NO_3$$

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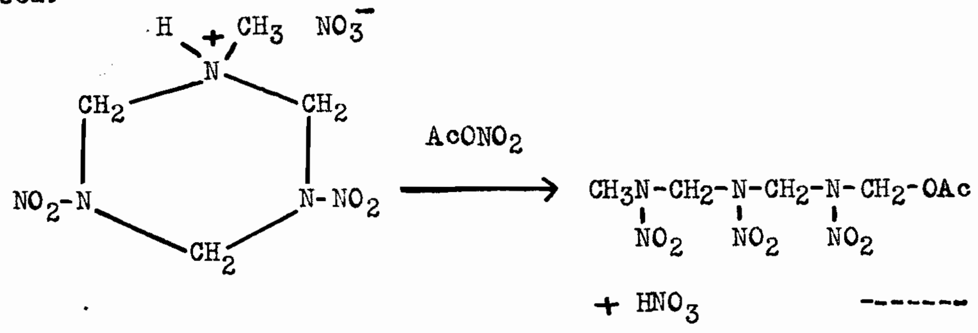
This secondary amine nitrate will be dehydrated* upon formation with the production of bis-methylaminonitramine dinitrate (see above) which will in turn undergo condensation and dehydration. PCX will be an intermediate in this process.

HMX in the Bachmann reaction probably arises through DNPT and by synthesis although there is some evidence (58) (see also p. 153) that it may arise by synthesis alone. BSX, AcAn, TAX and QDX are postulated to be products of the degradation of hexamine. It seems more likely, however, that TAX and QDX will be produced in the synthesis process by acetylation of PCX and the analogous eight-membered ring compound. MSX may be produced by the synthesis reaction when monomethylammonium nitrate is used:



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* Since chloride catalysts are considered necessary for this reaction, this mechanism has often been questioned. However, Wright (101) has preliminary evidence that certain types of disubstituted amine nitrates may be dehydrated in yield in the absence of chlorides. The case of PCX itself may also be cited.

SUMMARY

The experimental results of these researches may be summarized as follows:

1. When the ammonium nitrate of the standard Bachmann reaction is replaced with various amine nitrates, RDX may be produced in considerable quantity, but never in a quantity exceeding one mole per mole of hexamine.

2. When the ammonium nitrate of the standard conversion of DNPT to HMX (and RDX) is replaced with various amine nitrates, HMX may be produced in considerable quantity but RDX is not produced.

3. When the Bachmann reaction is carried out in the absence of ammonium or amine nitrates, a very small yield of RDX is obtained. This base value is unaffected by changes in temperature. In this reaction large yields of BSX may be produced.

4. When the DNPT conversion is carried out in the absence of ammonium or amine nitrates, a very small yield of HMX is obtained. The magnitude of this yield appears to be only slightly affected by temperature. In this reaction large yields of AcAn may be produced.

5. When ammonium nitrate is withheld from the Bachmann reaction until the other reagents have been added, considerable quantities of RDX may still be produced.

6. If ammonium nitrate is omitted from a Bachmann run and if an amine

nitrate is added after the complete addition of all the other reagents, little or no RDX is produced.

7. A Bachmann run carried out at 40°C. gives small yields of RDX and BSX. These yields increase slowly with increased holding time.

8. When less than the theoretical requirement of ammonium or amine nitrate is added to a Bachmann reaction in the usual manner, considerable RDX is produced; if the deficiency is made up by adding ammonium nitrate in the later stages of the reaction, the yield of RDX is increased; if, however, the deficiency is made up by adding an amine nitrate, the yield of RDX is not increased.

9. In a modified Bachmann run, the sum of the BSX yield plus one-half of the RDX yield may exceed one mole per mole of hexamine.

10. In a modified DNPT conversion, the yield of RDX plus the yield of HMX plus the yield of AcAn may exceed one mole per mole of DNPT.

11. In the Bachmann run where the addition of the ammonium nitrate is delayed, the yield of BSX appears to be relatively independent of the presence of ammonium or amine nitrates in the later stages of the reaction.

12. When monomethylammonium nitrate is substituted for the ammonium nitrate of a regular Bachmann reaction, large yields of MSX are produced in addition to the RDX.

13. When monomethylammonium nitrate is substituted for the ammonium

nitrate of a regular Bachmann reaction, very little by-product HMX is produced.

14. When urea nitrate is added belatedly to the reaction mixture of a run into which no ammonium nitrate was introduced, large quantities of urea-formaldehyde polymer are produced.

15. The yield of RDX in the Bachmann and modified Bachmann reactions is found to vary with the following factors: the mole ratio of ammonium nitrate to hexamine, the mole ratios of ammonium nitrate and acetic anhydride, the reaction temperature both at zero and at high mole ratios of ammonium nitrate, the holding time before dilution at low temperatures, the quantity of ammonium or monomethylammonium nitrate added belatedly to the reaction mixture (when the initial reaction was carried out in the absence of ammonium nitrate), and the mole ratio of nitric acid to hexamine. The RDX yield does not vary with the length of holding time after dilution when no ammonium nitrate is introduced, nor with the holding time before dilution for a 75°C. run into which only 0.5 moles ammonium nitrate was introduced per mole of hexamine.

16. The yield of BSX varies with the mole ratio of ammonium nitrate, with the mole ratios of ammonium nitrate and acetic anhydride, with the reaction temperature both at zero and at high mole ratios of ammonium nitrate and with the quantities of ammonium or monomethylammonium nitrate introduced belatedly. The yield of BSX does not vary with the holding time after dilution for runs of zero mole ratio of ammonium nitrate.

17. The yield of HMX varies with the mole ratio of ammonium nitrate, with the mole ratios of ammonium nitrate and acetic anhydride, with the reaction temperature at high ammonium nitrate mole ratios, and with the quantity of ammonium nitrate added belatedly. The yield of HMX apparently does not vary with the reaction temperature at a zero mole ratio of ammonium nitrate.

18. The quantity of formaldehyde which can be shown to be present in the diluted mother liquor varies with the mole ratio of ammonium nitrate, with the mole ratiosof ammonium nitrate and acetic anhydride, with the reaction temperature at high mole ratios of ammonium nitrate, with the holding time after dilution at a zero mole ratio of ammonium nitrate and with the quantity of ammonium or amine nitrate added belatedly. The quantity of formaldehyde recovered does not vary with the reaction temperature for a zero mole ratio of ammonium nitrate.

19. In general, approximately 100 percent of the formaldehyde introduced can be accounted for in terms of solid products and formaldehyde in the mother liquor. The total recovery of formaldehyde, however, varies slightly with the mole ratio of ammonium nitrate, with the reaction temperature both at zero and at high mole ratios of ammonium nitrate, with the holding time after dilution for a zero mole ratio of ammonium nitrate and with the quantities of ammonium or monomethylammonium nitrate added belatedly.

20. The quantity of distillable amino nitrogen which can be shown to be present in the diluted mother liquor varies with the mole ratio of

ammonium nitrate, with the mole ratios of ammonium nitrate and acetic anhydride, with the reaction temperature at high mole ratios of ammonium nitrate, with the holding time before dilution at 40°C. for high mole ratios of ammonium nitrate, with the holding time after dilution for a 40°C. zero mole ratio of ammonium nitrate run, with the quantity of ammonium or monomethylammonium nitrate added belatedly, and with the mole ratio of nitric acid. The quantity of amino nitrogen recovered does not vary with the reaction temperature at a zero mole ratio of ammonium nitrate or with the holding time before dilution at a high temperature and a low mole ratio of ammonium nitrate. Amino nitrogen may be recovered from the diluted mother liquor even when no ammonium nitrate is introduced.

21. The amino nitrogen balance cannot be made unless the quantity of nitrous oxide evolved is measured. The quantity of amino nitrogen accounted for in terms of solid products and distillable amino nitrogen in the diluted mother liquor is always less than 100 percent and varies with all of the reaction variables studied except that of holding time before dilution at 40°C. for high mole ratio of ammonium nitrate runs.

22. The quantity of free (titratable) nitric acid present in the diluted mother liquor varies only slightly with the various procedures used. The recovery corresponds, in general, to a nitric acid consumption of a little less than four moles per mole of hexamine.

23. The quantity of combined nitric acid present in the diluted mother liquor varies considerably as the Bachmann procedure is varied. The curve representing this factor is always found to parallel the curve for the recovery of amino nitrogen from the diluted mother liquor for a corresponding series.

24. The nitric acid balance, like the amino nitrogen balance, cannot be made unless the quantity of nitrous oxide evolved is measured. The quantity of nitric acid accounted for in terms of solid products and nitrate ion in the mother liquor is always less than 100 percent and is found to approximate the value for the amino nitrogen recovery (total) under corresponding conditions.

25. The quantity of acetic acid in the diluted mother liquor and the total recovery of acetic anhydride factors are found to vary at random and the results are not believed to be significant.

26. The ratio of the quantity of formaldehyde in the diluted mother liquor to the quantity of amino nitrogen in the diluted mother liquor is found to be a constant (in the runs not involving belated addition of ammonium or amine nitrates) provided that ammonium nitrate is not present in excess of the actual requirement.

27. The ratio of amino nitrogen in the mother liquor to combined nitric acid in the mother liquor approximates unity in the presence of a large excess of ammonium nitrate but is otherwise greater than unity.

28. The ratio of amino nitrogen unaccounted for to nitric acid unaccounted for is, in general, equal to unity.

29. The apparent ammonium nitrate consumption varies widely with all reaction variables studied. This apparent consumption may be negative at low mole ratios of ammonium nitrate (either in the regular or belated addition of this substance) and in runs characterized by low reaction temperatures and short holding times before dilution even in the presence of excess ammonium nitrate.

30. The corrected ammonium nitrate consumption varies widely with changing conditions. This corrected consumption is never negative in value and is always greater than the apparent consumption of ammonium nitrate.

31. The uncorrected ratio of RDX production to ammonium nitrate consumption varies widely with all reaction variables studied. It may be negative (corresponding to negative ammonium nitrate consumptions) or greater than unity at low mole ratios of ammonium nitrate (for either regular or belated addition) or for runs characterized by low temperatures and short holding times before dilution. It may be much less than unity for reactions characterized by low temperatures and long holding times and for reactions characterized by the belated addition of ammonium or amine nitrates. It is seldom equal to unity (except while changing from high to low values) but may be somewhat less than unity at high mole ratios of ammonium nitrate and at high temperatures (i.e. optimum conditions) and for the belated addition of large quantities of ammonium nitrate at high temperatures.

32. The value of the ratio of RDX production to ammonium nitrate consumption corrected with respect to the latter factor is never negative and is always less than unity. It may, however, approach unity at optimum conditions of temperature and ammonium nitrate concentration.

33. The value of the ratio of RDX production to ammonium nitrate consumption corrected with respect to both factors is never negative and is always less than the value corrected with respect to the ammonium nitrate consumption alone.

34. Monomethylammonium nitrate is consumed when added belatedly to a Bachmann run carried out in the absence of ammonium nitrate. The ratio of RDX produced to monomethylammonium nitrate consumed is generally less than the corresponding value in a run characterized by the belated addition of ammonium nitrate.

35. When the amino nitrogen unaccounted for in terms of RDX, HMX and distillable amino nitrogen in the mother liquor is calculated as yield of linear nitramine, the calculated total conversion of hexamine may be less than, equal to, or greater than 100 percent.

The majority of these facts can be successfully interpreted in terms of a mechanism for RDX formation involving the two processes of "catalysed nitrolysis" and "synthesis". HMX may be produced either by catalysed nitrolysis (of DNPT) or by synthesis. Some RDX (the base value) is produced by uncatalysed (direct) nitrolysis. BSX and AcAn are produced by uncatalysed nitrolysis modified by intermediate O-acetylation, but the possibility of some BSX and AcAn arising through synthesis is not excluded. QDX and TAX result from the process of acetolysis (analogous to and competing with nitrolysis), but the possibility of these compounds arising by the synthesis process (through PCX) is not excluded.

The proposed "catalysed nitrolysis - synthesis" mechanism is schematically similar to that of Linstead except with respect to the synthesis process. Since secondary amine nitrates can undergo dehydration in the presence of acetic anhydride (even in the absence of chloride catalyst (101)), it seems unlikely that hexamine or hexamine dinitrate are intermediates in the synthesis process. It seems more likely that intermediates will be of the nature of methylenediamine, the "ammonium nitrate derivative" of dimethylolnitramine, and PCX. The proposed mechanism also differs with that of Linstead in respect to the specific role assigned to the ammonium nitrate in the degradation of hexamine. Linstead believes that the sole function of the ammonium nitrate is to modify the nature of the reaction mixture. The proposed catalysed nitrolysis process holds that the ammonium nitrate actually alters the nature of the intermediate compounds.

Many of the experimental results listed above cannot be explained on the basis of any other mechanism hitherto proposed.

CLAIMS TO ORIGINAL RESEARCH

1. The effect of temperature, holding time and mode of addition on yields of RDX, HMX, BSX and MSX has been investigated for the normal Bachmann reaction and for the modified reactions involving omission of the ammonium nitrate and substitution of amine nitrates for the ammonium nitrate. The experiments involving the belated addition of ammonium nitrate are based on similar studies by Winkler. Experiments involving the substitution of certain amine nitrates were also carried out at the Pennsylvania State College, but the experiments reported herein were independently conceived and executed.

2. The effect of temperature, holding time and mode of addition on yields of HMX, RDX and AcAn has been investigated for the standard DNPT - HMX conversion and for the modified reactions involving omission of the ammonium nitrate and substitution of amine nitrates for the ammonium nitrate.

3. The yields of RDX, HMX and BSX and the concentrations of formaldehyde, amino nitrogen, free nitric acid, total nitrate ion, acetic acid and acetic anhydride in the mother liquor have been measured as the following factors were varied:

(a) the mole ratio of ammonium nitrate,
(b) the mole ratios of ammonium nitrate and acetic anhydride,
(c) the temperature (for zero moles of ammonium nitrate),
(d) the temperature (for excess ammonium nitrate),

(e) the holding time after dilution (for zero moles of ammonium nitrate at 40°C.),

(f) the belated addition of various quantities of ammonium nitrate (reaction temperature 40°C., holding temperature 70°C.),

(g) the belated addition of various quantities of ammonium nitrate (reaction temperature 70°C., holding temperature 70°C.), and

(h) the addition of various quantities of monomethylammonium nitrate to a Bachmann run carried out in the absence of ammonium nitrate (reaction temperature 40°C., holding temperature 70°C.).

From the above analyses, reagent consumptions and material balances have been calculated. In addition, the ratios of formaldehyde to amino nitrogen in the mother liquor, amino nitrogen to combined nitric acid in the mother liquor and amino nitrogen unaccounted for to nitric acid unaccounted for have been evaluated. The ratios of RDX production to ammonium nitrate consumption have been calculated and a method for correcting these ratios for the amount of hexamine amino nitrogen in the diluted mother liquor has been devised.

4. The interpretations placed on these experimental results are unique.

5. A mechanism has been proposed for the Bachmann reaction. This "catalysed nitrolysis - synthesis" mechanism incorporates features of both the mechanisms of Linstead and Davy but is distinct from either and from any other mechanism thus far proposed for the Bachmann reaction.

APPENDIX

Attempts to Demonstrate the Presence of New By-Products in Modified Bachmann Reactions

Two experiments are described which were designed to demonstrate the presence of a by-product in the reaction liquor of a modified Bachmann run into which no ammonium nitrate is introduced. It has been observed (64) that, on dilution, the reaction products of this type of run settle out as an oil rather than as an insoluble solid; this oil, however, rapidly changes over into a solid mass. If this solid is filtered off after only a short time in contact with the diluted mother liquor, the crude product is sticky in consistency, slightly yellow in colour and smells strongly of formaldehyde. If the solid is allowed to stand in contact with the diluted mother liquor for several days, however, the crude yield decreases considerably but the product can be shown to consist of only BSX and RDX(B). This behavior indicates that some easily-decomposable by-product is precipitated on dilution.

It was considered possible that this by-product might be the precursor of the RDX obtained in runs characterized by the belated addition of ammonium nitrate. In order to test this point, the oily substance was extracted out of the crude solid product and was treated with the Bachmann reagents. No RDX was obtained.

In view of the experimental data reported in Section III-F, it was thought that the by-product might be bis-acetoxymethylnitramine. Since this substance was known to decompose in the presence of the diluted mother liquor, it was considered that there would be a better chance of isolating the methoxy derivative (bis-methoxymethylnitramine);

this compound may easily be prepared from the diacetoxy derivative by treatment with strong nitric acid and then methanol. While this research was never concluded, there were indications that these transformations were successfully carried out.

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1. A modified Bachmann run was carried out at 40°C. in the absence of ammonium nitrate; (this run was identical with the run described in Table II, Run 6). The reaction mixture was diluted with 1500 ml. of cold water, stirred vigorously for twenty seconds and allowed to settle for two minutes. At the end of this time the supernatant liquid and the suspended solid were decanted away from the gummy mass which had settled to the bottom of the beaker. This material was extracted with three 250 ml. volumes of ether. The ether-insoluble fraction was a white solid smelling strongly of formaldehyde. The yield was 31 g. (Softens 105°C., melts 114-115°C.).

On evaporation of the etherous solution to half-volume, 2.5 g. of a white, crystalline solid was obtained (Softens 125°C., melts 129-132°C.). Evaporation to one-quarter of the original volume yielded 1.4 g. of a sticky, solid material (Softens 85°C., melts 90-100°C.). Complete evaporation of the ether left a residue of 50 g. of a yellowish liquid which smelled strongly of nitrous and acetic acids. To this residue was added 28.6 g. acetic acid and 10 g. acetic anhydride. This solution was treated with the Bachmann reagents (nitric acid, ammonium nitrate and acetic anhydride) at 70°C. in exactly the same manner as is the hexamine-acetic acid solution in the regular Bachmann reaction. Near the end of the reaction, a decomposition reaction set in. This reaction was not violent but the temperature rose to 100°C. and large volumes of a colourless gas were given off. The undiluted reaction liquor was filtered but the solid product obtained dissolved readily in hot water; this substance was believed to be unreacted ammonium nitrate. On dilution of the filtrate, no precipitate appeared immediately, but after three days at room temperature, a yellow gum appeared. The yield was 6 g. (Softens 85°C., melts 90-100°C.).

2. In another run, instead of being extracted with ether, the gummy residue was treated with 200 g. of strong nitric acid at - 40°C. The material readily dissolved and the resulting solution showed no tendency to decompose even when heated to 0°C.. On dilution with ten volumes of ice-water, a large quantity of white precipitate separated out and was filtered off immediately. This substance could not be dried since it began to decompose with evolution of formaldehyde. The dry weight was estimated at about 100 g. This material dissolved readily in 500 ml. methanol at 60°C. On evaporation of the methanol, about 20 g. of material melting around 100°C. was filtered off (1,7-dinitroxy-1,3,5,7-tetramethylene-2,4,6-trinitramine (?)). Evaporation on a steam cone over a period of ten hours gave a liquid residue of about ten grams. This product was not characterized.

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