THE PREPARATION OF R.D.X. BY THE McGILL PROCESS.

A THESIS

by

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Submitted to the Faculty of Graduate Studies
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The author wishes to take this opportunity of acknowledging his indebtedness to Dr. J. H. Ross and Dr. R. Boyer. Without their patient training and generous help this thesis would never have been written.

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Ph. D. CHEMISTRY

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"The Preparation of R D X by the McGill Process"

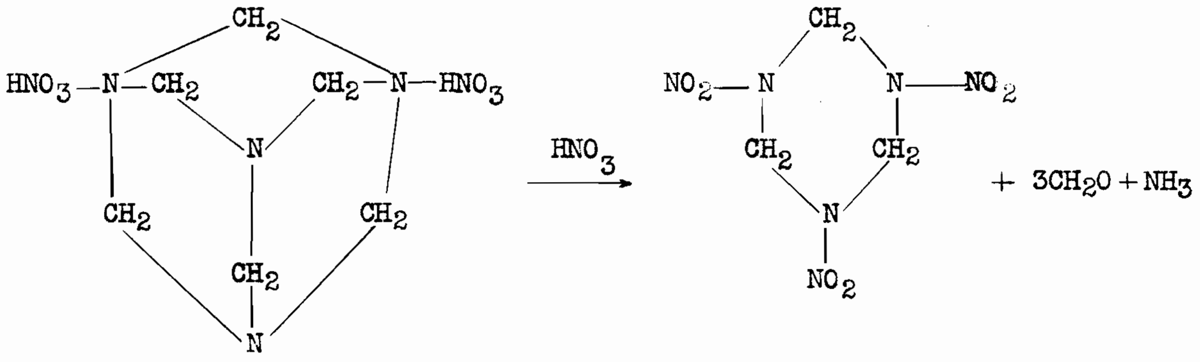
The synthesis of RDX, a powerful high explosive, was accomplished in 1940 at McGill by reaction of a mixture of paraformaldehyde, ammonium nitrate, and acetic anhydride.

A study was made of the conditions affecting the yield of RDX from the reaction, and a new method of conducting it found which enabled the reaction to be controlled when run in large batches, and which increased the yield to 50%. No means of purification was found yielding a product melting above 200° (British Specifications) without involving a large loss of material.

From a study of the consumption of reactants and thermal phenomena of the reaction, a mechanism is advanced for the McGill process. This mechanism predicts the formation of many as yet unisolated by-products.

I. HISTORICAL INTRODUCTION

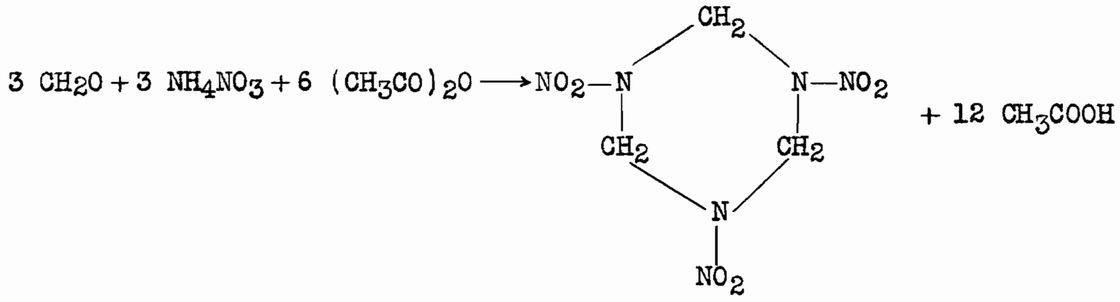
R.D.X. or cyclonite is one of the most powerful high explosives known today. It was first prepared in 1899 by Henning (1) by the nitration of hexamethylenetetramine - dinitrate (I) with fuming nitric acid (d = 1.52). It was later investigated by von Herz (2), who appears to have been the first to assign to it the structure generally accepted today, namely, that of cyclotrimethylenetrinitramine (II).



I II

Since then the material has been manufactured on a large scale in Italy and Great Britain for military purposes. Very little of the research done on it has been published: notable exceptions are the article of Hale (3) and the monograph of Linstead (4). In the latter is contained much of the material presented in this thesis.

Until 1939 no other method of preparing R.D.X. had been found. In that year Robert W. Schiessler, working under Dr. J. H. Ross of McGill University (5), discovered a means of preparing this compound which has come to be known as the McGill Process, and which ushered in a new era of R.D.X. research. It consisted of heating together paraformaldehyde and ammonium nitrate in the presence of acetic anhydride, a few drops of sulphuric acid being used as a catalyst.



The mixture on being heated to about 90° C. suddenly gives evidence of a vigorous reaction; the temperature rises and the so-called "kick-off" occurs, with frothing and the evolution of brown fumes. When it is over, the solids have gone into solution.

Schiessler's usual procedure was to maintain the mixture for a further fifteen minutes at 90° to 100° and then to pour it into a large excess of water. A white or cream-coloured solid precipitated out. The aqueous suspension was neutralized with sodium carbonate, heated for several hours on the steam-cone, and then cooled and filtered. The product thus obtained was impure R.D.X.

Purification was generally accomplished by dissolving the crude material in acetone, filtering from it a dark impurity melting above 300°, and then adding water to the hot solution until it showed first signs of cloudiness. On cooling, crystals of R.D.X. were deposited. These were still impure, melting at about 195° (British Ordnance Specifications call for a melting point above 200°).

The yield of material by this method was low. In more than forty runs Ross and Schiessler attempted to improve it by altering conditions, but it never rose above 40% (based here and always on the amount of formaldehyde used). They found that an excess of ammonium nitrate and acetic anhydride and a temperature of 65° gave the best results. Several catalysts (iron oxide, ferric nitrate, aluminium nitrate, and iodine) were tried but proved ineffective.

The yields often varied in erratic and unpredictable fashion, however, and frequently could not be repeated. The desirability of a changed mode of operation was clearly indicated.

The mechanism advanced for the reaction by Schiessler, which actually led to its discovery, postulated the dehydration of the ammonium nitrate by acetic anydride to form nitramide:

$$NH_4NO_3 + (CH_3CO)_2O \longrightarrow NH_2NO_2 + 2\ CH_3COOH$$

This compound then condensed with formaldehyde to form the methylolnitramine:

$$CH_2O + NH_2NO_2 \longrightarrow CH_2OH—NHNO_2$$

which then by dehydration and trimerization, or by cyclodehydration, could form R.D.X.

On the basis of such a mechanism, one might expect that the reaction could proceed when dehydrating agents other than acetic anhydride are used. Ross and Schiessler tried anhydrous glycerol, glacial acetic acid, and toluene under reflux, but none proved effective.

Since it has often been assumed (6) that the thermal decomposition of ammonium nitrate to nitrous oxide and water occurs by the formation first of nitramide:

$$NH_4NO_3 \longrightarrow NH_2NO_2 + H_2O$$

$$NH_2NO_2 \longrightarrow N_2O + H_2O$$

it seemed possible that R.D.X. might be formed simply by fusing paraformaldehyde and ammonium nitrate together. However, the melt so formed, even on the addition of a dehydrating agent such as phosphoric acid, gave nothing but water-soluble products.

Another attempt to verify this mechanism consisted of the "dearrangement" of nitrourea (7) by sulphuric acid in formalin solution. Such a dearrangement should give nitramide:

$$NH_2CONHNO_2 \longrightarrow NH_2NO_2 + HOCN$$

but no R.D.X. was obtained.

Such was the status of the problem when the author began research in it in January, 1941. It is obvious that the reaction involves the condensation of formaldehyde with an amide or an ammonium compound, and the formation of a nitramine (the order in which these changes take place is discussed later). Consequently, a brief survey of some of the reactions of formaldehyde with amides and amines follows, together with such of the methods of preparation of nitramines as appear relevant. In both of these fields the work done so far has been exceedingly scanty, and much of it is old. The McGill Process is unique, in that the condensation takes place in acetic anhydride,and may well yield in time a host of new compounds. This use of acetic anhydride is at the same time its most serious fault commercially, and so in the following research the possibility of replacing it was constantly kept in mind.

II THEORETICAL DISCUSSION

A. Condensation Reactions of Formaldehyde with Amides

The first mechanism advanced for the McGill Process postulated the condensation of formaldehyde with nitramide, the amide of nitric acid.

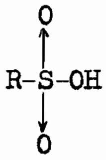
It is now known that such a method fails to give R.D.X. (8,9), It is not impossible, however, that a condensation of this type occurs during the reaction. Unfortunately, the products of the condensation of formaldehyde with nitramide or with substituted nitramides are not known, although Wright has inferred from various reactions that the first two compounds form the hypothetical monomer of R.D.X., methylenenitramine (III) (9).

$$CH_2O + NH_2NO_2 \longrightarrow \underset{\text{III}}{CH_2 = N - NO_2} + H_2O$$

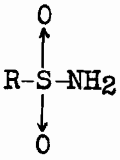
During the past forty years, a vast amount of work has been done on the condensation of formaldehyde with other amides, because of the importance of the products in the preparation of synthetic resins. Most of the work is of no theoretical interest in the present problem, and so the survey of these reactions shall be brief. Three types of amides will be considered: those of sulphonic, carboxylic, and carbamic acids.

1. Condensation with Sulphonamides.

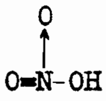
Sulphonic acids (IV) are strong, like nitric acid (VI), and so their amides (V) might be expected to be similar to nitramide (VII) and substituted nitramides (although the presence of a double bond between the nitrogen and oxygen in the latter, giving rise to the possibility of tautomerism and of resonance, may be of some importance). They are, in fact, the only amides which condense with formaldehyde to give a cyclotrimethylenetriamine derivative.


$R-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-OH$

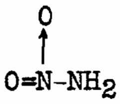
IV


$R-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-NH_2$

V

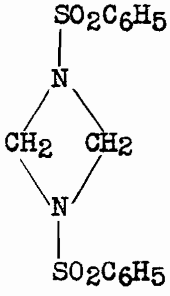

$O{=}\overset{\overset{O}{\uparrow}}{N}-OH$

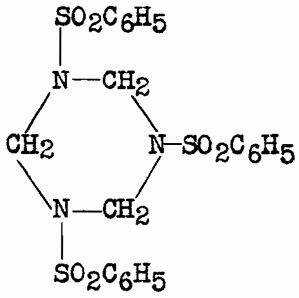
VI


$O{=}\overset{\overset{O}{\uparrow}}{N}-NH_2$

VII

The reaction of benzenesulphonamide with formaldehyde was first studied by Magnus-Levy (10). He found that on repeated evaporation of a solution of benzenesulphonamide, formaldehyde, and hydrochloric acid, followed by extraction of any unchanged sulphonamide with alkali, two compounds were obtained which were separable by fractional crystallization. They were shown by analysis and by molecular weight determinations to be a dimer and a trimer of methylenesulphonamide and were assigned the formulae (VIII), (IX), by analogy with other polymers containing the methylene group, such as trioxymethylene.


VIII


IX

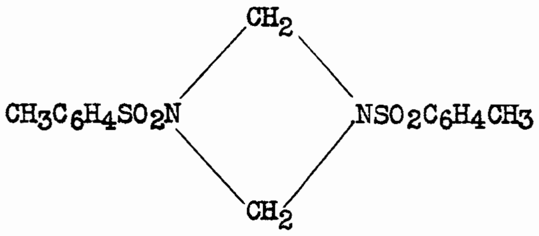
Since that time the most thorough investigation of the condensation of arylsulphonamides with formaldehyde has been made by Hug (11). He found that the following compounds could be obtained, using p-toluenesulphonamide:

1. N-methylol-p-toluenesulphonamide (X) by condensations

$$CH_3C_6H_4SO_2NHCH_2OH$$

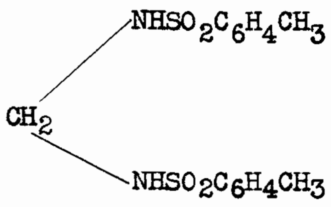
X

in neutral or slightly alkaline solution. Compounds of this type are quite unstable. Boiling water, acid or alkali cause complete hydrolysis. Attempts at benzoylation and alkylation caused the splitting of the molecule, accompanied by the formation of the dimer (XI); attempts at



XI

acylation with acetyl or benzoyl chloride led to the formation of di(p-toluenesulphonyl)methylenediamine (XII). No condensation with



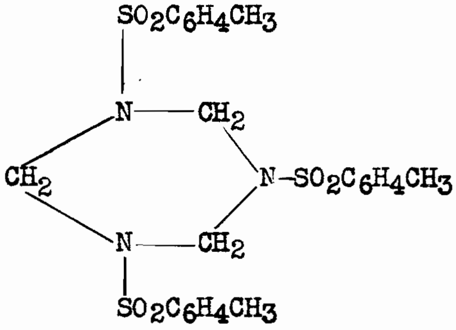
XII

amines or phenols was possible.

2. Di(p-toluenesulphonyl)methylenediamine (XII) could also be formed by boiling the methylol compound in anhydrous solvents. It is more stable than the methylolsulphonamide, but is still easily hydrolyzed. On heating it in acid or alcoholic solution it forms

3. Di(p-toluenesulphonyl)dimethylenediamine (XI), the dimer, and

4. Tri(p-toluenesulphonyl)trimethylenetriamine (XIII), the trimer.

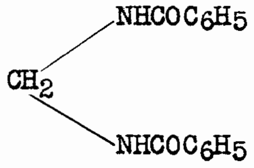


XIII

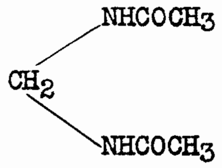
These latter two compounds may also be formed directly by condensation of p-toluenesulphonamide with an excess of formaldehyde in the presence of hydrochloric acid. They are insoluble in alkali and are fairly stable.

2. <u>Condensation with Carbonamides</u>.

Pulvermacher (12) found that the condensation of formaldehyde with benzamide and acetamide in the presence of acid gave methylenedibenzamide (XIV) and methylenediacetamide (XV) respectively.



XIV



XV

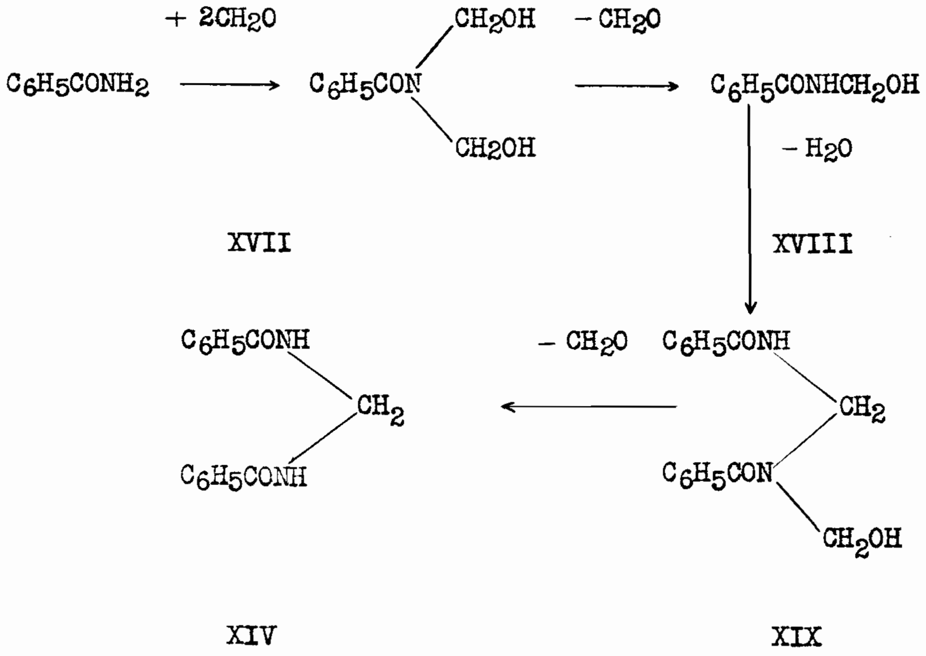
In 1905 a patent granted to Kalle and Co. (13) described the formation of methylolamides (XVI) by heating amides and paraformaldehyde

$$CH_2O + RCONH_2 \longrightarrow RCONHCH_2OH$$

XVI

together at 120-150°. No condensing agent was needed. Heating for a longer time at a higher temperature gave the methylenediamides in good yields.

These and other condensations were studied exhaustively by Einhorn and coworkers (14), who advanced the following mechanism for the formation of methylenediamides:



While it seems unnecessary to postulate these intermediates for condensation in acidic media, all of these compounds can be isolated by varying the conditions of the condensation.

N,N-dimethylol benzamide (XVII) was formed by slight warming (to body temperature) for one hour of benzamide in formalin solution with a small amount of dilute sulphuric acid. A completely clear solution was gradually obtained. Sodium acetate was then added to hinder the continuance of any condensation process. On dilution with water an oil was obtained, which after washing with water was taken up in ether and dried over sodium sulphate. The oil was then obtained by evaporation of the ether: analysis showed it to be the dimethylol derivative. It could not be further purified because of the ease with which it lost formaldehyde to give N-methylolbenzamide.

For most amides, the dimethylol derivative could not be isolated. Only with the amide of camphoric acid was a crystalline derivative obtained. The presence of two methylol groups in this compound was verified by forming a dibenzoate from it.

Most of Einhorn's work was done on the N-methylolamides. These compounds could be prepared by the condensation of amides with formaldehyde in aqueous solution, in the presence of a small amount of potassium carbonate. This proved to be a perfectly general reaction.

These compounds are very unstable. On dry heating, or on evaporation of an aqueous solution, the methylolamide breaks down into its components.

That, however, they are condensation compounds rather than loose addition products Einhorn adduced from the following evidence:

1. They give a positive Tollens test not immediately like formaldehyde, but only after a certain length of time, corresponding

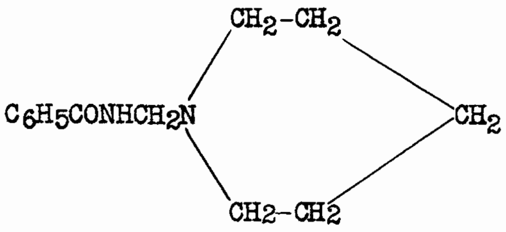
to the stability of the methylolamide.

2. Derivatives can be prepared, proving the existence of a carbon-nitrogen link. Thus on oxidation with dilute chromic acid N-methylolbenzamide gives N-formylbenzamide (XX):

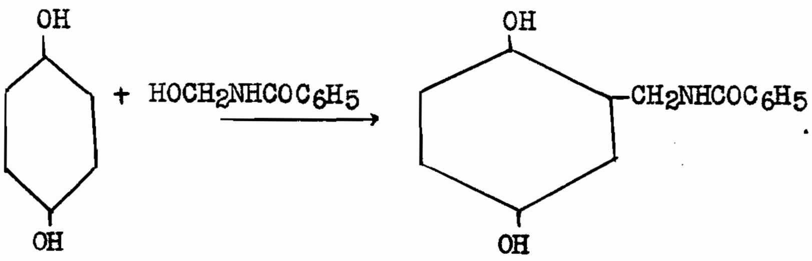
$$C_6H_5CONHCH_2OH \xrightarrow{\text{Oxidation}} C_6H_5CONHCHO$$

XX

Derivatives of methylenediamine can be formed by reaction with secondary amines, such as piperidine (forming N-piperdylmethylbenzamide (XXI)), and with amides. And with aromatic compounds tolyl or xylyl derivatives are formed, as in the synthesis of 2,5-dihydroxy-N-benzoylbenzylamine (XXII).

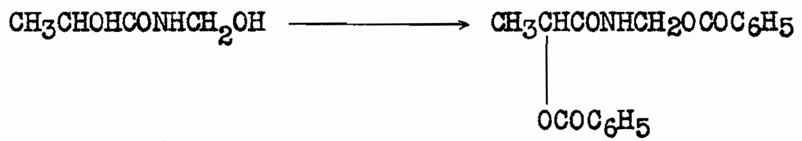


XXI



XXII

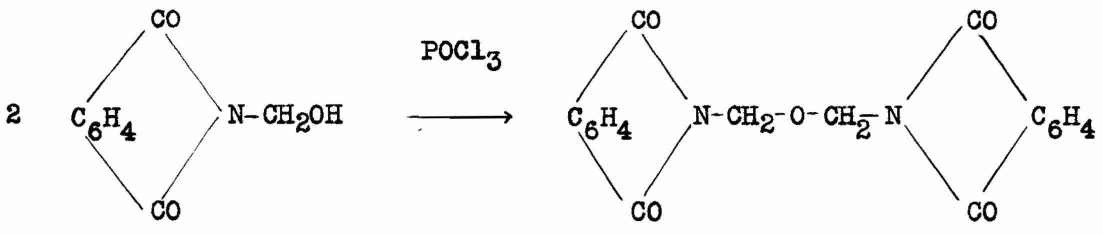
However, the instability of these compounds is such that many other derivatives cannot be made. Thus they will not form salts with acids. They form methylenediamides on being heated with acetic anhydride or benzoyl chloride. If acylation is attempted by the Schotten-Baumann procedure in alkaline solution, they form methylolmethylene compounds (such as XIX), except in a few cases, such as the dimethylol derivatives of camphoric acid amide already mentioned,or N-methylollactamide (XXIII).



$$CH_3CHOHCONHCH_2OH \longrightarrow CH_3\underset{\displaystyle OCOC_6H_5}{\underset{|}{C}}HCONHCH_2OCOC_6H_5$$

XXIII

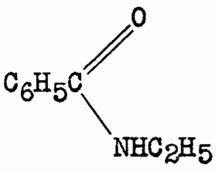
The N-methylolimides, as exemplified by N-methylolphthalimide (XXIV), discovered by Sachs (15), are much more stable. This compound forms salts, can be acylated with boiling acetic anhydride, and forms an ether (XXV) on treatment with phosphorus oxychloride.

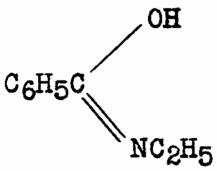


XXIV XXV

Strangely enough, Einhorn could not form a methylol derivative of a N-alkylated amide. Although he did not attempt to explain this fact, it may be accounted for on the assumption that amides have an aci-structure

(XXVII) rather than the one usually assigned them (XXVI) (16).

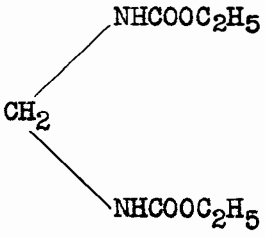

XXVI

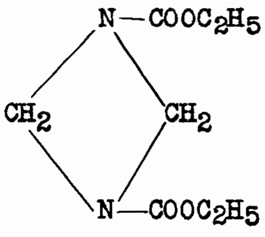

XXVII

N-methylolmethylenedibenzamide (XIX) can be prepared from N-methylolbenzamide by warming it to 30° in formalin solution with a small amount of sulphuric acid. It loses formaldehyde on heating, dry or in solution, to give methylenedibenzamide (XIV).

3. Condensation with Carbamic Esters and Carbamides.

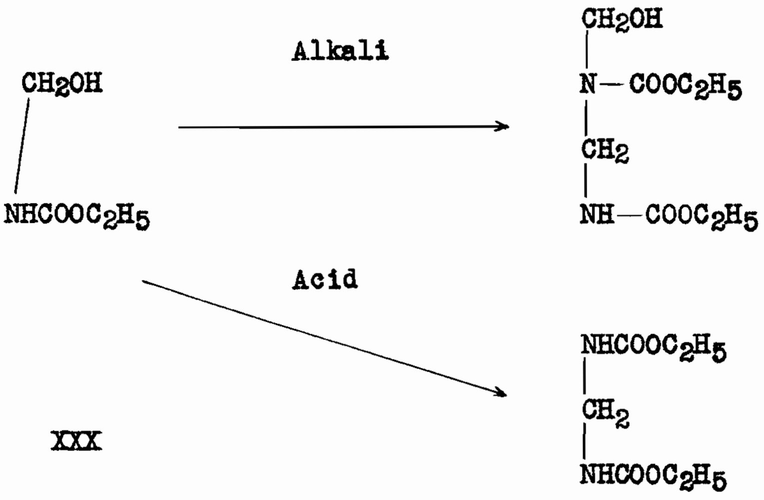
By the action of urethane (2 moles) on formaldehyde (1 mole) in aqueous solution, in the presence of hydrochloric acid and with vigorous cooling, Conrad and Hock (17) obtained methylenediurethane (XXVIII). With a molar ratio of 1 : 1, with more acid and at a temperature of 70-80°, they obtained anhydroformaldehydeurethane as a dimer (XXIX).


XXVIII


XXIX

Einhorn and coworkers (14) found that in basic solution

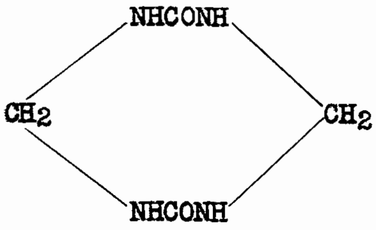
N-methylolurethane (XXX) could be formed, which condensed further as shown:



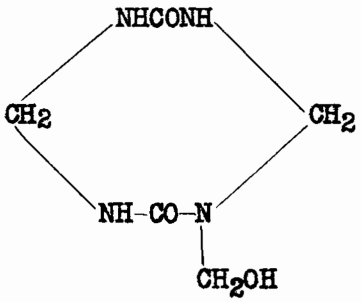
XXX

The condensation of urea or carbamide with formaldehyde follows the same essential course as previous condensations, but must be more carefully controlled because of the ease of polymer formation.

Methylol- or dimethylolcarbamide may be made simply by exposing in an evacuated desiccator for a few days a neutralized solution of urea containing one or two equivalents of formaldehyde (18). Alkaline condensation gives more complex products (14). If the ratio of formaldehyde to urea is 0.75 : 1, then acid condensation gives methylenecarbamide (XXXI); if it is 1.5 : 1, a methylol derivative (XXXII) is formed (18).

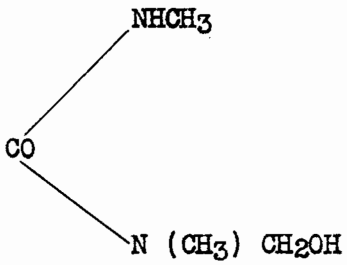


XXXI

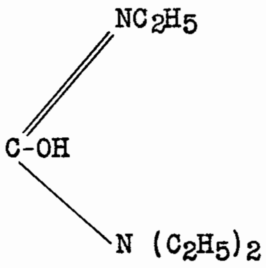


XXXII

Substituted carbamides, unlike substituted carbonamides can form methylol derivatives (e.g. XXXIII), except when trisubstituted. Einhorn advanced as an explanation the possibility that the trialkyl urea existed in the "pseudo form" (XXXIV) (14).



XXXIII



XXXIV

B. Condensation Reactions of Formaldehyde with Ammonia and Amines

1. Condensation with Aliphatic and Aromatic Amines

Another possible mechanism in the McGill Process is the condensation of formaldehyde, not with an amide, but with ammonia or an amine.

Our knowledge of this condensation is surprisingly small. It is, however, fairly generally accepted that the condensation proceeds first by addition of the amine to the carbonyl group (19) :

$$RCHO + R'NH_2 \longrightarrow RCHOH-NHR'$$

XXXV

The α-hydroxy amine (XXXV) so formed can then react in different ways to give imines, cyclic compounds, etc.

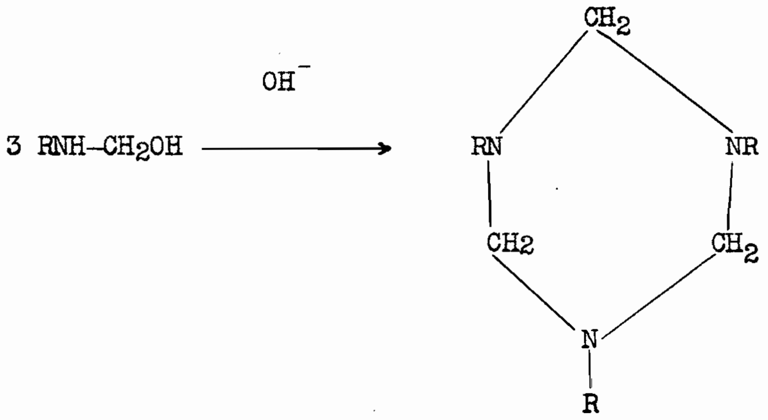
These α-hydroxy amines can be isolated when formaldehyde is allowed to react with aliphatic amines in the presence of alkali (20). The methylolamines derived from methyl- , ethyl- , propyl- , isobutyl- ,

$$RNH_2 + CH_2O \xrightarrow{OH^-} RNHCH_2OH$$

isoamyl- , and benzyl- amines and from piperidine are colourless liquids. They may react with another molecule of amine to give bis(alkylamino)methanes (XXXVI) :

$$RNHCH_2OH + R'NH_2 \longrightarrow \underset{\text{XXXVI}}{RNHCH_2NHR'}$$

When distilled over potassium hydroxide, the methylolalkylamines lose water to form the corresponding alkylmethyleneimines, usually as cyclic trimers (XXXVII)



XXXVII

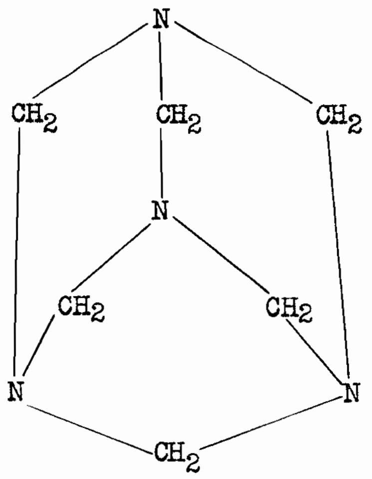
These products are also formed by the condensation of formaldehyde with aromatic amines under carefully controlled conditions, although the intermediate compounds have not been isolated (21). The molecular weight of the vapour of anhydroformaldehyde aniline, on the other hand, is reported to correspond to that of the monomer. (This behaviour is analogous to that of formaldoxime, which normally exists in the trimeric form, but can be isolated as an unstable monomer (22)).

2. Condensation with Ammonia and Ammonium Salts.

The condensation of formaldehyde with ammonia is rather more complex. When the two compounds are mixed in aqueous solution, they react to form hexamethylenetetramine (abbreviated to hexamine in this thesis) (23).

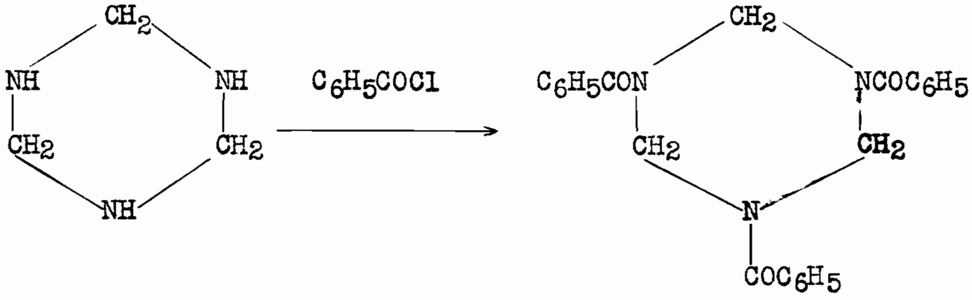
$$6CH_2O + 4NH_3 \longrightarrow \underset{\text{XXXVIII}}{(CH_2)_6N_4} + 6H_2O$$

The empirical formula (XXXVIII) for this compound was settled by analysis and by molecular weight determinations (24). Many different structures were proposed for it, however, the generally accepted one today being that of Duden and Scharff (XXXIX) (25).



XXXIX

These authors considered the precursor of hexamine to be cyclotrimethylenetriamine (XL) by analogy with the formation of cyclotrimethyltrimethylenetriamine on reacting formaldehyde with methylamine (25,26), and because on adding benzoyl chloride to a solution of equimolecular amounts of formaldehyde and ammonia they obtained the tribenzoyl derivative (XLI)



XL

XLI

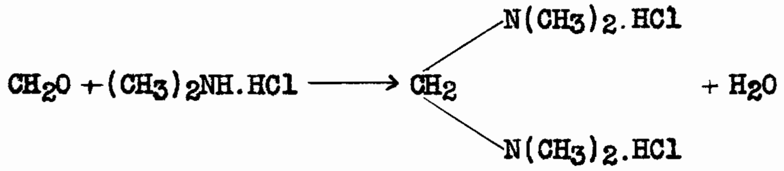
Cyclotrimethylenetriamine could not be isolated from solution, however. Because of the active hydrogen remaining on the nitrogen, further reaction with formaldehyde and then ammonia is possible, leading to hexamine.

The first reaction of formaldehyde with ammonia is probably the formation of methylolamine (27), which reacts by further condensation with ammonia or formaldehyde until hexamine is formed. If formaldehyde and ammonia are allowed to condense in the presence of sodium bisulphite, then the bisulphite esters of mono- , di- , and trimethylolamine can be prepared (28).

When ammonium salts are dissolved in formalin solution, the solution becomes acid: on heating, carbon dioxide, formic acid, and mono-, di-, and trimethylamine salts are formed (29). The salts of amines can be methylated in the same fashion.Werner (30) advanced the following mechanism for the reaction:

1. $CH_2O + NH_3.HCl \longrightarrow CH_2OHNH_2.HCl \longrightarrow CH_2{=}NH.HCl + H_2O$
2. $CH_2{=}NH.HCl + H_2O + CH_2O \longrightarrow CH_3NH_2.HCl + HCOOH$
3. $CH_2O + CH_3NH_2.HCl \longrightarrow CH_2{=}NCH_3.HCl + H_2O$
4. $CH_2{=}NCH_3.HCl + H_2O + CH_2O \longrightarrow CH_3NHCH_3.HCl + HCOOH$

5.

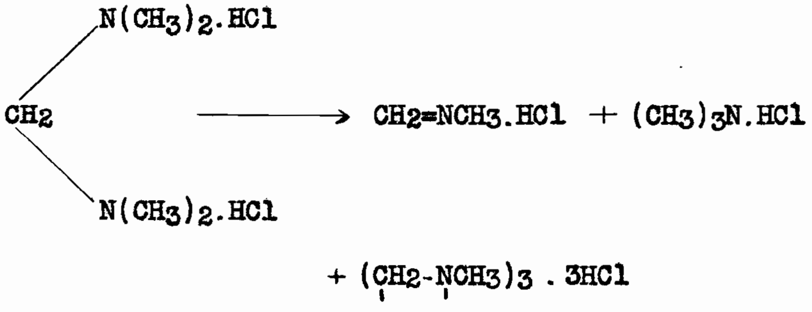


$$CH_2O + (CH_3)_2NH.HCl \longrightarrow CH_2\begin{array}{l} \diagup N(CH_3)_2.HCl \\ \diagdown N(CH_3)_2.HCl \end{array} + H_2O$$

XLII

Bis(dimethylamino)methane dihydrochloride (XLII) so formed is saturated, and so shows no tendency to be reduced. At high temperature it decomposes:

6.



$$CH_2\begin{array}{l} \diagup N(CH_3)_2.HCl \\ \diagdown N(CH_3)_2.HCl \end{array} \longrightarrow CH_2{=}NCH_3.HCl + (CH_3)_3N.HCl$$

$$+ (\underset{|}{C}H_2\text{-}\underset{|}{N}CH_3)_3 \,.\, 3HCl$$

XLIII

This mechanism explains why the formation of mono- and dimethylamine is accompanied by the formation of formic acid; and why the formation of tri- from dimethylamine hydrochloride and formaldehyde is accompanied by the production, not of formic acid, but of cyclotrimethyltrimethylenetriamine (XLIII). It is also obvious from equations (2) and (4) that water is needed for the oxidation-reduction to proceed. Werner found that this was so: when an attempt was made to react formaldehyde with methylamine hydrochloride in alcoholic solution, the amine salt was recovered unchanged and ethylal was formed:

$$CH_2O + C_2H_5OH \longrightarrow CH_2(OC_2H_5)_2 + H_2O$$

3. The Structure of Hexamethylenetetramine and its Derivatives

Duden and Scharff (25) inferred from the facts that hexamine (1) was a strong, tertiary base, and (2) on degradation in many different reactions gave formaldehyde, ammonia, sometimes methylamine, but never ethylamine, that it must be made up of nitrogen atoms and methylene groups alternately linked. Its structure they then deduced from the fact that it could be broken down by various reagents to form bicyclic compounds of two fused six-membered rings, or further to monocyclic compounds of six-membered rings. The parent compound they consequently considered best represented by a structure with three fused six-membered rings. This structure gives formal representation to the fact that all nitrogen and carbon atoms are equivalent, and possesses a high degree of symmetry.

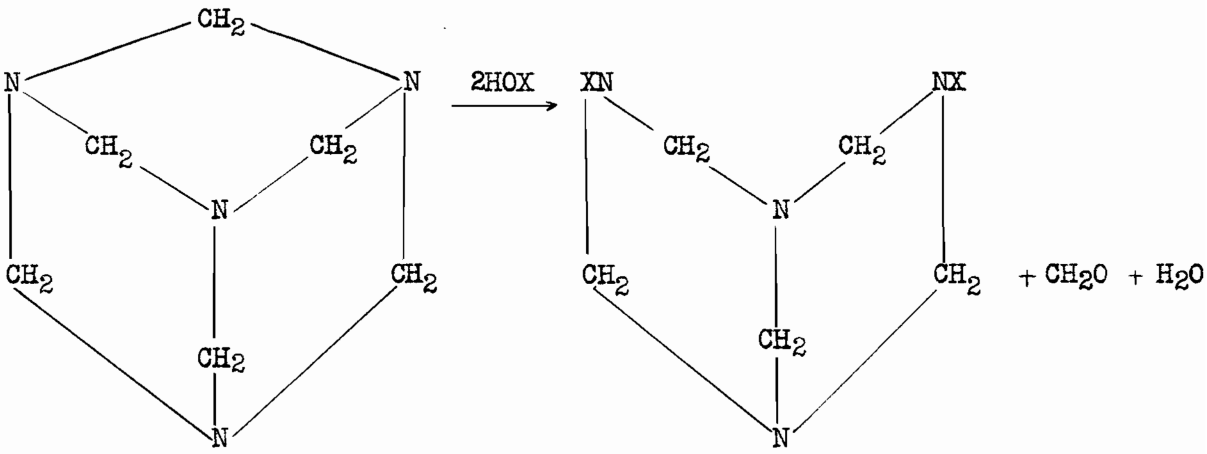
Later X-ray investigations (31) have tended to confirm Duden and Scharff's structure; but recently Wright (32) has offered chemical evidence against it.

In considering the derivatives formed from hexamine, one must bear in mind the fact that this compound is hydrolyzed in acid solution to formaldehyde and ammonia. It is possible that its derivatives are formed, not by partial breakdown of the molecule which still leaves some of the rings intact, as Duden and Scharff believed, but by a complete hydrolysis, followed by a synthesis of the derivative from formaldehyde, ammonia, and the specific reagent used (33).

In the following discussion we shall proceed on the assumption that the derivatives are formed by a partial rather than a complete breakdown of the hexamine molecule, although this question still lacks decisive chemical evidence for settlement one way or the other.

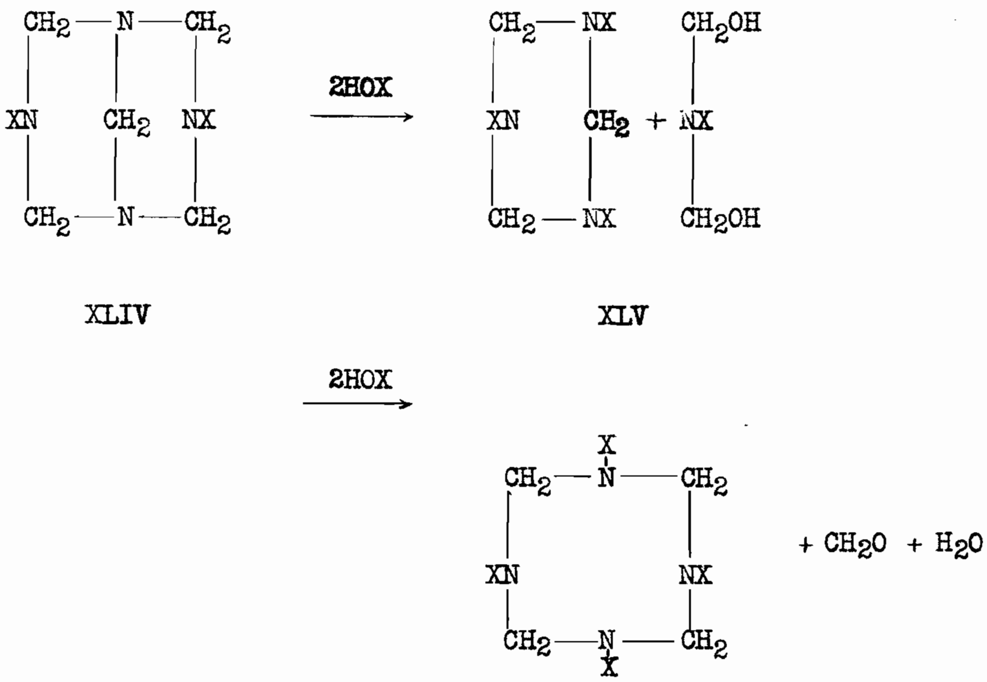
Hexamine is attacked by a variety of reagents of the general type HOX, where X may be H, NO, Cl, or NO_2. The breakdown may take place through two stages to give:

1. Pentamethylenetetramine derivatives (bicyclic compounds) (XLIV)



XLIV

2. Cyclotrimethylenetriamine (XLV) or cyclotetramethylenetetramine (XLVI) derivatives(monocyclic compounds).



XLIV

XLV

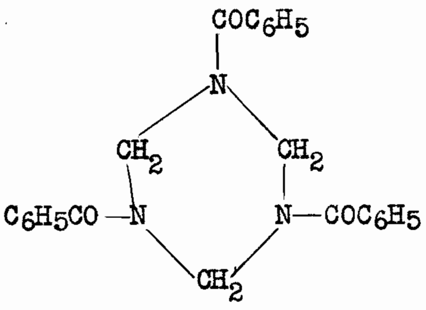
XLVI

The formation through a bicyclic intermediate of the monocyclic derivatives was postulated by Duden and Scharff (25) but has been shown to take place in only a few cases. The factors governing the mode of breakdown to give the trimer (XLV) or the tetramer (XLVI) are not known.

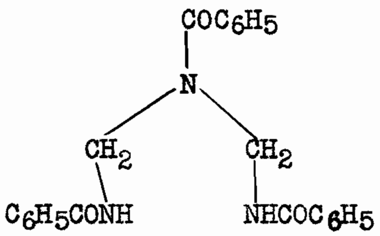
The first reagent to give cyclic degradation products was nitrous acid. When only a small amount of sodium nitrite was added to an acid solution of hexamine, dinitrosopentamethylenetetramine was formed (34); an excess of the reagent led to the formation of cyclotrinitrosotrimethylenetriamine (35).

Hexamine may be degraded by various reagents in aqueous solution. Strong acids lead to a complete hydrolysis to formaldehyde and ammonia, and no intermediate products have been isolated (25). In the presence of diazo salts, diazo-pentamethylenetetramine derivatives may be formed; the reagent is apparently not vigorous enough to give monocyclic derivatives (25).

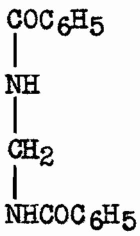
With benzoyl chloride in alkaline solution, on the other hand, the reaction proceeds considerably further, to give cyclotribenzoyltrimethylenetriamine (XLVII), tribenzoyldimethylenetriamine (XLVIII),



XLVII



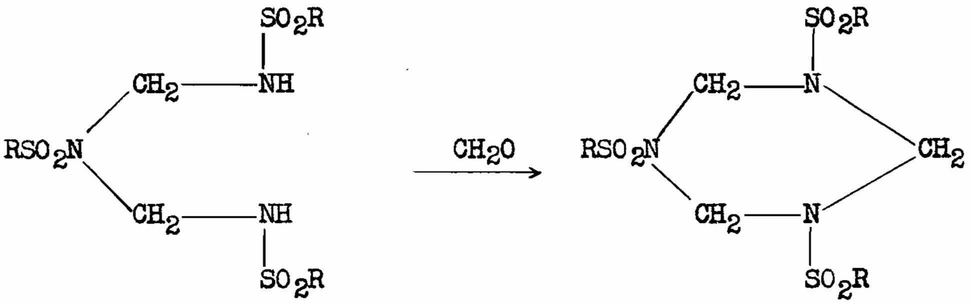
XLVIII



XLIX

and methylenedibenzamide (XLIX).

The action of sulphonyl chloride on hexamine in alkaline solution results in the formation of disulphonylpentamethylenetetramine (36) and cyclotrisulphonyltrimethylenetriamine derivatives (37). Hug explained the non-formation of a dimethylenetriamine derivative such as (XLVIII) by the fact that the hydrogen atoms on the nitrogen of such a compound (L) would be very active and so would condense with the formaldehyde present in the solution from the degradation of the hexamine to form a cyclic compound (LI).

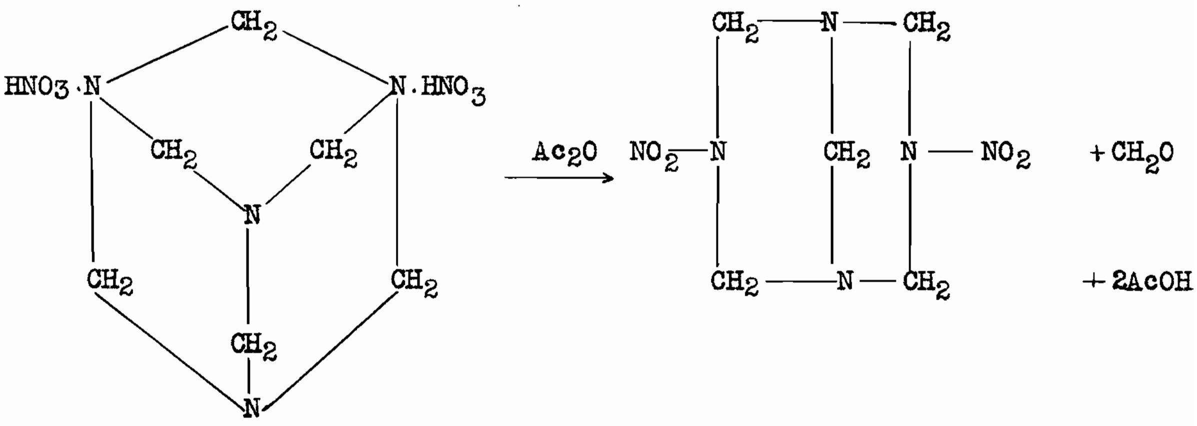


L LI

The action of sulphonyl chlorides provides fairly convincing evidence for the mechanism postulating the formation of derivatives of hexamine by a partial breakdown of the molecule, rather than a complete decomposition to formaldehyde and ammonia followed by resynthesis. For in the latter case one should expect the formation of a dimer as well as a trimer of the methylenesulphonamide (c.f. page 6); actually, only the trimer is found.

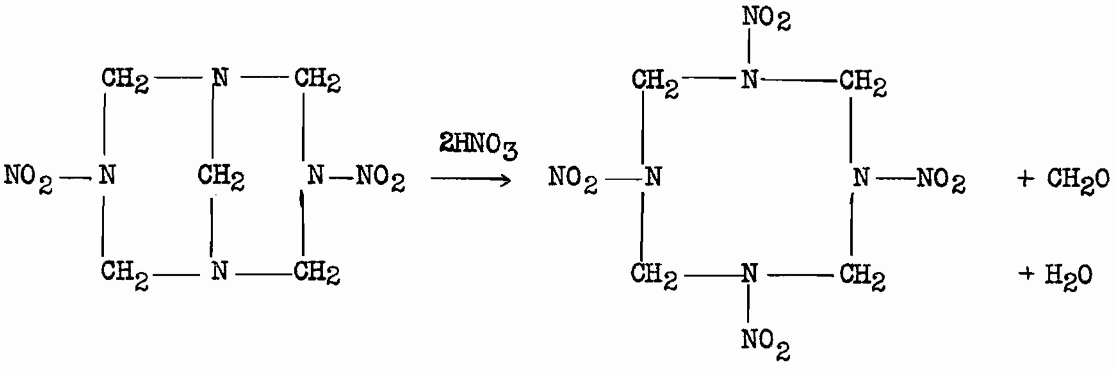
The behaviour of hypochlorous acid is similar to that of nitrous acid. Treatment of hexamine with sodium hypochlorite solution gives dichloropentamethylenetetramine; in acetic acid solution cyclotrichlorotrimethylenetriamine instead is formed. The latter compound can also be formed by dissolving dichloropentamethylenetetramine in acetic acid (38).

The formation of nitro-derivatives differs from previous reactions in that it can take place only in relatively anhydrous media. Thus R.D.X. can be formed only by nitrolysis of hexamine in nitric acid containing less than 20% water (39). Dinitropentamethylenetetramine (LII) (40) has recently been prepared in several ways, notably by the action of acetic anhydride on hexamine dinitrate.



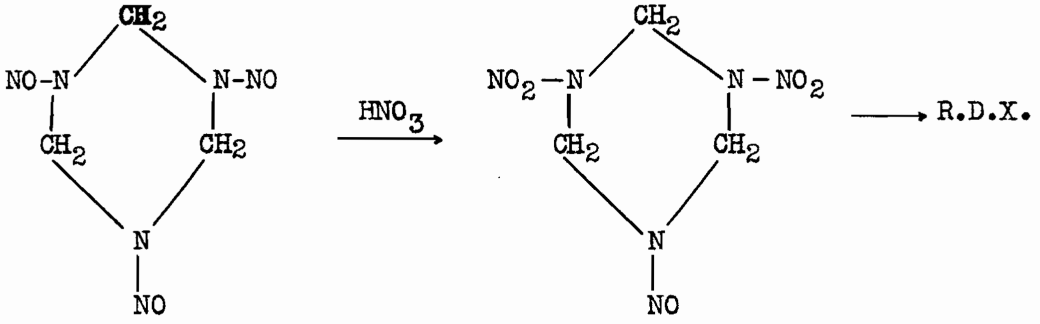
LII

The nitration of dinitropentamethylenetetramine can yield R.D.X. (41), but more often H.M.X. (LIII) (42), according to the conditions employed. The latter is the only eight-membered ring yet derived from hexamine.



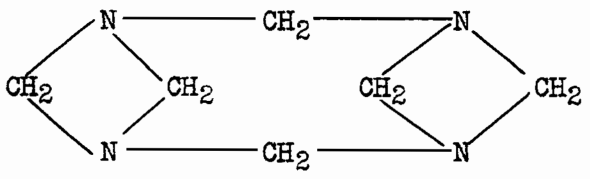
LIII

Several attempts have been made to interrelate these derivatives of hexamine, most of which have failed because of the instability of the compounds to the reagents used. Nitrolysis of cyclotribenzoyl- and cyclotri-p-toluenesulphonyltrimethylenetriamine in concentrated nitric acid has so far failed to yield R.D.X. (43). Attempts to convert the trichloro- derivative to R.D.X. have been unsuccessful (44). The action of a mixture of hydrogen peroxide and nitric acid on dinitrosopentamethylenetetramine gave, not dinitropentamethylenetetramine, but R.D.X. (45). Only the oxidation of cyclotrinitrosotrimethylenetriamine has yielded the desired nitro-analogue. Dinitromononitrosotrimethylenetriamine (LIV) is formed, which can be further oxidized to R.D.X. (46).



LIV

From the foregoing summary it is seen that the formation of all the degradation products of hexamine so far discovered may be explained by a partial breakdown of the hexamine molecule as pictured by Duden and Scharff. This furnishes strong evidence that their structure is correct. The only other completely polycyclic structure, that of van't Hoff and later of Delepine (LV) (47), would give rise to the formation of four-membered rings. On the other hand, the objection to the structure of

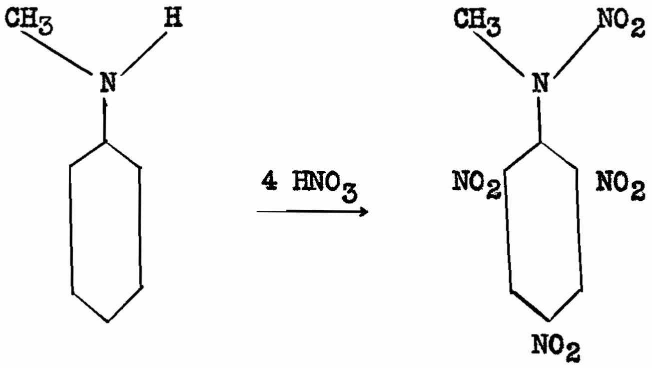


LV

Duden and Scharff voiced by Delepine, that it predicted the formation of eight-membered rings, has become with the discovery of H.M.X. one of its most powerful supports.

C. The Formation of Nitramines.

The nitration of mono- and dimethylaniline was found by van Romburgh (48) to lead to a compound (LVI) in which one nitro group was attached to the nitrogen atom of the amine.



LVI

The significance of this discovery was grasped immediately by Franchimont (49), who named this new type of compound a nitramine. The parent compound, nitramide, might be expected by the loss of water from ammonium nitrate on heating. If formed, however, it decomposes for only nitrous oxide is obtained.

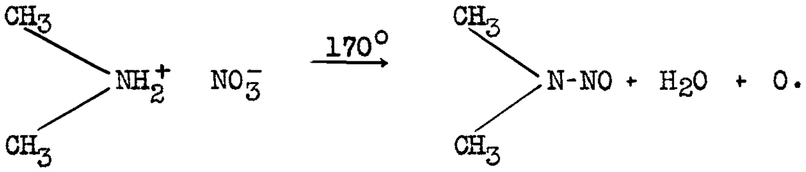
$$NH_4NO_3 \longrightarrow NH_2NO_2 + H_2O$$

$$NH_2NO_2 \longrightarrow N_2O + H_2O$$

There is some evidence, however, that ammonium nitrate forms nitramide in solution in concentrated sulphuric acid (50).

The thermal decomposition of dialkylamine nitrates

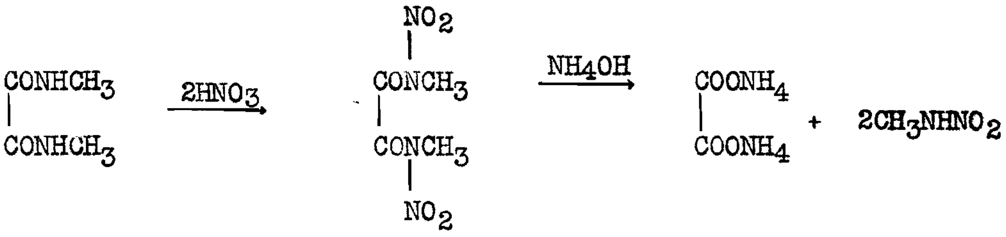
(LVII) gives dialkylnitrosamines (LVIII), not dialkylnitramines (51).



LVII LVIII

Since dimethylnitramine is stable above 200°, the formation of a nitrosamine cannot be due to the decomposition of a nitramine first produced.

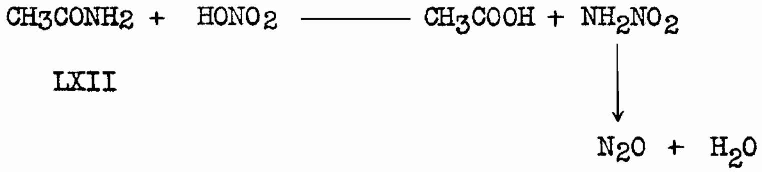
Franchimont first succeeded in preparing a nitramine by the action of concentrated colourless nitric acid (d = 1.52) on N,N'- dimethyloxamide (LIX) (49). The N,N'- dinitro- N,N'- dimethyloxamide (LX) on hydrolysis furnished methylnitramine (LXI); by varying the alkyl substituent on the oxamide, different alkylnitramines could be prepared in a similar way (52).



$$\begin{array}{l}\mathrm{CONHCH_3}\\ |\\ \mathrm{CONHCH_3}\end{array} \xrightarrow{2HNO_3} \begin{array}{l}\mathrm{NO_2}\\ |\\ \mathrm{CONCH_3}\\ |\\ \mathrm{CONCH_3}\\ |\\ \mathrm{NO_2}\end{array} \xrightarrow{NH_4OH} \begin{array}{l}\mathrm{COONH_4}\\ |\\ \mathrm{COONH_4}\end{array} + 2\mathrm{CH_3NHNO_2}$$

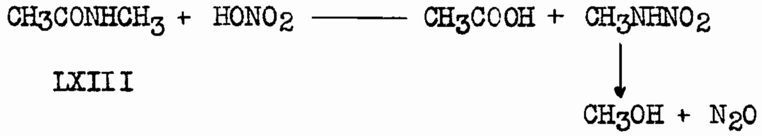
LIX LX LXI

With simpler amides, (LXII,LXIII) Franchimont by this procedure did not obtain nitramide or alkylnitramines, but nitrous oxide. Presumably they were formed as intermediates (49).



$$CH_3CONH_2 + HONO_2 \longrightarrow CH_3COOH + NH_2NO_2 \downarrow N_2O + H_2O$$

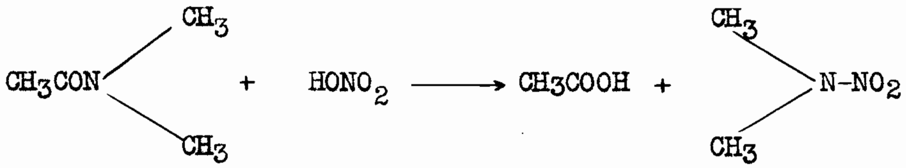
LXII



$$CH_3CONHCH_3 + HONO_2 \longrightarrow CH_3COOH + CH_3NHNO_2 \downarrow CH_3OH + N_2O$$

LXIII

With N,N- dimethylacetamide (LXIV), however, dimethylnitramine (LXV) was formed. Van Romburgh found that N,N'- dimethylbenzenesulphonamide on treatment with nitric acid also gave dimethylnitramine (53).



LXIV LXV

Thiele and Lachmann (54) later showed that in many cases Franchimont failed to obtain nitro- derivatives of the simpler amides because of the excess of nitric acid he employed. When only the theoretical amount of nitric acid was used, nitrourea and nitrourethane were easily formed. Thiele and Lachmann hydrolyzed the latter and succeeded in finally isolating nitramide (55).

Bamberger (56) found that by the action of acetic anhydride on several amine nitrates nitramines could be formed. By this method he prepared dimethylnitramine, N- nitropiperidine, and the N- nitro derivatives of aniline and of several substituted anilines. Recently, Wright (57) has in this way prepared nitramines from aliphatic primary amine nitrates: the yield, however, is very low.

III NOTE ON REAGENTS USED.

In the early period of research on the McGill Process there was insufficient appreciation of the great effect of the type of reagent employed on the yield of R.D.X.

In some cases, this effect has been related to the physical state, reactivity or purity of the reagent; but in many cases there is as yet no explanation for it.

The source of the paraformaldehyde (abbreviated to paraform in this thesis) used in the work described in Chapter IV, Section A, is not known. For the greater part of the research, Eastman Kodak (EK) paraform m.p. (in a sealed tube) 131° - 168°, was used. The work in Chapter IX and in a few other isolated cases was done with Roessler and Hasslacher (R & H) paraform, m.p. (in a sealed tube) 129° - 131°. In all such cases the type of paraform will be designated; otherwise as paraform will be understood the Eastman Kodak product.

Throughout this thesis the yields of R.D.X. are calculated from the weight of paraform used. Actually, analysis showed the formaldehyde content of Eastman Kodak paraform to be 96.6%. On the basis of the amount of formaldehyde used, the yields would consequently be slightly higher. Similarly, molar quantities of formaldehyde have been calculated from the weight of paraform, except in Chapter VIII where a quantitative study is made of the reaction.

Two types of acetic anhydride were used, designated as O and N. Type O had been in the stores for several years, and was coloured brown with impurities. Type N was water-white. Both were the technical product of the Shawinigan Chemical Co. Direct titration* indicated a 3% acetic acid content in Type O. However, determinations of the strength of acetic anhydride are subject to large errors, and this figure is in some doubt. Throughout the thesis molar quantities of acetic anhydride are calculated on the basis of a pure anhydride, and so are slightly high.

When the type of acetic anhydride is not specified, it is understood to be Type O.

The ammonium nitrate used was the commercial grade supplied by Consolidated Mining and Smelting Co. It was a fine powder, and contained small amounts of metallic salts (see page 77). A few runs in Chapter IV,Section A, were made with Merck Reagent crystalline ammonium nitrate.

All temperatures are recorded in degrees centigrade. Those between 150° and 250° are corrected; those below 150° are uncorrected, but are not in error by more than 1°.

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* By R. W. Schiessler.

IV The Preparation of R.D.X. by the McGill Process

A. The Total Addition Method

The name "total addition method" is given to the method originally employed by Ross and Schiessler for the preparation of R.D.X. In it, all the paraformaldehyde and ammonium nitrate were added to the acetic anhydride before reaction. The mixture was then heated with stirring in a three-necked flask, fitted with a thermometer, reflux condenser, and mercury-sealed stirrer. At about 80° - 90° the kick-off occurred, and the solids went into solution. The mixture was heated a further fifteen minutes to complete the reaction.

1. Preliminary Investigation of Reaction Conditions.

The following runs are in the nature of a preliminary investigation, in an attempt to duplicate the yield of 40% reported by Schiessler. This attempt was unsuccessful.

All runs were made using 3.0 gms. (0.1 mole) of paraform (m.p. 168 - 173°), 16.0 gms. (0.2 mole) of ammonium nitrate, and 29 cc. (0.3 mole) of acetic anhydride (Type O), except in Run 4 where the theoretical amount (8.0 gms.; 0.1 mole) of ammonium nitrate was used.

Two types of ammonium nitrate were used: coarse crystalline material (Merck reagent), and finely pulverized material (Consolidated Mining and Smelting Co.).

Three methods of isolating the R.D.X. were followed:

A. The reaction mixture was diluted with approximately six times its volume of water, thereby precipitating the R.D.X.; after neutralizing with sodium carbonate the suspension was heated for two hours on the steam cone. The material so obtained was light tan in colour, and contaminated with a dark, high-melting impurity insoluble in acetone. The method was abandoned when it was found that if the R.D.X. were filtered from the neutralized reaction mixture, the filtrate on being heated on the steam cone precipitated a yellow-brown gum.

B. The R.D.X. was filtered from the diluted reaction mixture. It was then washed with boiling water. The melting point was raised a few degrees by this treatment. The wash-waters on cooling precipitated a solid with a melting point close to that of the paraform used. It burned, however, like R.D.X., and undoubtedly contained some of this compound because of the appreciable solubility (0.15%) of R.D.X. in boiling water (58). About 25% of the crude R.D.X. was lost by this treatment.

AB. The diluted reaction mixture was neutralized and heated, as in method A; and the R.D.X. after filtration was washed with hot water, as in method B.

The results in Table I indicate that higher yields of R.D.X. are obtained from the powdered than from the crystalline ammonium nitrate, and with a lower temperature of reaction. These runs were made following the usual procedure as outlined above.

Table I

Effect of Temperature upon Yield of R.D.X.

Using Crystalline NH_4NO_3							Using Powdered NH_4NO_3						
Run No.	Temp. °C	Purification Method	Wt, gms.	Yield %	M.P. °C	Remarks	Run No.	Temp. °C	Purification Method	Wt. gms.	Yield %	M.P. °C	Remarks
1	90-100	A	1.5	20	-	(1)	7	90	B	2.4	32	192-196	
2	87- 95	AB	1.2	16	188-192								
3	83- 87	A	1.7	23	177-180	(2)							
4	80	AB	0.9	12	171-174	(3)	8	75	AB	1.7	23	187-191	
5	65- 70	AB	2.0	27	187-190	(4)	9	65	B	2.8	37	190-192	(4)
6	55	AB	0.7	9	178	(4)							

Remarks

(1) 2 drops of 74% H_2SO_4 used

(2) 1 drop of 74% H_2SO_4 used

(3) Half the usual amount of NH_4NO_3 used. R.D.X. was darker in colour than usual.

(4) No kick-off at this temperature.

It is evident that the trace of sulphuric acid (Runs 1 and 3) employed by Ross and Schiessler as a catalyst for the depolymerization of paraform is unnecessary, and that use of only the theoretical amount of ammonium nitrate (Run 4) greatly reduces the yield.

It was found that when the reaction was run on this scale, stirring caused a definite increase in yield. This is shown by the yields of Runs 1 - 3 in Table 2. In these runs the mixture of the reactants was heated without stirring in a flask fitted with an air condenser until effervescence was noted. The heating was then stopped: the reaction proceeded with increasing vigour until violent frothing occurred. When it had subsided the product was poured into water and worked up as before.

However, the necessity for stirring appears to be dependent on the size of the run: if the quantities are small enough, the turbulence caused by the kick-off is sufficient to keep the reactants well mixed. This is shown in runs 4-6 in Table 2. These runs were made using 0.75 gms. (0.025 mole) of paraform, 4.0 gms. (0.050 mole) of ammonium nitrate, and 6.25 cc. (0.066 mole) of acetic anhydride. This reaction mixture was heated until effervescence was noted, and ninety seconds later was poured into 100 cc. of water. The crude R.D.X. was filtered off, dried, and weighed without any attempt at purification.

Table 2.

Effect of Stirring on Yield of R.D.X.

Run No.	Size of Run	Type of NH_4HO_3	Conditions	Temp. °C	Purification Method	Wt. gms.	Yield %	M.P. °C
1	large	crystalline	No stirring	-	B	1.3	18	191-194
2	large	powder	No stirring	-	B	2.0	27	190-193
3	large	powder	No stirring	-	B	1.7	23	188-193
4	small	powder	No stirring	79	-	0.71	38	182-186
5	small	powder	Stirring	84	-	0.72	39	190-193
6	small	powder	Stirring	76	-	0.76	41	191-194

2. Effect of Proportions of Reactants.

From Table 1 it is evident that using only the theoretical amount of ammonium nitrate rather than an excess results in a lowered yield and a more impure product.

Consequently, a series of runs was made to determine the optimum proportions of reagents for the Total Addition Method. A fixed amount of paraform (0.75 gms.; 0.025 mole) and varying amounts of ammonium nitrate and acetic anhydride were used. The reactants were placed in a flask fitted with an air-condenser by a ground-glass joint, and heated on the steam cone with shaking. The agitation was continued for 90 seconds after the kick-off had occurred,and then the mixture was poured into 100 cc. of water. The suspension formed was stirred, allowed to stand for 5 minutes, and then filtered into a tared Gooch crucible. The precipitate was washed with 100 cc. of water,and dried for 24 hours at 85°.

In order that the results might be significant, the procedure was standardized as much as possible. It is evident, however, from Runs 17 and 18 that the reaction does not give exactly reproducible yields.

Table 3.

Effect of Proportions of Reactants on Yields.

Run	Ammonium	Nitrate	Acetic	Anhydride	Ac_2O/CH_2O	R.D.X.	% Yield	M.P.
No.	gms.	moles	cc.	moles	mole ratio	gms.		in °C
1	2.00	0.025	5.00	0.053	2.12	0.40	22	172-177
2	2.00	0.025	5.50	0.058	2.33	0.52	28	165-174
3	2.00	0.025	6.00	0.063	2.54	0.50	27	170-174
4	2.00	0.025	6.50	0.069	2.85	0.53	29	169-172
5	2.00	0.025	7.00	0.074	2.97	0.48	26	156-170
6	2.00	0.025	7.50	0.079	3.18	0.44	24	151-168
7	2.00	0.025	8.00	0.085	3.39	0.46	25	153-168
8	2.00	0.025	8.50	0.090	3.60	0.47	25	161-169
9	3.00	0.037	5.00	0.053	2.12	0.32	17	190-195
10	3.00	0.037	5.50	0.058	2.33	0.47	25	191-196
11	3.00	0.037	6.00	0.063	2.54	0.66	36	185-190
12	3.00	0.037	6.50	0.069	2.84	0.66	36	186-189
13	3.00	0.037	7.00	0.074	2.97	0.55	30	186-189
14	3.00	0.037	7.50	0.079	3.18	0.54	29	185-189
15	3.00	0.037	8.00	0.085	3.39	0.47	25	174-184
16	3.00	0.037	8.50	0.090	3.60	0.48	26	185-192
17	4.00	0.050	5.00	0.053	2.12	0.38	20	188-191
18	4.00	0.050	5.00	0.053	2.12	0.33	18	187-190
19	4.00	0.050	5.50	0.058	2.33	0.37	20	189-192
20	4.00	0.050	6.00	0.063	2.54	0.63	34	188-191
21	4.00	0.050	6.50	0.069	2.84	0.69	37	184-187
22	4.00	0.050	7.00	0.074	2.97	0.62	33	189-194
23	4.00	0.050	7.50	0.079	3.18	0.55	30	188-190
24	4.00	0.050	8.00	0.090	3.39	0.56	30	190-193
25	8.00	0.100	5.00	0.053	2.12	0.25	13.5	191-194
26	8.00	0.100	6.50	0.069	2.84	0.76	41	190-193
27	8.00	0.100	8.00	0.090	3.39	0.62	34	188-192
28	8.00	0.100	9.50	0.101	4.02	0.55	30	191-195
29	8.00	0.100	13.00	0.138	5.52	0.38	20	192-194

These results are shown graphically in Fig. 1. An examination of this graph shows that for 1.0 mole of paraform, the optimum amount of acetic anhydride is approximately 2.6 moles, the curves showing quite definite maxima in this region.

Effect of Proportions of Reactants on Yield of R.D.X.

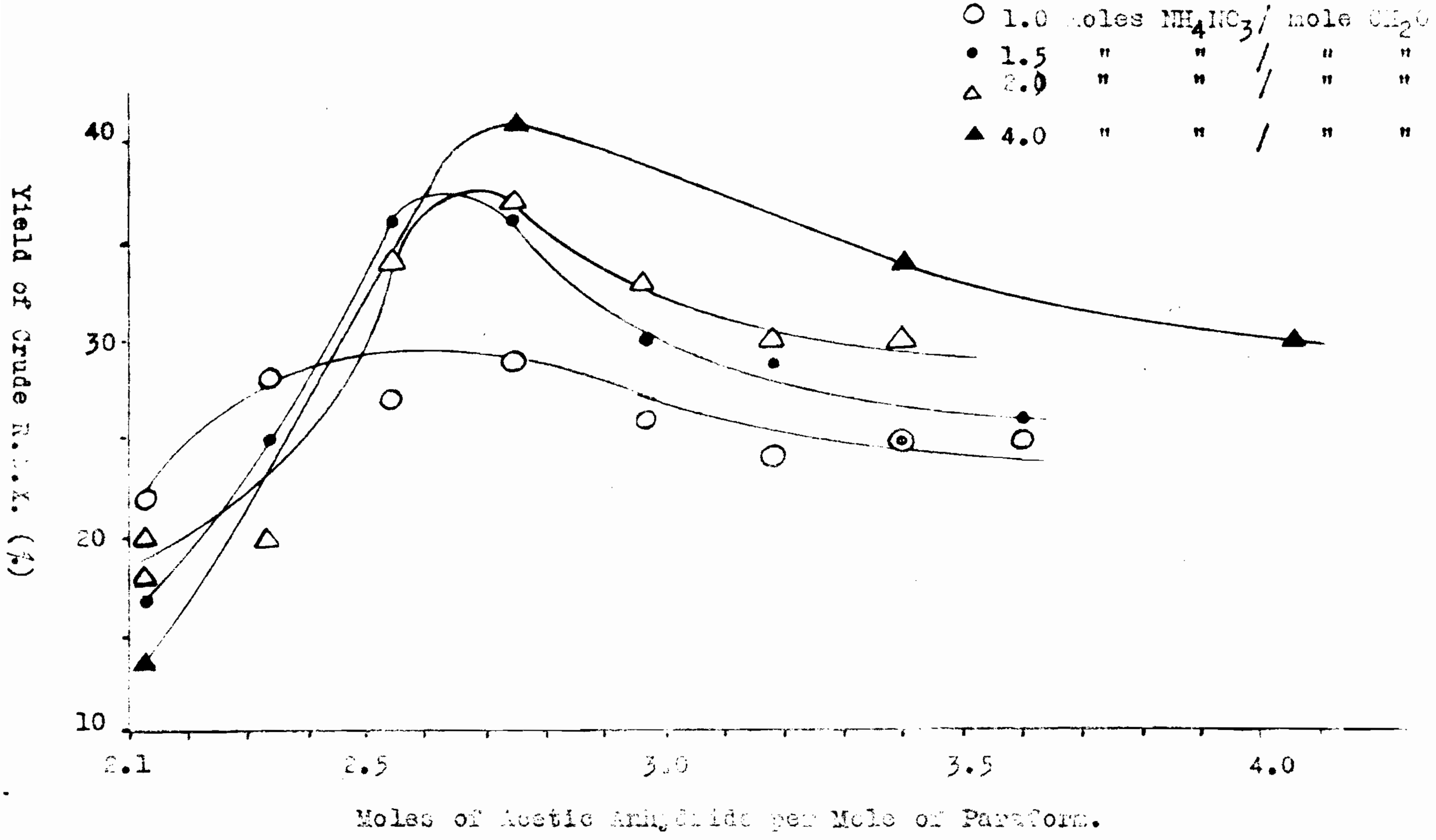

Figure 1

The optimum amount of ammonium nitrate, on the other hand, is indefinite. If the theoretical amount is used, the yield is low and the product is yellow and very impure. With increasing amounts of ammonium nitrate the yield increases at first sharply and then more slowly, and the product becomes purer, as shown by the higher melting points.

In further work, 4.00 gms. of ammonium nitrate and 6.25 cc. of acetic anhydride were used for 0.75 gms. of paraform. This gives a mole ratio of paraform: ammonium nitrate: acetic anhydride of 1 : 2 : 2.6.

3. Effect of Temperature and Time of Reaction.

The data in Table I indicate that temperatures below that causing a kick-off result in larger yields of R.D.X. Accordingly, an investigation of the effect of the time and temperature of the reaction upon the yield was made in a series of runs using 0.75 gms. of paraform, 4.0 gms. of ammonium nitrate, and 6.25 cc. of acetic anhydride. The mixture was stirred in a 100 cc. round-bottom flask which was heated in a water-bath maintained at the desired temperature. After a measured time, the contents of the flask were poured in 100 cc. of water, and the crude R.D.X. was isolated as described in the previous section.

Because of the exhaustion of the paraform used up to this time (Type I), the later runs were made with a fresh stock (Type II). Using the new paraform the yields obtained with the old paraform could not be duplicated.

Table 4.

Effect of Temperature and Time of Reaction on Yield of R.D.X.

Type I Paraform						Type II Paraform					
Run No.	Temp. °C	Time mins.	Wt. gms.	Yield %	M.P. °C	Run No.	Temp. °C	Time mins.	Wt. gms.	Yield %	M.P. °C
1	70	5	0.01	0.5	160-						
2	70	10	0.66	37	190-193	14	70	10	0.07	4	176-178
3	70	10	0.72	39	191-194	15	70	10	0.09	5	176-179
4	70	10	0.79	43	187-188						
5	70	10	0.75	40	178-180						
6	70	15	0.73	39	187-190						
7	70	25	0.77	42	186-190						
8	65	5	trace	-	160-						
9	65	10	0.74	40	188-192						
10	65	15	0.78	42	187-189						
						16	65	25	0.06	3	174-
11	60	5	trace	-	160-						
12	60	15	0.33	18	185-189						
13	60	30	0.74	40	185-187						
						17	60	60	0.20	11	175-178

Actually, the solid obtained from Runs 14-17, using Type II paraform was probably unchanged paraform (m.p. 175-181°) as shown by its failure to deflagrate when heated on a spatula.

The results in Table 4 are subject to some uncertainty. The time recorded is the period of heating the reaction flask by the water-bath, and does not take into account the time needed for the reactants to warm up from room temperature; and the temperature is that of the water-bath, and does not take into account the increase in temperature of the reaction mixture due to the exothermic nature of the reaction. The results have comparative value, and show that:

1. an induction period exists for the reaction;
2. the rate of the reaction is greatly dependent on temperature;

3. the reaction is complete in about ten minutes at 70°; and

4. the type of paraform used has an enormous effect on the yield of R.D.X..

The time of contact of paraform and ammonium nitrate before use in the action also has an effect on the yield of R.D.X. When 0.75 gms. of paraform and 4.0 gms. of ammonium nitrate were mixed and allowed to stand at room temperature overnight in a stoppered flask, it was found that on addition of acetic anhydride heating occurred spontaneously. In two runs 1.90 cc. of acetic acid was added. The mixture was heated for 10 mins. at 70°, and then poured into 200 cc. of water and the R.D.X. isolated as in Subsection 2.

Table 5

Effect of Time of Standing of Ammonium Nitrate-Paraform Mixture upon Yield of R.D.X.

Time of Standing hours	Addition of Acetic Acid cc.	Wt.of R.D.X. gms.	Yield %
0	0	0.65	35
0	1.9	0.65	35
12	0	0.57	31
12	1.9	0.54	29

This decreased yield caused by prolonged contact of the paraform with the ammonium nitrate has been noted by many other workers, and is so far without explanation.

4. Effect of Type of Paraform

The work in the preceding section has shown the great effect of the type of paraform used on the yield of R.D.X.. An attempt was consequently made to relate this effect to the composition and degree of polymerization of the paraform.

Paraform (59) is composed of a mixture of polyoxymethylene glycols, containing from six to fifty formaldehyde molecules. The commercial product usually contains 5% water as the end hydroxyl groups, and melts at 120-130°. It dissolves slowly in water. Different samples of paraform vary considerably in their properties, depending on the average length of the polymers making it up. For in general the solubility and reactivity decrease, and the melting point increases, with increasing size of the polyoxymethylene glycol chain.

Methylation of the end hydroxyl groups in a polyoxymethylene glycol, to form a compound such as γ- polyoxymethylene, has an enormous effect on decreasing the reactivity of the polymer and increasing its stability.

Four types of paraform (Types I , II, III, and IV) were examined for their physical properties and their yield of R.D.X. Except for Type IV, their melting points all indicated a higher degree of polymerization than usually found in commercial paraforms. This may have been due to the slow continued polymerization on "ageing" of Types I, II, and III, (60).

The lower degree of polymerization of Type IV was also indicated by its limited solubility in water; the other types were relatively insoluble. These solubilities were determined by shaking 25 gms. of the sample of paraform with 100 cc. of water for two hours. The undissolved paraform was then filtered off, dried in a desiccator over calcium chloride for over fourteen hours, and weighed.

The filtrates on evaporation gave a strong odour of formaldehyde, but only from that of Type IV was an appreciable residue (m.p. 120-125°) left.

The yield of R.D.X. was found by reacting 0.75 gms. of paraform with 4.0 gms. of ammonium nitrate and 6.25 cc. of acetic anhydride. Two methods were used:

A. The reaction mixture was heated until a kick-off occurred;

B. The reaction mixture was heated to 70° for 10 minutes.

In either case, the reaction mixture was poured into 100 cc. of water, and worked up as in runs in Subsection 2.

Table 6

Effect of Type of Paraform on Yield of R.D.X.

Phys Props of Paraform			Method A				Method B		
Type	Solubility in gms/100 gms H_2O	M.P. in °C	Kick-off Temp. in °C	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C
I	?	168-173	84	0.72	39	190-193	0.66	37	190-193
			76	0.76	41	191-194	0.79	43	187-188
							0.75	40	178-180
II	trace	175-181	$>$ 90	0.38	20	188-191	0.07(1)	4	176-178
				0.44	24		0.09(1)	5	176-179
III	trace	165-172	87	0.70	38	184-188			
IV	12	135-145	87	0.58	31	192-196	0.72	39	191-194

(1) Probably unchanged paraform

It is apparent that the yield of R.D.X. is not greatly affected by the polymer type within certain limits, the typical "paraformaldehyde" of Type IV giving substantially the same results as the α- polyoxymethylenes (59) of Types I and III. Type II might be a γ- or δ- polyoxymethylene, accounting for its lack of reactivity except at high temperatures, when the whole molecule is disrupted and the formaldehyde made available for reaction.

5. Effect of Size of Run

The runs so far described have been small, the largest using only 3.0 gms. (0.10 mole) of paraform. It was found that when 12.0 gms. (0.40 mole) of paraform, 64.0 gms. (0.80 mole) of ammonium nitrate, and 100 cc. (1.06 mole) of acetic anhydride were used, then if the temperature of the heating bath were kept below 65° a violent kick-off ensued after four to eight minutes. Excessive frothing resulted in some losses of material. It is evident that in a larger run the heat generated in the kick-off is larger and less readily dissipated, and so the reaction is disproportionately more violent.

Table 7

Yield of R.D.X. from Larger Runs

			First Crop of R.D.X.			Second Crop of R.D.X.			R.D.X.
Run No.	Temp. °C	Time mins.	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C	Total Yield %
1	70	4	8.0	27	190-192	0.35	1.2	182-187	28
2	65	7	8.2	28	188-190	0.37	1.2	181-182	29
3	63	8	7.3	25	186-191	0.06	0.2	210	25

B. The Continuous Addition Method*

It soon became obvious that the Total Addition Method was unsuitable for any but small runs because of the vigorously exothermic nature of the McGill Process. It was found that by the Continuous Addition Method the reaction could be controlled well enough to run large batches without a kick-off. The yield of R.D.X. was higher, approximating 50% under optimum conditions.

In the Continuous Addition Method, a mixture of the paraform and ammonium nitrate was added continuously to the hot stirred acetic anhydride during the reaction. By this means it was possible to avoid the presence of a large excess of unreacted material at any time, and so lessen the rate of evolution of heat. The temperature of the reaction mixture was observed by means of a thermometer dipping into the stirred acetic anhydride.

It was found that for a short time after addition of the solid reactants to the acetic anhydride had commenced, no heat was evolved (the first "No-Heating Period" or N.H.P. (1)). A vigorous reaction then set in, and heat was evolved until after the addition was complete (the Heating Period or H.P.).

The temperature of the reaction was first controlled by heating the reaction flask with a water-bath, and adding the solid reactants at such a rate as to maintain the temperature at the desired level. This necessitated a slow addition.

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* Much of the work in developing this method was done in collaboration with Mr. A. Gillies, whose help is gratefully acknowledged.

Later it was found that the yield of R.D.X. was not decreased by a shorter time of reaction, and so the heating-bath was dispensed with. The reaction flask was heated with a Bunsen flame during the N.H.P.(1); as soon as the H.P. had commenced, the flask was cooled frequently with a beaker of cold water. The control of the reaction by this method required considerable skill and experience. For a run at 70°, it was found that if the temperature rose above 75° it frequently became uncontrollable. In some instances, (e.g. Run 1 , Table 24 , page 67), while the temperature and other conditions had been regulated in the usual way, the yield dropped off without apparent reason.

The R.D.X. was usually isolated in two crops. The first crop was obtained by diluting the reaction mixture to give an acetic acid concentration of 40-60%, and cooling to room temperature. The filtrate from this crop, on further dilution to an acetic acid concentration of 20-30%, precipitated a second crop of more impure R.D.X. At this concentration the precipitation of R.D.X. is substantially complete (61). All crops obtained after dilution and boiling, following the Shawinigan Method of Purification (page 66), are designated by the letter "S" following the weight of the crop.

Occasionally the reaction mixture was at once diluted to 20-30% acetic acid, and the crude R.D.X. filtered off in one crop.

1. Effect of Proportions of Reactants.

The three runs in Table 8 were made at 70°. In this and in succeeding tables, "Addition" refers to the time required to add the mixture of paraform and ammonium nitrate to the acetic anhydride; "Heating" to the length of time after addition for which the reaction mixture was heated.

Table 8

Effect of Proportions of Reactants on Yield of R.D.X.

Run No.	Amounts of Reactants: Paraform gms.	Amounts of Reactants: NH_4NO_3 gms.	Amounts of Reactants: Ac_2O cc.	$(CH_2O)_x$:NH_4NO_3:Ac_2O mole ratio	Addition mins.	Heating mins.	First Crop Wt. gms.	First Crop Yield %	M.P. °C
1	6.0	16.0	96	1 : 1 : 5.1	24	20	5.4	36	190-193
2	6.0	32.0	100	1 : 2 : 5.2	86	-	4.5	30	195-198
3	12.0	64.0	100	1 : 2 : 2.6	17	8	14.5	49	190-192

In this method, as in the older one, the optimum mole ratio of paraform: acetic anhydride appears to be 1 : 2.6 (Run 3). However, an excess of ammonium nitrate decreases rather than increases the yield (compare Runs 1 and 2). This result has been confirmed by Johnson (62), who found the optimum ratio of paraform : ammonium nitrate : acetic anhydride to be 1 : 1.25 : 2.6. For the greater part of the investigations on this method the old ratio of 1 : 2 : 2.6 was used.

2. Effect of Temperature of Reaction

In all the runs in Table 9 the ratio of paraform : ammonium nitrate : acetic anhydride was 1 : 2 : 2.6.

Table 9

Effect of Temperature on Yields of R.D.X.

Run No.	Paraform Wt. gms.	Addition Temp. °C	Addition Time mins.	Heating Temp. °C	Heating Time mins.	First Crop Wt. gms.	First Crop Yield %	First Crop M.P. °C	Second Crop Wt. gms.	Second Crop Yield %	Second Crop M.P. °C	Total Yield %
1	12.0	65-80	30	-	-	14.5	49	189-194	2.0	6.6	165-	56
2	30.0	67	60	-	-	36.3	49	189-194	1.0	1.3	202-205	50
3	12.0	70	17	70	8	14.5	49	190-192	-	-	-	49
4	24.0	70-74	60	-	-	25.5	43	192-194	2.1	3.5	150-160	46
5	30.0	80-85	20	80	15	30.8	42	193-198	-	-	-	42
6	12.0	90	30	-	-	10.0	34	193-197	1.1	3.7	187-192	38

It is apparent that, in the temperature range 65-90°, the highest yields of R.D.X. are obtained at the lower temperature. Below 65°, however, the rate of the reaction drops off rapidly (Table 4), and so continuous addition within a reasonable length of time is in effect little different from total addition at the beginning of the experiment. Hence in Run 2 (Table 10), a small amount of the solid was added to the anhydride at 70°, and stirred for 6 mins. By this time the induction period (page 40) is over at this temperature. The temperature was then lowered to 50°, and the solids added in 5 equal portions at intervals of 15 minutes. Only after 60 minutes did the evolution of heat become noticeable.

It has been noticed that when the formaldehyde is contained in a reactive paraform, a reaction temperature of 65° gives the optimum yield of R.D.X., but when it is held in a more inert polymer a higher temperature is necessary to make it available for reaction (page 43). To see whether the paraform not used in the formation of R.D.X. had reacted to form a heat-labile compound, the reaction mixture in Run 3 was heated to 115° ; the failure to obtain an increased yield indicates that this formaldehyde has formed a stable by-product.

The runs in Table 10 were made using 12.5 gms. (0.42 mole) of paraform, 40 gms. (0.50 mole) of ammonium nitrate, and 100 cc. (1.06 mole) of acetic anhydride, the mole ratio thus being 1 : 1.2 : 2.6.

Table 10

Effect of Temperature upon Yield of R.D.X.

		Addition		Heating		First Crop			Second Crop			Total
Run No.	Ac_2O Type	Temp. °C	Time mins.	Temp. °C	Time mins.	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C	Yield %
1	N	70	11	70	20	13.1S	44.3	191-195	1.0	3.4	180-186	47.7
2	0	51-53	75(1)	53	120	13.5S	45.6	191-196	0.8	2.7	170-173	48.3
3	N	70	10	(70 (115	(15 (20(2)	12.6	42.5	191-195	0.2	0.7	-	43.2

(1) Addition in 5 equal portions at intervals of 15 mins.

(2) During this time 20 cc. of 97.5% HNO_3 and 10 cc. of Ac_2O were added in small portions

It is shown in the following subsection that Type 0 anhydride gave yields of R.D.X. about 5% higher than those obtained with Type N. Hence it appears that neither a temperature of reaction lower than 65° (Run 2) nor a temperature in the heating period higher than 70° (Run 3) results in an increased yield of R.D.X.

3. Effect of Type of Acetic Anhydride

The results in Table II below, and in Table 24 on page 67, show that a consistently higher yield of R.D.X. was obtained with Type 0 acetic anhydride than with Type N. Run 1 was made with 12.0 gms. and Run 2 with 3.0 gms. of paraform. In both cases the mole ratio was 1 : 2 : 2.6.

Table II

Effect of Type of Acetic Anhydride on Yield of R.D.X.

		Addition		Heating				
Run No.	Ac_2O Type	Temp. °C	Time mins.	Temp. °C	Time mins.	Wt. gms.	Yield %	M.P. °C
1	0	70	17	70	8	14.5	49	190-192
2	N	65-70	15	70	5	3.08	41.6	182-187

The difference in yields (see Table 24) was usually smaller than this. There is as yet no satisfactory explanation for this effect.

4. Effect of Type of Formaldehyde

The investigations so far described on the effect of reaction conditions on the yield of R.D.X. were done with Eastman Kodak paraform. Roessler and Hasslacher paraform, which has become standard for R.D.X. research in North America, gave a very slightly lower yield. The two runs in Table 12 were made with 12.5 gms. (0.42 mole) of paraform, 40 gms. (0.50 mole) of ammonium nitrate, and 100 cc. (1.06 mole) of acetic anhydride (Type N), the mole ratio thus being 1 : 1.2 : 2.6.

Table 12

Effect of Type of Paraform on Yield of R.D.X.

	Para-	Addition		Heating		First Crop			Second Crop			Total
Run No.	form Type	Temp. °C	Time mins.	Temp. °C	Time mins.	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C	yield %
1	EK	70	11	70	20	13.15	42.5	191-195	1.0	3.3	180-186	45.8
2	R&H	70	10	70	20	13.4	43.5	189-194	-	-	-	43.5

Dupont paraform was found to give a slightly higher yield of R.D.X. than E.K. paraform (Table 24, page 67).

The use of gaseous formaldehyde in the McGill Process was investigated. This had been tried by Ross and Schiessler (65) and later, with improved control, by Wright (65). The following work was done later, and confirms Wright's results.

To measure the amount of formaldehyde introduced into the reaction, two methods were tried:

1. An attempt was made to prepare anhydrous liquid formaldehyde, using an apparatus modified after that of Spence and Wild (66) and of

Walker (67). It was hoped to use for each run a fixed volume of liquid formaldehyde, whose weight could be determined by analytical methods. However, it was not found possible to obtain more than a small amount of liquid formaldehyde before the apparatus became clogged with solid polymer. This may have been due to a failure to use alkali-precipitated paraform. The practical difficulties of this method caused it to be dropped.

2. A weighed amount of paraform was volatilized in a current of nitrogen, using the apparatus described by Wright (65). The weight of the formaldehyde was then regarded as that of the paraform (the 4-5% water content was ignored in this as in previous cases in the calculation of the yield).

It was noticed, however, that on volatilization of the paraform a small carbonaceous residue was always left behind. This must have come from the decomposition of some δ-polyoxymethylene making up a part of the paraform. In this polymer some of the carbon atoms are linked directly together, rather than through oxygen atoms, and so complete depolymerization to formaldehyde is impossible (68).

An attempt was made to find the amount of formaldehyde liberated by the sublimation of 3.000 gms. of paraform (2.895 gms. of HCHO by analysis*) in a stream of nitrogen. This was done by passing the mixed gases through a solution of sodium sulphite, and then titrating the liberated alkali with standard acid, thymolphthalein being used as an indicator * (69). It was found that the amount of formaldehyde accounted for was always less than that calculated. That this discrepancy did not

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* The author is indebted to Mr. D. Robinson for these formaldehyde determinations.

arise entirely from a non-volatile fraction such as δ polyoxymethylene in the paraform was shown by the variability of the loss. As other possible sources of loss, the following were eliminated:

1. Oxidation by traces of oxygen in the nitrogen (Runs 5 and 6, Table 13);

2. leakage from the apparatus : in Runs 5 and 6 all connections were pointed with collodion;

3. failure of the sodium sulphite solution to absorb completely the gaseous formaldehyde : in Run 4 the gases were passed through a second solution of sodium sulphite, which on analysis showed no formaldehyde present;

4. too rapid volatilization of the paraform (Run 2) ;

5. too rapid a nitrogen stream (Run 4) ;

6. heating of the sodium sulphite solution (Run 3).

Table 13

Recovery of Formaldehyde after Volatilization of 3.00 gms. of Paraform in a Stream of Nitrogen.

	Amount of Formaldehyde						
Run No.	Calcd. gms.	Anal. gms.	loss gms.	loss %	Rate N_2 flow cc/mins.	Time of Volatilization mins.	Remarks
1	2.895	2.504	0.391	13.5	150	-	
2	2.895	2.443	0.452	15.6	150	20	
3	2.895	2.370	0.525	18.1	150	10	Soln. of Na_2SO_3 stirred and cooled by ice bath.
4	2.895	2.185	0.710	24.5	25	-	
5	2.895	2.325	0.570	19.7	150	3	N_2 passed through alkaline pyrogallol
6	2.895	2.527	0.368	12.3	150	15	N_2 passed through alkaline pyrogallol

Hence in the runs made using gaseous formaldehyde, the yield was based on the weight of paraform volatilized. The yield was about the same as with the use of solid paraform. All runs were made at 70°. In all the runs the mixture of formaldehyde and nitrogen was passed into a stirred suspension of ammonium nitrate in acetic anhydride, except in Run 2, in which the ammonium nitrate was fed into the acetic anhydride simultaneously with the gaseous formaldehyde. This method offers no advantages, as seen by the yield.

In all runs, the NHP (1) appeared to be practically eliminated, and heat was evolved from the beginning of addition of the gaseous formaldehyde. A slight excess of ammonium nitrate over the theoretical is necessary to give a yield of 50%.

Table 14

Yield of R.D.X. using Gaseous Formaldehyde

Run No.	Paraform Wt. gms.	$(CH_2O)_x$:NH_4NO_3:Ac_2O mole ratio	Time Addition mins.	Time Heating mins.	First Crop Wt. gms.	First Crop Yield %	First Crop M.P. °C	Second Crop Wt. gms.	Second Crop Yield %	Second Crop M.P. °C	Total Yield %
1	6.0	1 : 1 : 2.6	10	10	6.38	43.1	188-190	-	-	-	43.1
2	12.0	1 : 1 : 2.6	10	20	12.2S	41.3	190-193	1.0	3.4	170-173	44.7
3	12.0(1)	1 :1.25 : 2.6	15	20	13.8S	46.7	190-194	1.2	4.1	169-	50.8
4	12.0	1 : 2 : 2.6	22	10	13.0S	43.9	195-200	2.1	7.1	174-	51.0

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(1) N_2 bubbled through alkaline pyrogallol used as formaldehyde diluent.

C. The Reversed Addition Method

It has been shown that continuous addition of a mixture of paraform and ammonium nitrate to acetic anhydride leads to a 50% yield of R.D.X. **Wright** showed that addition of paraform to a stirred mixture of the ammonium nitrate in acetic anhydride gave the same result (70). On the other hand, continuous addition of ammonium nitrate to a stirred suspension of paraform in acetic anhydride leads to a lowered yield. This mode of operation is known as the Reversed Addition Method.

The Reversed Addition Method is of no practical value ; but it was investigated in order to gain information on the side reactions in the McGill Process which cause a decreased yield of R.D.X. The study did little to elucidate this problem. The results show that an excess of paraform over ammonium nitrate, such as exists for the greater part of the reaction time with this method , leads to am increased consumption of paraform in side reactions and a lowered yield of R.D.X.: this **is believed** to hold in the Continuous Addition Method also (71). That, however, the side-reaction does not consist of a simple reaction between paraform and acetic anhydride, as was believed at one time in this and other laboratories (72) was shown by the fact that when these two compounds were heated for 60 mins. alone, or with a small amount of ammonium nitrate, no further decrease in yield of R.D.X. was observed, using Type N anhydride : a slight decrease occurred with Type O anhydride, however. It is now believed that the excess of paraform favours a side reaction in which paraform, ammonium nitrate, and acetic anhydride are all involved: for increased time of addition of ammonium nitrate (i.e. increased proportion of reaction time for which the paraform is present in excess) leads to a lowered yield of R.D.X.

In runs using the Reversed Addition Method, the following procedure was followed, except as otherwise noted: A stirred suspension of 12.5 gms. (0.42 mole) of paraform in 100 cc. (1.06 mole) of acetic anhydride was heated to 70°. Immediately (Run Type A) or after 60 minutes time (Run Type B), 40.0 gms. (0.50 mole) of ammonium nitrate was added over a period of 10 minutes at as uniform a rate as possible. After three or four minutes from the start of addition, the reaction became suddenly **exothermic** ; cooling by an ice-water bath at frequent intervals was necessary to keep the temperature at 70° and prevent a kick-off. After addition was complete, the mixture was stirred for a further 20 minutes at 70°. The crude R.D.X. was isolated in one or two crops in the same fashion as in the Continuous Addition Method (page 46). These crops were combined for purification from 70% nitric acid, which was used in the ratio of 7 gms. (5 cc.) of acid for 1 gm. of solid. On heating up such a mixture, the solids went into solution; then a "fume-off" occurred in which the oxidation of the impurities took place with the evolution of copious brown fumes. The nitric acid solution was heated a further ten minutes. On cooling, the first crop of R.D.X. was obtained; dilution of the filtrate gave a second more impure crop.

1. Effect of Type of Paraform.

Changes in the types of reagent used had a much greater effect on the yield of R.D.X. in this method than in the Continuous Addition Method. Thus R. & H. paraform gave a more exothermic reaction than E.K. paraform, and a reduced yield of R.D.X.: this yield, however, appeared more independent of the temperature.

Table 15

Effect of Type of Paraform on Yield of R.D.X.

				Crude R.D.X.						Purified R.D.X.		
				First Crop			Second Crop					
Run No.	Paraform Type	Ac_2O Type	Addition Temp.	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C
1	E.K.	N	70(95)(1)	4.8	15.6	193-200	-	-	-	4.2	13.5	192-199
2	E.K.	N	70	8.3	27.0	190-198	-	-	-	7.4	24	191-196
3	R.& H.	N	70(90)(1)	- S	-	-	5.5	17.9	183-190	3.8	12.5	201-204
4	R. & H.	N	70	4.2S	13.5	183-190	1.5	4.9	184-194	4.4	14.3	196-200

(1) Reaction momentarily escaped control, heated to temperature in parentheses.

In all succeeding runs, E.K. paraform was used.

2. Effect of Acetic Anhydride.

In Runs 1 and 3 of Table 16, the ammonium nitrate was added to the suspension of paraform in acetic anhydride as soon as it had been heated to 70° (Run Type A); in Runs 2,4 and 5, the suspension was heated with stirring for 60 mins. before addition of the ammonium nitrate (Run Type B).

Table 16

Effect of Type of Acetic Anhydride on Yield of R.D.X.

			Crude R.D.X.						Purified R.D.X.					
			First Crop			Second Crop			First Crop			Second Crop		
Run No.	Type	Ac_2O Type	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C
1	A	0	12.6	41.0	165-170	-	-	-	9.1	29.6	191-193	-	-	-
2	B	0	10.2	32.8	180-183	-	-	-	8.3	27.0	191-193	-	-	-
3	A	N	8.3	27.0	190-198	-	-	-	7.4	24.0	191-196	-	-	-
4	B	N	8.9	28.9	189-195	-	-	-	8.2	26.6	191-196	-	-	-
5	B	N	9.7(S)	31.5	186-190	0.8	2.6	182-190	8.4	27.3	193-197	0.4	1.3	192-196

From the results of Table 16 it is apparent that while the yield of R.D.X. is decreased by a Type B Run when Type O anhydride is used, it is increased by a Type B Run when Type N anhydride is used. Like the other effects produced by the two types of anhydrides, this is without satisfactory explanation at the moment. It is evident that, for Type N anhydride at least, no side reaction between the paraform and acetic anhydride was taking place during the contact for 1 hour at 60°.

3. Effect of Rate of Addition of Ammonium Nitrate.

In Runs 3 and 6 of Table 17, 0.5 gm. of the 40.0 gms. of ammonium nitrate was added to the stirred suspension of paraform in acetic anhydride before heating it for one hour to 70°: this is indicated in the column "Wt. NH_4NO_3 Added" of the Table. This procedure caused a decreased yield of R.D.X. when Type O anhydride was used.

Table 17

Effect of Rate of Addition of NH_4NO_3 on Yield of R.D.X.

						Crude R.D.X.						Purified R.D.X.		
						First Crop			Second Crop					
Run No.	Type	Wt. NH_4NO_3 Added gms.	Ac_2O Type	Addition Time mins.	Temp. °C	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C
1	A	-	O	10	70	12.6	41.0	165-170	-	-	-	9.1	29.6	191-193
2	B	-	O	10	70	10.2	32.8	180-183	-	-	-	8.3	27.0	191-193
3	B	0.5	O	10	70	9.4	30.6	178-181	-	-	-	7.1	23.0	191-196
4	A	-	N	11	70	8.3	27.0	190-198	-	-	-	7.4	24.0	191-196
5(1)	A	-	O	20	65	7.6(S)	25.7	186-187	0.5	1.7	-	-	-	-
6(1)	B	0.5	O	20	65	5.8(S)	19.6	188-190	1.0	3.4	-	-	-	-
7	A	-	N	60	70	0.3(2)	0.8	187-197	3.0	9.7	189-193	-	-	-

(1) 12.0 gms. paraform used instead of the usual 12.5 gms.
(2) Obtained by filtering solids from cooled reaction mixture without dilution, then washing these solids with water to remove water-soluble materials.

From this Table it is evident that increasing the time of addition of ammonium nitrate, as in Run 7, greatly reduces the yield of R.D.X.

4. Effect of Small Amounts of Ammonium Nitrate on Paraform-Acetic Anhydride Mixture.

In Table 17 it was seen that the addition of small amounts of ammonium nitrate to the paraform-acetic anhydride mixture before heating it with stirring for one hour at 70° (Type B Run) caused an apparent increase in the side reaction, i.e. a decrease in the yield of R.D.X. With Type N anhydride, on the other hand, the effect is the opposite with small amounts of ammonium nitrate. With larger amounts of ammonium nitrate a decrease in yield of R.D.X. is indeed noted: but in these cases interpretation of the results becomes difficult. For the decreased yield can be attributed to slower rate of addition of NH_4NO_3, the material being added in two portions at an interval of 60 minutes.

Table 18

Effect on Yield of R.D.X. of Addition of Varying Amounts of NH_4NO_3 to Acetic Anhydride-Paraform Suspension (Type N Ac_2O)

			Crude R.D.X.						Purified R.D.X.					
			First Crop			Second Crop			First Crop			Second Crop		
Run No.	Wt. NH_4NO_3 Added gms.	Addition Temp. °C	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C
1	-	70	8.9	28.9	189-195	-	-	-	8.2	26.6	191-196	-	-	-
2	-	70	9.7(S)	31.5	186-190	0.8	2.6	182-190	8.4	27.3	193-197	0.4	1.3	192-196
3	1.0	70(2)	4.8(S)	15.6	194-198	1.2	3.9	180-	4.6	14.9	193-195	0.4	1.3	192-198
4	1.0	70(3)												
5	1.0	70	10.5(S)	34.2	187-193	0.6	2.0	179-184	9.3	30.2	195-199	0.5	1.6	205-225
6	4.0	70	7.1(S)	23.0	193-197	0.7	2.3	181-185	6.1	19.8	193-195	0.3	1.0	192-198
7	(1)	70	8.5(S)	27.6	187-193	0.8	2.6	183-188	7.6	24.7	195-199	0.4	1.3	191-195

(1) 12 gms. acetic acid added: this is the amount formed if 4.0 gms. of NH_4NO_3 is dehydrated completely to give R.D.X. and similar by-products.

(2) Reaction became uncontrollable during addition, and temperature rose momentarily to 110°.

(3) Kick-off occurred at the end of the 20 min. heating period following addition.

The kick-off occurring in Run 4 is noteworthy. The by-products whose formation is favoured by the Reversed Addition Method must be highly unstable: it has already been shown (page 48), that if the reaction mixture after Continuous Addition of the reagents is heated up to 110°, no kick-off occurs.

V. The Isolation and Purification of R.D.X.

British Ordnance Specifications call for a melting point of R.D.X. above 200°. Material of this purity is produced by the nitration of hexamine: and for some time much effort was expended in attempting to purify the product of the McGill Process to meet this specification. It was found that one of the impurities lowering the melting of R.D.X. was very similar in physical properties and chemical stability, and so could not be separated sharply from the R.D.X. . This is now believed to be H.M.X. discovered later by **Wright** (73). This appears always to be formed with R.D.X. in the McGill Process (74).

Crude R.D.X. can be isolated from the reaction mixture of the McGill Process by:

1. Cooling the mixture to room temperature, and filtering off the solids: when these are washed with water to remove water-soluble material, crude R.D.X. is left behind. Some R.D.X. remains in solution in the filtered reaction mixture, and must be precipitated by diluting it with water.

2. Dilution of the reaction mixture with water. In a 50% AcOH - 50% water mixture, R.D.X. is soluble to the extent of 0.06%; in a 25% AcOH - 75% water mixture, to the extent of 0.03%(61). At the latter concentration, precipitation of R.D.X. is substantially complete.

3. Dilution of the reaction mixture with organic solvents in which R.D.X. is insoluble. These were found to offer no advantages over water (74A).

The crude product so obtained usually melts at 180-190°. It purified by what are classified as physical and as chemical methods of purification.

A. Physical Methods of Purification.

Physical methods of purification are defined here as methods depending on differences in physical properties of the compound and its contaminants. For crude R.D.X. three such methods are applicable: crystallization, extraction, and sublimation (75).

1. Crystallization.

Purification of R.D.X. by crystallization is made difficult by the relative insolubility of this compound in most organic solvents (58). Preliminary tests showed several organic solvents in which it is soluble to be unsuitable. In these and succeeding crystallizations, the standard method as described by Fieser (76) was followed. The following melting points were observed on crystallizing a crude R.D.X., m.p. 186-188°, from the specific solvent: ethanol, m.p. 192-195°; ethyl acetate, m.p. 201-203°; 50-50 benzene-acetone mixture, m.p. 195-198°. No R.D.X. was recovered on cooling a pyridine solution.

Ross and Schiessler's method of crystallizing R.D.X. from a hot acetone solution to which water had been added to give incipient cloudiness gave a crop melting below 200°. When the proportion of water is kept below 20%, however, a fair recovery of material melting above 200° is obtained.

Table 19

Crystallization of R.D.X. from Acetone-Water Mixtures

Crude R.D.X.		Solvent				First Crop			Second Crop (1)		
Wt. gms.	M.P. °C	Acetone %	Water %	Vol. cc.	Solubility cc/gm.	Wt. gms.	Recovery %	M.P. °C	Wt. gms.	Recovery %	M.P. °C
1.0	189-193	100	0	6.7	6.7	0.26	26	200-202	0.26	26	196-198
1.0	189-193	80	20	8.3	8.3	0.52	52	200-202	0.24	24	190-191
0.5	189-193	60	40	11.6	23.2	0.16	32	189-192			
0.5	189-193	40	20	34.9	69.8	0.19	38	193-196			
0.25	189-193	20	80	81.7	327.	0.11	44	189-191			

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(1) Obtained by addition of water to hot filtrate from first crop to incipient cloudiness, cooling.

The effectiveness of the 80.20 acetone-water mixture and of other solvents for crystallization is compared in Table 20. In Expts. 1-7, the standard procedure for crystallization was followed: in Expts. 8 and 9 the R.D.X. was dissolved in the minimum quantity of boiling solvent and the solution was then allowed to cool. The recovery of R.D.X. is considerably greater than when the hot solution is filtered (Expts. 6 and 7). A small part of this difference is due to the non-removal in Expts. 8 and 9 of some insoluble material: the greater part is due to the loss of R.D.X. by incrustation on the filter paper in Expts. 6 and 7. These losses are comparatively great in small-scale laboratory crystallizations, but would be negligible on an industrial scale.

Table 20

Recovery of R.D.X. on Crystallization for Various Solvents

	Crude R.D.X.		Solvent			Crystallized R.D.X.		
Expt. No.	Wt. gms.	M.P. °C	Name	Vol. cc.	Solubility^{-1} cc/gm.	Wt. gms.	Recovery %	M.P. °C
1	2.8	190-192	80-20 acetone-water	24.3	8.7	1.44	51.5	200-202
2	30	191-195	" " " "	265	8.8	16.0	53.3	202-203
3	3.0	190-192	ethyl acetate	90	30	1.37	46.5	201-202
4	30	190-192	" "	780	26	13.1	43.7	202-203
5	30	191-195	acetic acid	575	19	21.4	71.3	198-201
6	5.0	191-195	2-nitro-propane	25	5.0	2.69	53.8	198-201
7	5.0	184-187	" " "	16	3.2	3.02	60.4	194-196
8	5.0	184-187	" " "	-	-	4.16	83.2	-
9	4.0	198-200	" " "	-	-	3.64	91.0	200-201

From Expt. 9 it is apparent that the 90% recovery from 2-nitropropane claimed by Johnson is possible only from fairly pure R.D.X., and with no losses in filtration.

2. Extraction.

From Table 20 it appears that R.D.X. melting above 200° is obtained by crystallization from ethyl acetate. This material was found to have a very low sensitivity (Table 22). However, the recovery is poor.

Extraction of crude R.D.X. with a small volume of ethyl acetate, insufficient to dissolve it completely, gives a larger recovery of R.D.X., still meeting specifications for melting point (Expt.1, Table 21). However, repeated extraction using the filtrate from a previous experiment, as in Expts. 2-3, and 4-8, was unsuccessful.

Table 21

Extraction of R.D.X. with Ethyl Acetate

	Crude R.D.X.			Crystallized R.D.X.		
Expt. No.	Wt. gms.	M.P. °C	Extracting Liquid	Wt. gms.	Recovery %	M.P. °C
1	2.00	190-192	20 cc.ethyl acetate	1.45	72	200-202
2	2.00	188-190	40 cc.ethyl acetate	0.96	48	199-202
3	2.00	188-190	Filtrate from Expt.2	1.71	86	199-202
4	2.00	190-192	40 cc.ethyl acetate	0.61	31	199-202
5	2.00	190-192	Filtrate from Expt.4	1.19	59	198-201
6	2.00	190-192	" " " 5	1.53	76	197-201
7	2.00	190-192	" " " 6	1.31	65	197-201
8	2.00	190-192	" " " 7	1.96	98	185-188

The data on the explosive properties of samples of R.D.X. sent from this laboratory to Mr. Fletcher, at the Bureau of Mines, Ottawa, are tabulated below.

Table 22

Explosive Properties of Crude and of Crystallized R.D.X.

R.D.X. description	M.P.	Sensitivity		Trauzl Block Expansion	
	°C	Cms.	T.N.T.=1	cc.	TNN.T.=1
Crude	189-194	58	2.76	453	1.77
Crude	189-194	116	1.3	447	1.75
Crude boiled in water for 24 hours	195-198	74	2.16	-	-
Crystallized from Ethyl acetate	200-202	154	1.05	-	-
" " " "	202-203	170	0.94	472	1.84
Amorphous (R.D.X.,m.p.200-201, pptd.from cold acetone with water)	200-202	118	1.36	-	-
Crystallized from 80-20 acetone-water	202-203	60	2.7	443	1.73
Crystallized from acetic acid	198-201	62	2.6	446	1.74
STANDARD: T.N.T.		160	1.0	256	1.0

B. Chemical Methods of Purification.

By chemical method of purification is here understood any method which depends on chemical action (hydrolysis, decomposition,etc.) for removing impurities from a material by converting them into soluble or volatile products while leaving the material itself unchanged. It has been seen that the physical methods employed in purifying R.D.X. were not signally successful: a large recovery of R.D.X. on crystallization from a given solvent was accompanied by a low melting point, and vice versa. A chemical method of purification, if successful, would obviate these difficulties. It was suggested by the stability of R.D.X. to a great variety of reagents, recorded in Table 23, Expt. 1 is a control, and shows that with no chemical action a recovery of about 95% may be anticipated. Of the reagents below, only sulphuric acid attacks R.D.X. to any appreciable extent; it appears to attack the impurities more quickly.

In all experiments except Expt. 12 of Table 23 the R.D.X. after being exposed to the action of reagent, was recovered by dilution and filtration. In Expt. 11 it was found that this dilution of sulphuric acid, even with vigorous external cooling, caused the temperature to rise to 50°, so in Expt. 12 it was diluted by the addition of chopped ice.

Table 23

Stability of R.D.X. to Chemical Reagents

	Original R.D.X.			Exposure to Reagent				Recovered R.D.X.		
Expt. No.	Wt. gms.	M.P. °C	Solvent used	Reagent Formula	Vol. (cc)	Temp. °C	Time mins.	Wt. gms.	Recovery %	M.P. °C
1	0.80	200-202	-	Ac_2O	5	20	0	0.76	95	200-202
2	0.80	200-202	-	Ac_2O	5	70	30	0.74	92	201-202
3	0.50	203	-	Ac_2O	5	120	15	0.47	94	-
4	0.50	203	-	Ac_2O(1)	5	84	25	0.45	90	-
5	0.80	200-202	-	AcOH	5	70	30	0.76	95	200-202
6	0.50	203	-	AcOH	5	120	15	0.49	98	-
7	2.0	200-201	AcOH	HCI gas	-	20	120	1.92	96	202-203
8	2.0	200-201	acetone	HCl gas	-	20	120	1.92	96	203-204
9	0.20	188	-	HNO_3(85%)	3	20	-	0.17	85	196-
10	0.10	188	-	HNO_3(100%)	0.5	20	-	0.09	90	195-
11	0.10	188	-	H_2SO_4(96%)	3	-10	15	0.05	50	201-
12	0.10	188	-	H_2SO_4(96%)	3	-10	30	0.04	40	201-
13	0.10	188	-	H_3PO_4	3	20	30	0.09	90	193-

(1) 2 gms. NH_4NO_3 added, mixture stirred during 25 mins. at 84°.

It was found, however, that while the melting point of the crude R.D.X. could be raised by chemical methods, it was not possible except in a few cases to obtain material melting above 200°. Evidently some of the impurities are as stable as R.D.X. to the attack of various reagents. This is to be expected, in the light of the later discovery of H.M.X.: this material is actually more stable than R.D.X., and the only known chemical method of purification of a mixture of the two compounds involves the destruction of R.D.X. by boiling in concentrated ammonia solution (77).

1. The Shawinigan Method of Purification.

The Shawinigan Method of purification received its name from its discovery at the laboratory of the Shawinigan Chemicals Ltd. It was accomplished by adding 20 volumes of water to 52 volumes of the reaction mixture, and boiling vigorously. The solids went almost completely into solution: a small amount of solid remained undissolved and gave a slight cloudiness to the solution. On cooling, R.D.X. melting above 200° crystallized out. The recovery of pure R.D.X. from the crude product was about 90%.

It had been found empirically that if the reaction liquors were further diluted, the solids failed to go completely into solution on boiling. Assuming a complete conversion of active anhydride to acetic acid during the reaction or in subsequent hydrolysis, this gave a calculated 69% acetic acid - 31% water solution. When the molar ratio of reactants was 1 : 2 : 2.6, and the amount of solids (ammonium nitrate and by-products) was taken into account, the concentration of the acetic acid was calculated as 55%. Direct titration showed the concentration to be 53%.

Because of its seeming promise, the Shawinigan Method was thoroughly investigated. On a laboratory scale it failed to give R.D.X. melting above 200°. It has, however, been repeated successfully on a pilot-plant scale at Shawinigan and at Woolwich (78). The reason for this difference caused by the size of the run is not known.

The runs in Table 24 were all made by the Continuous Addition Method, using a molar ratio of paraform: ammonium nitrate: acetic anhydride of 1 : 2 : 2.6. In Run 1, 3.0 gms. of paraform, 16.0 gms. of ammonium nitrate, and 25.0 cc. of acetic anhydride were used; in all other runs, 12.0 gms. of paraform, 64.0 gms. of ammonium nitrate, and 100 cc. of acetic anhydride. Any significant variation in the procedure is recorded in the able.

The results substantiate previous findings on the optimum conditions of reaction, with the exception of the inexplicable falling-off of yield in Run 1.

Table 24

The Shawinigan Method of Purification of R.D.X.

Run	Type of Reagents		Addition		Heating		Boiling	First Crop			Second Crop		
No.	Paraform	Ac_2O	Temp. °C	Time mins.	Temp. °C	Time mins.	Time mins.	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C
1	E.K.	0	65-70	15	-	-	20	1.75	24	180-	-	-	-
2	E.K.	N	65	12	65	8	20	12.2	41.4	183-187	0.80	2.7	185-188
3	E.K.	0	67	10	67	10	20	13.7	46.4	185-192	0.55	1.8	187-192
4	E.K.	0	70	15	67	10	30	13.8	46.5	188-193	1.71	5.8	186-188
5	Dupont	N	70	10	67	10	30	12.0	40.5	187-189	1.88	6.3	183-187
6	E.K.	0	70	15	67	10	5(1)	14.0	47.5	185-190	1.49	5.0	179-182
7	E.K.	0	65	30	67	90	5			197-199			
							20			195-197			
							65			196-197			
							215	13.5	45.6	198-199	0.66	2.2	188-189
8	Dupont	N	75	60	(75	45)	120	11.2	37.7	198-200	1.10	3.7	170-175
					(85	15)							
9	E.K.	0	65	25	65-80	95	5	13.5(2)	45.5	190-192	1.23	4.1	175-180

(1) Reaction mixture diluted and boiled immediately after reaction over.
(2) Crystallized by rapid cooling of mixture after boiling.

It is evident from comparison of Runs 2 and 5 that Dupont paraform gives a slightly higher yield of R.D.X. than E.K. paraform.

2. Other Methods of Purification.

Digestion of crude R.D.X. with various reagents often gave a small increase in melting point, but left it far below 200°.

Table 25

Effect of Various Reagents on the Melting Point of Crude R.D.X.

	Crude R.D.X.		Digestion by Reagent				Treated R.D.X.		
Expt. No.	Wt. gms.	M.P. °C	Reagent	Vol. cc.	Temp. °C	Time mins.	Wt. gms.	Recovery %	M.P. °C
1	0.2	189-191	water	50	100	1200	0.17	85	189-191
2	4.18	188-190	water	100	100	1200	3.90	93.4	195-198
3	2.00	190-192	10% aq.H_2SO_4	20	25	120	1.94	97	194-195
4	2.00	190-192	10% aq.H_2SO_4	20	(100 (25	2) 120)	1.95	97	194-195
5	1.00	190-192	20% aq.H_2SO_4	20	(100 (25	45) 1200)	0.95	95	190-
6	1.00	190-192	1N NaOH aq.	40	25	1200	0.87	87	194-

It is apparent that digestion decomposes some of the impurities contaminating R.D.X. Its failure to remove them completely may be explained by the protection from attack of impurities within particles of R.D.X. Hence, in the experiments of Table 26 the R.D.X. was completely dissolved and subjected to oxidizing and hydrolytic agents.

Table 26

Effect of Reagents on Melting Points of Crude R.D.X. in Solution

Expt. No.	Crude R.D.X. Wt. gms.	Crude R.D.X. M.P. °C	Solvent	Solvent Vol. cc.	Action of Reagent	Vol. cc.	Temp. °C	Time mins.	First Crop Wt. gms.	Recovery %	M.P. °C
1	1.00	190-192	HNO_3	10		-	ca80	-	0.56(1)	56	199-20
2	1.00	190-192	acetone	-	H_2SO_4(16%)(2)	20	25	20	0.77	77	200-20
3	2.00	190-192	acetone	45	H_2SO_4(16%)(2)	70	(70 (25	15) 1200)	1.77	88	195-19
4	1.00	190-192	AcOH	20	$Na_2Cr_2O_7$	-	120	5	0.93(3)	93	196-
5	2.00	190-192	acetone	40	HCl gas	-	25	120	1.85(4)	92	190-19

---

(1) Obtained on cooling without dilution

(2) Caused precipitation of R.D.X. when added

(3) Obtained on dilution to 50% AcOH

(4) Obtained on dilution to 10% acetone

Precipitation from acetone with a 16% sulphuric acid solution (Expt.2: actually, a combination of physical and chemical methods of purification) gives the highest recovery of R.D.X. melting above 200° from the crude product of any method yet found.

VI The Effect of Added Compounds on the McGill Process

It was noted early by Ross and Schiessler (79) that the presence of acetic acid lowers the yield of R.D.X. from the McGill Process. Hence it seemed possible that the comparatively low yield from this process might be due to a progressive inhibition of the reaction by the acetic acid formed from acetic anhydride during its course.

This hypothesis was tested in this and in other laboratories in several ways:

1. Bases were added to neutralize the acetic acid;
2. More powerful anhydrides were added to reform acetic anhydride from acetic acid;
3. Metals were added to remove the acetic acid by reduction (80); and
4. The acetic acid ($B.P._{760}=118^{\circ}$) was removed from the acetic anhydride ($B.P._{760}=140^{\circ}$) by conducting the reaction under reduced pressure (81).

All methods proved ineffective in raising the yield of R.D.X.: the first two are considered in this chapter. The hypothesis itself was proved in error by a more quantitative study of the effect of acetic acid upon the yield of R.D.X. In large amounts the inhibitory effect observed by Ross and Schiessler was confirmed: in small amounts, however, it had no effect. The inhibitory effect of large amounts of acetic acid is not specific: dilution of the acetic anhydride with inert solvents to the same extent causes approximately the same decrease in yield of R.D.X.

The effect of salts on the yield of R.D.X. is variable: it has been explained by Johnson on the basis of their acidic or basic character in acetic anhydride (82). This explains the increased yield obtained with such compounds as **boron trifluoride** and zinc nitrate (which are electron acceptors, or acidic (83)). Their action is more complex than this, however. Aluminium chloride and other acids decrease the yield of R.D.X. (84). This is probably due to the presence of chloride ion. In large amounts, sodium chloride causes a violent kick-off, sodium fluoride a great amount of gassing, and in both cases no R.D.X. is obtained. Bromides and iodides have been found to have a similar inhibitory effect (85).

A. The Effect of Bases.

The effect of the addition to the McGill Process of pyridine, triethylamine, and urea is shown in Table 27. It should be noticed that bases which neutralize acetic acid by the formation of water are inapplicable, for they can react with acetic anhydride:

$$\begin{array}{l} MOH + AcOH \longrightarrow MOAc + H_2O \\ Ac_2O + H_2O \longrightarrow 2AcOH \\ \hline MOH + Ac_2O \longrightarrow MOAc + AcOH \end{array}$$

The use of the common inorganic bases (hydroxides, oxides, carbonates, etc.) is thus excluded.

In Runs 1 and 2, 3.0 gms. (0.10 mole) of paraform, 16.0 gms. (0.20 mole) of ammonium nitrate, and 29 cc. (0.30 mole) of acetic anhydride were used; in Runs 3, 4 and 5, 0.75 gms. (0.025 mole) of paraform, 4.0 gms. (0.050 mole) of ammonium nitrate, and 6.25 cc. (0.066 mole) of acetic anhydride.

Table 27

Effect of Bases on Yield of R.D.X.

Run No.	Base		Addition Method(1)	Temp. °C	Time mins.	Time of Addn. of Base mins.	Product		
	Name	Amount Moles					Wt. gms.	Yield %	M.P. °C
1	pyridine	0.8	TAM	105	20	0	4 (2)	-	-
2	pyridine	0.8	TAM	90-95	15	3-4	0.29	-	(181-185) (165-175)
3	triethylamine	0.2	TAM	70	10	10	0.07	4	177-179
4	triethylamine	0.13	TAM	70	15	0	trace	-	-
5	urea	0.037	CAM	65	20	5	0.79(3)		245

(1) TAM = Total Addition Method
CAM = Continuous Addition Method
(2) No R.D.X. on crystallization from acetone-water
(3) Did not deflagrate when heated

It is evident that R.D.X. is formed only in an acid medium in the McGill Process.

B. The Effect of Anhydrides

Phosphorus pentoxide and thionyl chloride are both stronger anhydrides than acetic anhydride, and so can reform it from acetic acid.

Five gms. of phosphorus pentoxide was added to 3.0 gms. of paraform, 16.0 gms. of ammonium nitrate, and 29 cc. of acetic anhydride, and the reaction was conducted following the Total Addition Method (page 32). A kick-off occurred at 75°. The product, isolated and purified by method AB (page 33), weighed 2.0 gms. (27% yield), m.p. 194-197. It was dirty-brown in colour. There had thus been no increase in yield.

In the run testing the effect of thionyl chloride, 3.0 gms. (0.10 mole) of paraform, 16.0 gms. (0.20 mole) of ammonium nitrate and

5.0 cc. (0.05 mole) (instead of the usual 25 cc.) of acetic anhydride were used. One-fifth of the solids was added to the acetic anhydride with stirring at 65°: the rest of the solids was added simultaneously with 16.0 cc. (0.22 mole) of thionyl chloride over a period of 15 mins. On dilution with water only 0.28 gms. (3.8% yield), m.p. 189-193, of solid was obtained.

The failure of thionyl chloride as a dehydrating agent in the McGill Process is without doubt related to the inhibiting effect of chlorides.

C. The Effect of Acetic Acid

The effect of acetic acid on the yield of R.D.X. was investigated by adding varying amounts to 0.75 gms. (0.025 mole) of paraform, 4.0 gms. (0.050 mole) of ammonium nitrate, and 6.25 cc. (0.066 mole) of acetic anhydride. The stirred reaction mixture was then heated to 70° for ten minutes. The product was worked up in the same fashion as runs of a similar size in Chap.IV Section A (page 35).

Table 28

Effect of Acetic Acid on Yield of R.D.X.
(by the Total Addition Method).

Run No.	Acetic Acid added gms.	Acetic Acid added moles	Acetic Acid formed in Reaction moles	Acetic Acid at End of Reaction moles	R.D.X. Wt. gms.	R.D.X. Yield %
1	0	0	0.132	0.132	0.65	35
2	2	0.033	0.132	0.165	0.65	35
3	4	0.066	0.132	0.198	0.63	34
4	4	0.066	0.132	0.198	0.63	34
5	8	0.133	0.132	0.265	0.58	31
6	16	0.266	0.132	0.398	0.25	13.5

Effect of the Addition of Acetic Acid on the Yield of R.D.X.

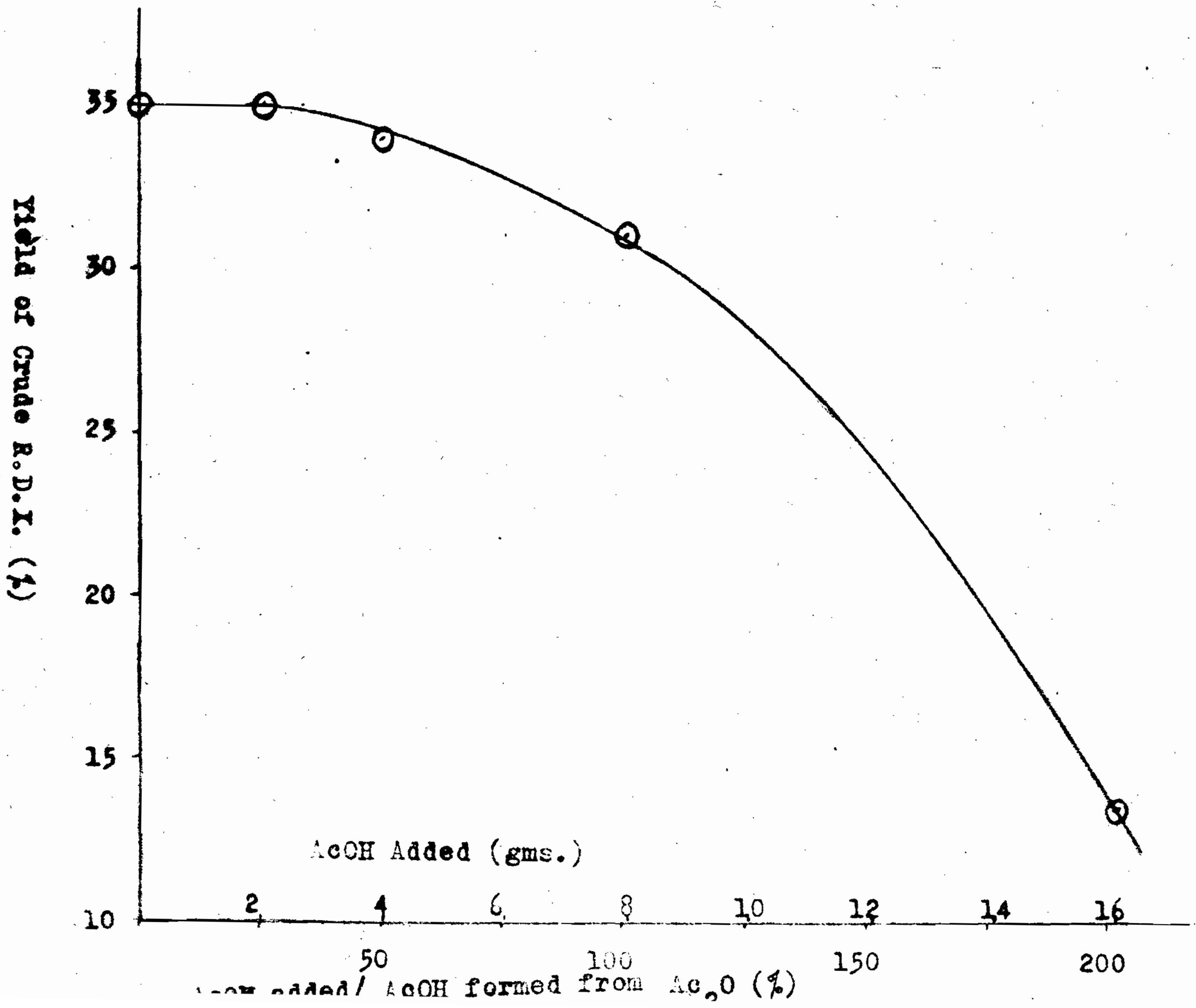


Figure 2

The amount of acetic acid formed in the reaction is calculated on the assumption of a complete conversion of acetic anhydride. The results are plotted in Fig.2 (Page 74).

D. The Effect of Diluents

The runs recorded in Table 29 were made with 3.0 gms.(0.10)mole) of paraform, 16.0 gms. (0.20 mole) of ammonium nitrate, 25 cc. (0.26 mole) of acetic anhydride, and 50 cc. of diluent. Run 3 was done under reflux because of the volatility of the diluent. In all runs the reaction mixture was diluted with 400 cc. of water and shaken well: the carbon tetrachloride and benzene formed a second liquid phase, but since R.D.X. is practically insoluble in these solvents (58) it could be filtered off in the usual fashion.

Table 29

Effect of Diluents on Yield of R.D.X. from McGill Process

Run No.	Diluent	Reaction Method(1)	Addition Temp. °C	Addition Time mins.	Heating Temp. °C	Heating Time mins.	Wt. gms.	Yield %	M.P. °C
1	Ethyl Acetate	CAM	63(2)	-	-	-	0.80	11	187-192
2	Benzene	CAM	65-70	5	65	25	1.59	21	(too sticky)
3	Acetone	TAM	-	-	62-70	60	-	-	-
4	Carbon tetrachloride	TAM	-	-	65-70	60	1.61	22	(too sticky)

(1) CAM = Continuous Addition Method; TAM = Total Addition Method

(2) After 4 mins. a violent kick-off caused temperature to rise to 90°

From Fig. 2 (Page 74) it can be estimated that acetic anhydride diluted with twice its volume of acetic acid gives an 18% yield of R.D.X., comparable to the yields of 21% and 22% obtained with benzene and carbon tetrachloride as diluents. Ethyl acetate and acetone are more reactive compounds, and it is possible that in decreasing the yield as drastically as they do they are not functioning solely as inert diluents.

E. The Effect of Salts

The effect of zinc nitrate hexahydrate on the McGill Process is shown in Table 30. The increased yields confirm the work of Johnson (82). In all runs, the Continuous Addition Method was used: 12.0 gms. (0.4 mole) of paraform and 64.0 gms. (0.8 mole) of ammonium nitrate were added to 100 cc. (1.06 mole) of acetic anhydride containing 1.0 gm. of the zinc salt. In the first two runs temperature control was poor, and the reaction mixture momentarily heated up to 80° (Run 1) and 90° (Run 2).

Table 30

Effect of Zinc Nitrate Hexahydrate on Yields of R.D.X.

Run No.	Addition Temp. °C	Addition Time mins	Heating Temp. °C	Heating Time mins	First Crop Wt. gms.	First Crop Yield %	First Crop M.P. °C	Second Crop Wt. gms.	Second Crop Yield %	Second Crop M.P. °C
1	62-65	25	-	-	16.3	55	179-182			
2	62-63	22	70-60	10	17.3	58.4	184-187			
3	67	17	67	10	14.3(1)	49.1	190-193	3.1	10.5	150-160

(1) Obtained on filtering undiluted reaction mixture, and then washing it with water. Dilution of the filtrate gave the second crop.

The possibility that part of the increased yield obtained with zinc nitrate might be due to contamination with zinc salts was disproved by

1. Burning 5 gms. of the R.D.X. of Run 2 under an iron crucible: no trace of white zinc oxide was noted; and

2. Decomposing 5 gms. of R.D.X. of Run 2 in 50 cc. of conc. sulphuric acid. The solution, on being neutralized with sodium carbonate and buffered with ammonium sulphate and acetate, failed to precipitate

white zinc sulphide when saturated with hydrogen sulphide. Instead 0.02 gms. of a black precipitate was obtained. The metals contaminating R.D.X. which give rise to this precipitate probably come from the ammonium nitrate used. This salt leaves a small inorganic residue when decomposed by heating on a spatula.

The effect of sodium fluoride and chloride was observed on runs made with 12.0 gms. (0.40 mole) of R. & H. paraform, 40.0 gms. (0.50 mole) of ammonium nitrate, and 100 cc. (1.06) mole of acetic anhydride. In each case 0.40 mole of the sodium halide (17 gms. of NaF; 23 gms. of NaCl) was used. The paraform and ammonium nitrate were added in 15 mins. to the acetic anhydride and salt at 70°: the mixture was then stirred a further 30 mins. at this temperature. With sodium fluoride, vigorous frothing but little heating took place; with sodium chloride, on the other hand, heating was so pronounced that a kick-off could not be avoided. In neither case was any R.D.X. obtained.

VII Attempted Modifications of the McGill Process

A. Attempts to Substitute for the Acetic Anhydride

The attempts of Ross and Schiessler to form R.D.X. from paraform and ammonium nitrate in the presence of dehydrating agents other than acetic anhydride have already been mentioned (page 3). All the dehydrating agents which they employed were weaker than acetic anhydride.

In this section are described further attempts to substitute for the acetic anhydride. Phosphorus pentoxide, maleic anhydride, acetyl chloride, acetyl bromide, and thionyl chloride were tried, but all proved unsuccessful.

The failure of other dehydrating agents to replace acetic anhydride caused doubt in some quarters as to its function as a dehydrating agent (87), and it was thought that possibly it was acting as an acetylating agent in the McGill Process. There is no evidence in support of this latter hypothesis. It seems possible that the specific action of acetic anhydride is due to its physical properties. The decreased yield on diluting it with inert solvents, and the failure of other anhydrides would then have a common cause. This view is strengthened by the recent discovery that R.D.X. can be prepared using propionic anhydride (88).

1. Phosphorus Pentoxide.

In all runs made with this reagent, 9.4 gms. (0.06 mole) of it was used with 3.0 gms. (0.10 mole) of paraform and 8.0 gms. (0.10) mole of ammonium nitrate.

On attempting to make a melt of the three solids by gentle heating, an explosive reaction took place which yielded only a small amount of black solid.

Accordingly, in the following three runs the phosphorus pentoxide was added to a stirred suspension of paraform and ammonium nitrate in an inert diluent. The mixture was heated for ten minutes, and then poured into a large excess of water and stirred to dissolve the phosphorus pentoxide.

Table 31

Attempt to Form R.D.X. Using Phosphorus Pentoxide

Run No.	Diluent	Temp. °C	M.P. of Solid Recovered °C	Remarks
1	chloroform	10	125-130	Solid Burned like Paraform
2	ethyl acetate	60-70	125-130	" " "
3	toluene	90	-	

The failure to obtain R.D.X. may be explained by the physical properties of phosphorus pentoxide. It is insoluble in organic solvents, and so tended to form a gummy mass.

2. Maleic Anhydride.

Two gms. (0.025 mole) of ammonium nitrate, 0.75 gms. (0.025 mole) of paraform, and 5 gms. (0.05 mole) of maleic anhydride (m.p.50-52°) were melted together and stirred for 50 mins. at 65°. No water-insoluble material was obtained on pouring the mixture into water. The same result was obtained in similar run to which 0.4 gms. of ammonium acetate was added.

3. Acetyl Chloride

A mixture of 0.75 gms. (0.025 mole) of paraform, 4.0 gms. (0.050 mole) of ammonium nitrate, and 4.7 cc. (0.066 mole) of acetyl chloride was stirred for 20 mins. at 40°. The mixture on dilution with water yielded

0.62 gms. of solid, m.p. 140°. This was shown to be paraform by its failure to deflagrate and its insolubility in acetone.

On running the reaction for 2 hours, 0.01 gms. of paraform but no R.D.X. was obtained on dilution with water,

4. Acetyl Bromide.

To 0.75 gms. of paraform and 4.0 gms. of ammonium nitrate, 5.4 cc. (0.066 mole) of acetyl bromide was added dropwise with stirring. A vigorous reaction ensued, but no solid was obtained on dilution with water.

5. Thionyl Chloride.

Three runs were made using 0.75 gms. of paraform, 4.0 gms. of ammonium nitrate, and 3.53 cc. (0.050 mole) of thionyl chloride. In the first run thionyl chloride was added to the stirred solids; in the second run to a stirred suspension of the solids in 10 cc. of benzene at 70°; and in the third run to a stirred suspension of the solids in 5 cc. of acetic acid at 65°. On dilution only the second run yielded any solid. This proved to be paraform.

B. Attempts to Substitute for Paraform.

Ross and Schiessler attempted to form 2,4,6-trimethyl-1,3,5-trinitro-sym-hexahydrotriazine by substituting paracetaldehyde for paraform in the McGill Process. They did not obtain any water-insoluble compound (89).

Since then numerous attempts have been made to substitute other aldehydes for paraform in the McGill Process, but always without success (90).

Use of the Fischer-Hirschfelder atomic models shows that theoretically almost any aldehyde, but no ketons , can form cyclotrimethylenetrinitramine derivatives, so this behaviour cannot be due to steric hindrance.

It has been suggested (91) that rather it is due to a specific chemical or stereochemical property of the methylene group. Formaldehyde is unique among the aldehydes in its tendency to polymerize.

On these grounds, it might be expected that trichloracetaldehyde, which like formaldehyde forms stable polymers, would react in similar fashion with ammonium nitrate in acetic anhydride. So far, however, there is no evidence that it forms a cyclotrimethylenetrinitramine derivative (92).

1. Acetaldehyde.

Gaseous acetaldehyde (0.4 moles), generated by warming 17.6 gms. of paraldehyde with a drop of sulphuric acid, was passed into a stirred suspension of 32 gms. (0.4 mole) of ammonium nitrate in 100 cc. (1.06 mole) of acetic anhydride, heated to 70°. In 20 mins. addition was complete. No solid was obtained on pouring the reaction mixture into a large excess of water.

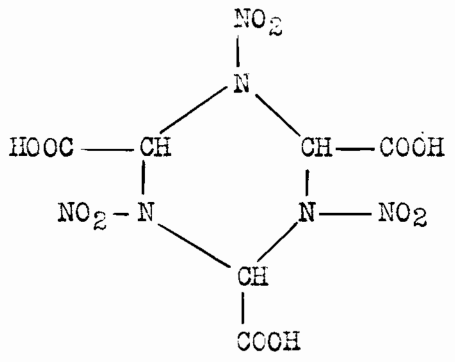
2. Benzaldehyde.

A mixture of 10.6 gms. (0.1 mole) of benzaldehyde, 8.0 gms. (0.1 mole) of ammonium nitrate, and 25 cc. (0.26 mole) of acetic anhydride was stirred for 10 mins. at 70°. At first there was no evidence of any reaction: then a violent kick-off occurred,

When the mixture was poured into water, a yellow oil but no solid separated.

3. Glyoxylic Acid.

If glyoxylic acid reacted like formaldehyde with ammonium nitrate in acetic anhydride, 2,4,6-tricarboxy-1,3,5-trinito-sym-hexahydro-triazine would be formed (LXVI):



LXVI

Such a compound might be expected to decarboxylate with great ease to give R.D.X.

That R.D.X. is not formed was shown in the first run. Eight gms. (0.1 mole) of ammonium nitrate, 7.4 gms. (0.1 mole) of glyoxylic acid, and 18.8 cc. (0.2 mole) of acetic anhydride were heated with stirring to 75°. In a short time a violent kick-off occurred, and a clear yellow solution formed. After the mixture had been heated for ten minutes it was poured into water. No solid separated out.

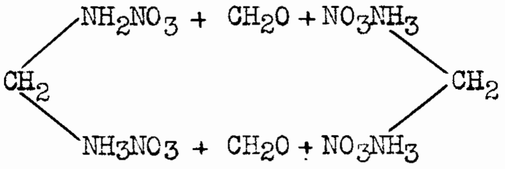
The tricarboxy- derivative, if formed, would be expected to be soluble in water. Hence in a second run, made in identical fashion with the first, the reaction mixture was not diluted with water. Several crops of solid were obtained by cooling and by evaporation of the acetic acid or anhydride under reduced pressure, but all appeared to be ammonium nitrate, from the m.p. (167-168°) and the manner of decomposing when heated on a spatula.

C. Attempts to Substitute for Ammonium Nitrate.

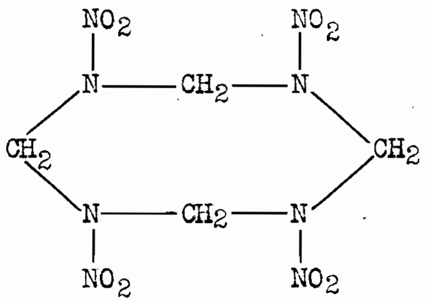
Studies of the McGill Process in which ammonium nitrate is replaced by another compound have so far proved most promising.

Mixtures of sodium nitrate with ammonium chloride and ammonium acetate failed to react with paraform in acetic anhydride to give R.D.X.. This is probably due to the inhibitory effect of chlorides (page 77) and acetates (82).

Methylenediamine dinitrate (LXVII), on the other hand, gave R.D.X., rather than the expected H.M.X. (LXVIII):



LXVII LXVII



LXVIII

However, the mechanism of this reaction is in some doubt because of the instability of methylenediamine dinitrate. It was found to break down in acetic anhydride in the absence of paraform to give R.D.X. and ammonium nitrate. This reaction occurred at temperatures as low as 40°.

1. Ammonium Chloride and Sodium Nitrate.

A mixture of 0.75 gms. (0.025 mole) of paraform, 4.2 gms. (0.050 mole) of finely pulverized sodium nitrate, 2.6 gms. (0.050 mole) of ammonium chloride, and 6.25 cc. (0.066 mole) of acetic anhydride was stirred for 15 mins. at 70°. After heating for 5 mins. a vigorous kick-off occurred.

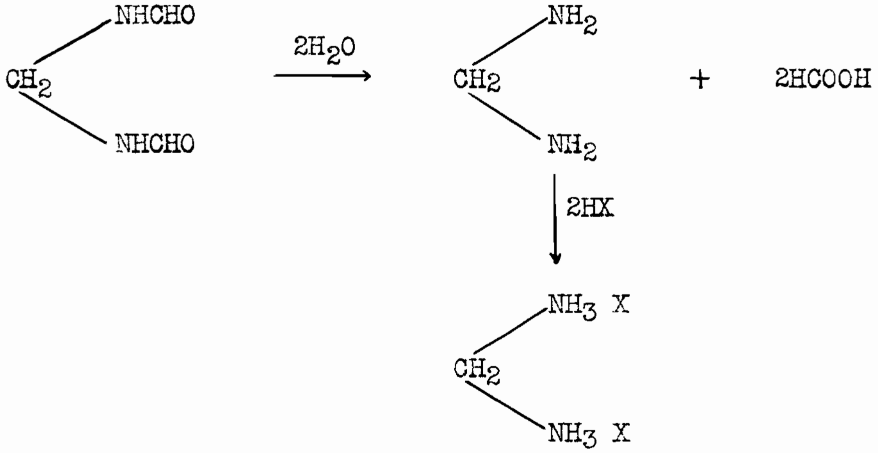
The reaction mixture on dilution with water precipitated no R.D.X.

2. Ammonium Acetate and Sodium Nitrate.

A mixture of 0.75 gms. (0.025 mole) of paraform, 2.1 gms. (0.025 mole) of finely pulverized sodium nitrate, 1.9 gms. (0.025 mole) of ammonium acetate, and 6.25 cc. (0.066 mole) of acetic anhydride was heated to 70° for 30 mins. with stirring. A slight kick-off occurred. When the reaction mixture was poured into water, 0.04 gms. of paraform was recovered.

3. Methylenediamine Dinitrate*.

The preparation of methylenediamine dinitrate is reported only once in the literature in an article by Knudsen (93). He prepared salts of methylenediamine by hydrolysis of methylene diformamide with aqueous solutions of hydrochloric, sulphuric and nitric acids:



Knudsen's description of methylenediamine dinitrate is meagre. It was formed by treatment of methylene diformamide with strong nitric acid at 12°. It crystallized in prisms. On being heated on a spatula these melted, then deflagrated. The composition of the compound was

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* The work on methylenediamine dinitrate was conceived and executed in collaboration with Miss Joan Romeyn. Her assent to its inclusion in this thesis is gratefully acknowledged.

checked by analysis for nitrogen.

The dihydrochloride hydrolyzed in water to give formaldehyde (93).

Methylenediformamide was prepared by heating together paraform (1 mole) and formamide (2 moles) in a round-bottom flask fitted with an air-condenser, following Knudsen's method. A vigorous reaction similar to the kick-off in the McGill Process, first occurred. When it had subsided the mixture was heated to maintain gentle ebullition for 4½ hours. An odour of formaldehyde was noticeable in the kick-off; later, the odour of amines became very strong.

On cooling the mixture in snow and salt, the first crop of methylenediformamide came down. It was filtered off, sucked as dry as possible, washed with a little ethanol and ether, and air-dried.

The excess of liquid in the filtrate was distilled off to the appearance of a reddish-brown colour. On cooling, a second crop of somewhat more impure methylenediformamide was obtained.

Knudsen claimed a yield of 38% of a crude product (m.p.142-143°), which after washing needed no further purification. Our yields were lower than his, and our product less pure (Table 32, page 86).

Because of the resemblance of this reaction in certain features to the McGill Process, it was studied in an attempt to improve the yield (Table 32). Actually, Knudsen's original method (Run 1) gave the highest yield.

An excess of paraform (Runs 2 and 3) decreased the yield of methylenediformamide and gave rise to a brown gum, possibly a polymer formed from N-methylolformamide. Stirring with continuous addition to avoid a kick-off (Run 4) and with a kick-off (Run 5) offered no advantages. The from pyridine gave methylenediformamide melting at 142-143°.

Methylenediamine dinitrate was prepared by dissolving methylenediformamide in 70% nitric acid with stirring or swirling. Only the theoretical amount of nitric acid was required, an excess actually lowering the yield (Run 4, Table 33). The optimum temperature of the reaction appeared to be somewhat above 25°, not 12° as Knudsen claimed (Run 3). After a varying length of time long needles of methylenediamine dinitrate crystallized from the solution. This solid was filtered off and air dried. Dilution of the filtrate with ethanol precipitated a second, less pure crop.

To obtain reasonably pure methylenediamine dinitrate, it was necessary to use pure methylenediformamide (Runs 5 and 6).

Table 33

The Preparation of Methylenediamine Dinitrate

	$CH_2(NHCHO)_2$							First Crop			Second Crop		
Run No.	gms.	moles	M.P. °C	70% cc.	HNO_3 moles	Temp. °C	Time hrs.	Wt. gms.	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C
1	5.0	0.05	132-135	8	0.13	20	24	4.2	50	92-94	-	-	-
2	17.0	0.17	137-139	27	0.44	15	-	13.0	44.5	88-90	4.0	14	-
3	7.0	0.07	132-135	11	0.18	25-30	24	8.0	74	91-92	-	-	-
4	14.8	0.15	126-	37	0.60	8-10	-	7.7	31	93	5.9	24	90-93
5	12.6	0.13	142-143	20	0.34	3- 5	48	11.7	50.5	95-97	1.3	6	-
6	21.	0.21	142-143	33	0.52	25-30	3	15.8	45	96-97	3.7	10.5	92-93

The first crop of Run 2 was analyzed for carbon by the dichromate method as described in R.D.X. specifications (94).

Calc'd. for $CH_2(NH_3NO_3)_2$: C, 6.97. Found, 7.13, 7.03

The outstanding property of methylenediamine dinitrate was its instability. Methylenediamine salts are decomposed by water (93), and so its instability in hydroxylic solvents such as ethanol was not unexpected. The decomposition in acetic anhydride was more surprising. Even on standing in the dry state the salt decomposed. Thus the first crop (m.p. 95-97°) of Run 5 (Table 33), after standing for six weeks in a cork-stoppered bottle melted between 115° and 125°.

Because of its instability, no method of purifying the compound was found. It dissolved in ethanol, acetic acid, 70% nitric acid, dioxane, acetylacetone, ethyl carbonate, and pyridine, but could not be recovered. It had little or no solubility in acetone, ether, ligroin, and chloroform. However, the first crop of Run 6 (Table 33) appeared to be reasonably pure from the sharpness of the melting point.

Except in acetic anhydride, methylenediamine dinitrate failed to yield R.D.X.. The procedures tried were: heating the compound in water and in acetic acid; heating it with paraform in acetic acid, and in acetic acid containing some anhydride; reacting it with sodium nitrite in acetic acid and in acetic anhydride; and fusing it with and without paraform.

When a mixture of methylenediamine dinitrate and acetic anhydride was heated to 70° with stirring, (Runs 1-3, Table 34) there was at first no sight of reaction. After a time a slight effervescence was noticed, and cooling was needed to maintain a temperature of 70°.

When the mixture was poured into water a gummy precipitate formed. This dissolved on boiling, and on cooling a white solid precipitated. It was shown to be R.D.X. by

1. Analysis for carbon by the dichromate method (94). (R.D.X. of Run 1).

For $C_3H_6N_6O_6$: Carbon calcd. 16.2%
found 16.4%

2. Crystallization (R.D.X.of Run 1) from 70% nitric acid. A solid was obtained, m.p. 195-199, which deflagrated like R.D.X. when heated on a spatula.

When the reaction mixture was not diluted with water, but was cooled and filtered, a mixture of ammonium nitrate and R.D.X. was obtained (Run 2), which partially melted at 163°, and became finally clear at 190°. The presence of R.D.X. was shown by washing one part of the precipitate with water to remove the soluble solids. The insoluble residue melted at 198-202°.

By washing another part of the residue with cold acetone, in which ammonium nitrate is only slightly soluble,the R.D.X. was extracted. It was precipitated from the acetone solution with water, and filtered. m.p.ca 200°. The residue melted at 166°; mixed m.p. with ammonium nitrate 165°. It was evidently ammonium nitrate (m.p. 169.6°).

The decomposition of methylenediamine dinitrate to R.D.X. and ammonium nitrate took place even at 40°, although at this temperature a rather long induction period is indicated (Runs 4 and 5, Table 34).

Methylenediamine dinitrate reacted with paraform in acetic anhydride to give R.D.X. (Table 35). The runs in which this reaction was carried out were conducted by the Continuous Addition Method (page 45),

Table 34

Reaction of Methylenediamine Dinitrate in Acetic Anhydride

Run No.	Reactants $CH_2(NH_3NO_3)_2$			Reactants Ac_2O		Addition		Heating		Products R.D.X.			Products NH_4NO_3			Products $CH_2(NH_3NO_3)_2$		
	gms.	moles	M.P. °C	cc.	moles	Temp. °C	Time mins.	Temp. °C	Time mins.	Wt. gms.	Yield(1) %	M.P. °C	Wt. gms.	Yield(1) %	M.P. °C	Wt. gms.	Recovery %	M.P. °C
1	1.8	0.010	88-90	5	0.05	-	-	70	20	0.23	15	187-192						
2	3.7	0.020	88-90	8.7	0.09	70	10	70	15	0.3	21	198-202	1.5	77	166			
3	8	0.046	96-97	17.4	0.18	70	15	70	15	1.7	25	194-199	2.7	73	-			
4	2.5	0.014	93	6	0.06			40	60	-	-	-	-	-	-	1.9	75	93-9
5	2.5	0.014	90-93	6	0.06	40	20	40	180	0.3	21	198-201	1.2	70	156-168			

(1) These yields are calculated on the basis of the equation:

$$3CH_2(NH_3NO_3)_2 \longrightarrow (CH_2{=}N{-}NO_2)_3 + 3\ NH_4NO_3$$

Table 35

Reaction of Methylenediamine Dinitrate with Paraform in Acetic Anhydride

Run No.	$CH_2(NH_3NO_3)_2$			**Paraform (R&H)**		Ac_2O		Addition		Heating		R.D.X.		
	gms.	moles	M.P. °C	gms.	moles	cc.	moles	Temp. °C	Time mins.	Temp. °C	Time mins	Wt. gms.	Yield(1) %	M.P. °C
1	1.7	0.010	92-94	0.3	0.010	7.5	0.08	70	40	70	20	0.4	27	179-
2	8.6	0.050	88-90	1.5	0.050	14.1	0.15	90	30	90	10	2.6	35	190-199
3	1.8(2)	0.010	88-90	0.3	0.010	5	0.05	70	5	70	10	1.0	62	187-191
4	4.3	0.025	88-90	0.75	0.025	10.1	0.11	70	25	70	20	1.8	50	192-200
5	2.5	0.014	88-90	0.44	0.014	5.9	0.06	70	10	70	13	1.1	52	189-197
6	2.5	0.014	88-90	0.44	0.014	6	0.06	40	20	40	180	1.1	52	192-200
7	8.	0.046	96-97	1.4	0.047	17.4	0.18	70	20	70	8	3.7	54	190-197

(1) Calculated on the basis of the equation:

$$3CH_2(NH_3NO_3)_2 + 3CH_2O \longrightarrow 2(CH_2{=}N{-}NO_2)_3$$

(2) This figure is only approximate

with the exception of Runs 3 and 5. In these the methylenediamine dinitrate and acetic anhydride were heated to 70° for 20 mins. before addition of the paraform. This modification does not increase the yield appreciably. After reaction, the mixture was poured into a large excess of water and boiled.

The identity of the product obtained in Run 1 was established by crystallizing it from 2 cc. of 61% nitric acid. A solid melting at 190° was obtained. The mixed m.p. with R.D.X. (m.p.200°) was 193°.

In Run 2 the presence of H.M.X. was demonstrated. The crude product on crystallization from 70% nitric acid gave two crops: 1.8 gms. (24% yield), m.p. 193-198°, and 0.3 gms. (4% yield), m.p. 194-235°. This latter melting point corresponds to a 65% H.M.X.-35% R.D.X. mixture (95). The second crop was boiled under reflux with 30 cc. of conc. ammonia solution for 3 hours: 0.11 gms. (1.5% yield) of a solid m.p. 270-272° (uncorr.) was obtained. The mixed m.p. with an authentic sample of H.M.X. was 270-272° (uncorr.).

VIII. Side-Reactions in the McGill Process

A. The Fate of the Ammonium Nitrate.

No attempts have been made to discover the fate of the ammonium nitrate used in the McGill Process since some early work of Ross and Schiessler (96). This work was done on reactions in which a kick-off had occurred, and so part of the ammonium nitrate was lost as nitrogen or nitrous oxide.

Later, a careful study of the gases evolved during the reaction was made by A. Gillies (97). The reaction was carried out by the Total Addition Method, but since the temperature was 60° no kick-off occurred. Only a small amount of gas was evolved, at a constant rate independent of the rate of formation of R.D.X. Analysis showed the gas to be made up of 95% nitrous oxide and a trace of carbon dioxide. The amount of the former gas evolved in one hour corresponded to a decomposition of only 2% of the ammonium nitrate present.

It is evident that if a kick-off is avoided the proportion of the reactants forming gaseous products is negligible.

The ammonium nitrate not consumed in the formation of R.D.X. can be accounted for in three possible ways:

1. it can react with acetic anhydride;
2. it can react with paraform; or
3. it can remain unreacted, part of it dissolving in the reaction liquor.

It was shown that the first of these possibilities could be excluded. When ammonium nitrate was heated in acetic anhydride for 15 mins. at 70° with stirring, no change was noted, and the melting point of the recovered ammonium nitrate was unaltered.

The other possibilities will now be considered.

1. The Solubility of Ammonium Nitrate in the Reaction Liquor*

Davidson and Greer (98) found the solubility of ammonium nitrate in acetic acid at 27° to be 0.3916 mole percent, or 0.535 gms. per 100 gms. of acetic acid.

The solubility of ammonium nitrate in acetic anhydride is not reportedin the literature. It was found, using glacial acetic acid and Type N acetic anhydride that its solubility in 100 gms. of solvent at room temperature was as follows:

in acetic acid, 1.79 gms.;
in 50-50 acetic acid-acetic anhydride, 0.66 gms.;
in acetic anhydride, 0.11 gms.

These values are all too high, because of the presence of water in the acetic acid and of acetic acid in the anhydride. They are of comparative value, however, and show that the solubility is far less in acetic anhydride than in acetic acid.

Since the composition of the reaction liquor is not known, the solubility of the ammonium nitrate in it cannot be determined accurately. The most recent work indicates an anhydride content of about 15% (99). The solubility in such solvent could not be greatly different from that in acetic acid, 0.5 gms./100 gms. of solvent. Since the reaction of 12.0 gms. of paraform and 64.0 gms. of ammonium nitrate

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* In this Thesis, the liquid obtained after filtering off the solids from a cooled, undiluted reaction mixture is referred to as the "reaction liquor".

in 100 cc. of acetic anhydride yields about 145 cc. of reaction liquor, the amount of dissolved ammonium nitrate at room temperature is about 0.7 gm. This is rounded off to 1.0 gm. in subsequent calculations.

2. The Recovery of Ammonium Nitrate in the McGill Process.

The runs in which the recovery of unreacted ammonium nitrate was studied were carried out at 70°, the first three Runs by the Continuous Addition Method and the fourth by the Reversed Addition Method. All relevant details of the Runs are furnished in Table 36.

At the end of the reaction, the mixture was not diluted with water. Instead, it was cooled, and allowed to stand. The solid precipitating out was filtered off in glass wool (Runs 1 and 2) or hardened filtered paper (Runs 3 and 4). It was then dried in the oven at 90° and weighed as "Total Solids".

By washing the Total Solids with water, the soluble material was dissolved. The R.D.X. was then filtered off, dried and weighed (First Crop). The difference in weight between the Total Solids and the R.D.X. gave the weight of Water-Soluble Solids.

Dilution with water of the filtrate from the Total Solids gave the Second Crop of R.D.X.

Table 36

Reaction Conditions of Ammonium Nitrate Recovery Runs

	Amounts of Reactants						First Crop R.D.X.				Second Crop R.D.X.		
Run No.	$(CH_2O)_x$ gms.	NH_4NO_3 gms.	Ac_2O cc.	Addition Time mins.	Heating Time mins.	Total Solids gms.	Wt. gms.	Yield %	M.P. °C	Water-Sol. Solids gms.	Wt. gms.	Yield %	M.P. °C
1(1)	12.0	64.0	100	17	10	45.2	14.3	49.1	190-193	30.9	3.1	10.5	150-160
2	12.0	64.0	100	15	10	41.3	12.4	42	187-188	28.9	2.8	9.5	160-165
3	124.4	400.	1000	50	20	244	159	51.6	181-183	84.	12.9	4.2	187-196
4(2)	12.5	40.0	100	60	20	14.9	0.25	0.8	187-197	14.6	3.0	9.7	189-193

(1) 1 gm. of zinc nitrate hexahydrate used as a catalyst
(2) R. & H. paraform, Type N acetic anhydride used

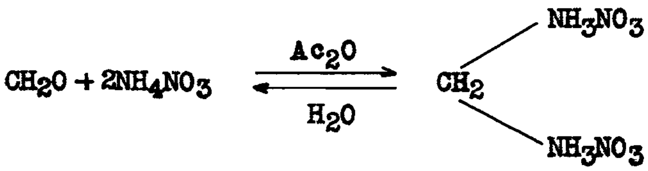
By evaporation of the filtrate containing the Water-Soluble Solids, and then cooling, crops of crystals were obtained. In Run 4 this procedure was varied by evaporating to dryness, taking up the residue in boiling ethanol, and obtaining one crop on cooling. Further crops were thrown down by the addition of ether to the filtrate. The recovery of ammonium nitrate from these solutions is shown in Table 37.

Table 37

Recovery of Ammonium Nitrate from Water-Soluble Solids of McGill Process

Run No.	Water-Sol. Solids gms.	Crop 1		Crop 2		Crop 3		Crop 4		Total Recovery	
		Wt. gms.	M.P. °C	Wt. gms.	M.P. °C	Wt. gms.	M.P. °C	Wt. gms.	M.P. °C	Wt. gms.	%
2	28.9	18.7	165	6.2	140					24.9	86
3	84	33.6	167-169	6.8	167-169	29.6	165-167	7.1	-	77.1	92
4	14.6	7.4	168-169	2.3	166-169	2.6	168-169	0.8	166-169	13.1	90

From the recovery of ammonium nitrate, it appears that most of the Water-Soluble Solid was composed of this compound. There is the possibility that some of it was composed of soluble compounds like methylenediamine dinitrate, which can be formed during the reaction:



$$CH_2O + 2NH_4NO_3 \underset{H_2O}{\overset{Ac_2O}{\rightleftarrows}} CH_2(NH_3NO_3)_2$$

The hydrolysis of this compound would proceed readily on evaporating the aqueous solution, and the loss in weight caused by the elimination of the formaldehyde would amount only to 7%. Actually, the difference between the weight of Water-Soluble Solid and of the ammonium nitrate was always greater than this, although due in part to the usual losses in manipulation. Furthermore, the odour of formaldehyde was noted on evaporating the aqueous solution.

However, until quantitative analysis has shown the presence of appreciable amounts of formaldehyde in the aqueous extract, this view is unproven; and so the Water-Soluble Solid will be regarded as ammonium nitrate.

3. The Reaction of Ammonium Nitrate with Paraform to Give By-Products.

Since no by-products of the McGill Process have yet been isolated, their nature at the moment necessarily remains speculative. However, it is possible to gain an estimation of their over-all composition by drawing up a balance-sheet for the fate of the reactants in the McGill Process.

It is first necessary to discuss the fate of the formaldehyde not consumed to form R.D.X. Work in this laboratory (100) has shown that only a negligible amount of formaldehyde (0.1-0.2% of the total amount used) is present in the crude R.D.X., whence it may be removed by steam-distillation. (This may actually come from the hydrolysis of compounds containing formaldehyde during steam-distillation). Hence the formaldehyde not forming R.D.X. is in the reaction liquor at the end of the reaction. There it may exist as free formaldehyde or as formaldehyde in by-products. Because of the reactivity of formaldehyde and because of the absence of any noticeable odour of it in the fresh reaction-liquor, it is assumed to have reacted to form by-products. After the reaction liquor has been allowed to stand for some time, the odour of formaldehyde becomes noticeable.(101)

Table 38

Balance Sheet for the Fate of the Paraform and Ammonium Nitrate in the McGill Process

	Run 1		Run 2		Run 3		Run 4	
	gms.	moles	gms.	moles	gms.	moles	gms.	moles
Starting Materials:								
CH_2O	11.5	0.38	11.5	0.38	120	4.0	12.0	0.40
NH_4NO_3	64.0	0.80	64.0	0.80	400	5.0	40.0	0.50
End Products:								
CH_2O in R.D.X.	7.1	0.24	6.2	0.21	70	2.3	1.3	0.04
CH_2O in sol. By-Products	4.4	0.15	5.3	0.18	50	1.7	10.7	0.36
Total	11.5	0.39	11.5	0.39	120	4.0	12.0	0.40
NH_4NO_3 in water-soluble solids	30.9	0.39	28.9	0.36	84	1.0	14.6	0.18
NH_4NO_3 in R.D.X.	18.9	0.24	16.4	0.20	186	2.3	3.6	0.04
NH_4NO_3 in soln-in Reaction Liquor	1	0.01	1	0.01	10	0.1	1	0.01
NH_4NO_3 in sol. By-Products	13.2	0.16	17.7	0.22	120	1.5	20.8	0.26
	64.0	0.80	64.0	0.79	400	4.9	40.0	0.49
Mole Ratio CH_2O/NH_4NO_3 in By-Products		0.9		0.8		1.1		1.4

The determination of the fate of the reactants in Run 1 will be given as an example of the methods of calculation.

The equation

$$3CH_2O + 3NH_4NO_3 \longrightarrow (CH_2{=}NNO_2)_3 + 6H_2O$$

calls for the formation of 222 gms. of R.D.X. from 90 gms. of paraform and 240 gms. of NH_4NO_3 . Hence the total yield of 17.4 gms. of R.D.X. (See Table 36) in Run 1 must have been formed from

$$\frac{90}{222} \times 17.4 = 7.1 \text{ gms. of } CH_2O\text{, and}$$

$$\frac{240}{222} \times 17.4 = 18.9 \text{ gms. of } NH_4NO_3\text{.}$$

It is assumed that the crude R.D.X. (i.e. the impurities) has about the same composition as pure R.D.X.. This is supported by analyses of crude R.D.X. done at Shawinigan (102).

Since 11.5 gms. of formaldehyde (12.0 gms. of paraform, having a 96% CH_2O content) was added during the reaction, 11.5 - 7.1 = 4.4 gms. must have gone into by-products soluble in the reaction liquor.

The consumption of ammonium nitrate is calculated in similar fashion, the assumptions being made (a) that all the Water-Soluble Solid is ammonium nitrate, and (b) that the solubility of the ammonium nitrate in the reaction liquor is 1 gm. per 150 cc. of liquor.

Obviously, the number of assumptions makes the results only approximate. However, these indicate unmistakeably that the molar proportions of the reagents in the by-products depend on the conditions of the reaction: when a large excess of ammonium nitrate is used, the by-products contain a higher mole percentage of ammonium nitrate. This is summarized in Table 39.

Table 39

Relationship between Composition of By-Products and Proportions of Reagents in McGill Process

Run No.	Reactants $(CH_2O)_x : NH_4NO_3 : Ac_2O$ mole ratio	Addition mode (1)	By-Products $(CH_2O)_x : NH_4NO_3$ mole ratio
1	1 : 2 : 2.6	CAM	0.9
2	1 : 2 : 2.6	CAM	0.8
3	1 : 1.2 : 2.6	CAM	1.1
4	1 : 1.2 : 2.6	RAM	1.4

(1) CAM = Continuous Addition Method

RAM = Reversed Addition Method

In Run 4, although the mole ratio of formaldehyde to ammonium nitrate is the same as in Run 3, the mode of addition ensures that for the greater part of the reaction time the formaldehyde is present in excess. All the results, then, show a definite trend. The possible significance of this is discussed later. (Chapter XI).

The consumption of ammonium nitrate in the formation of by-products is also of interest because of the light it may shed on the fate of the third reactant, acetic anhydride.

If each mole of ammonium nitrate which has gone into by-products has lost two moles of water to form soluble nitramines, then in Run 1 0.24 mole (forming R.D.X.) and 0.16 mole (forming by-products) have reacted to give 2 x (0.24 + 0.16) = 0.80 mole of water. This would combine with 0.80 mole of acetic anhydride to form acetic acid. The latest work in this laboratory indicates that Type N acetic anhydride contains 15% acetic acid. Assuming this value for Type O, this would mean that the amount of acetic anhydride in 100 cc. was 0.90 mole, not 1.06 mole. At the end of the reaction, 0.90 - 0.80 = 0.10 mole of acetic anhydride would be left unhydrated: the acetic anhydride content of the liquor would be only about 10%. This is close to the most recent values obtained in this laboratory (99).

B. The Fate of the Paraform.

The fate of the paraform in the McGill Process was first studied by Johnson (103). By distillation of the diluted reaction liquor, he obtained a distillate containing acetic acid and about 12% of the original formaldehyde; and a viscous residue. This residue on treatment with ammonia gave hexamine and a small amount of impure R.D.X. The formaldehyde accounted for in the distillate, in the hexamine, and in the total yield of R.D.X. amounted to 85% of the amount originally used. This experiment does not show whether the formaldehyde in the reaction liquor is free or in the form of some easily hydrolyzable compound.

Ross, Boyer, and coworkers (104) later found that this formaldehyde in the reaction liquor could be removed by steam-distillation. It was analyzed in the distillate by a method modified after that of Walker (105). The formaldehyde in the distillate and that consumed in forming R.D.X. together amounted to 93% of the formaldehyde used. Here again the experiment does not show whether the formaldehyde is free or combined.

Wright (106) on distillation of the reaction liquor obtained some as yet unidentified products. These gave formaldehyde on hydrolysis, and contained nitrogen.

At the present moment there is no evidence as to the state of the formaldehyde in the reaction liquor. For the reasons given on page 96 , it is believed to be in chemical combination in by-products; but decisive evidence will be lacking until the compounds in which it is present have been isolated and characterized.

The possible reactions by which formaldehyde can form by-products rather than R.D.X. are:

1. Reaction with acetic anhydride; or
2. Reaction with ammonium nitrate; or
3. Reaction with ammonium nitrate and acetic anhydride.

1. Reaction of Formaldehyde with Acetic Anhydride.

It has already been shown (107; pages 54,57, this thesis) that experimental evidence does not indicate a side-reaction between paraform and acetic anhydride to give polyoxymethylene diacetates. This is to be expected, because of the drastic conditions needed to obtain these compounds (108).

This view was confirmed by investigating the action of acetic anhydride on paraform at 70°. A mixture of 31.1 gms. of paraform and 250 cc. of acetic anhydride (Type N) was stirred for one hour at 70°. The mixture was then cooled to 40°, filtered through a hardened filter paper, and the solid was sucked as dry as possible. It was washed twice with 10 ml. portions of ligroin, but still smelled strongly of anhydride and weighed 31.5 gms. After standing in a vacuum desiccator for 12 hours over P_2O_5 and paraffin it weighed 29.2 gms. The odour of formaldehyde in the desiccator was strong. The properties of the solid were almost identical with those of the untreated paraform, as shown in Table 40.

Table 40

Comparison of Properties of Paraform (EK) Before and After Treatment with Acetic Anhydride (Type N) for One Hour

Properties	Treated Paraform	Untreated Paraform
1. M.P. (in a sealed tube)	131-168	131-168
2. Acidity* (cc. of 0.1N NaOH per 5.0 gms.of solid)	0.4 cc.	0.2 cc.
3. Yield of R.D.X.		
First Crop	13.1 gms.(42.5%) M.P.191-195	13.5 gms.(44.0%) M.P.190-195
Second Crop	1.0 gms.(3.3%) M.P.180-186	0.01 gms. M.P.172-177

The R.D.X. in both cases was prepared by the Continuous Addition Method: 12.5 gms. of the paraform and 40.0 gms. of ammonium nitrate were added over a period of 10 mins. to 100 cc. of acetic anhydride (Type N) at 70°, with stirring. After addition was complete the mixture was stirred a further 20 mins. at 70°, then diluted and boiled according to the Shawinigan Method of Purification.

2. Formaldehyde Balance in Runs Made by the Reversed Addition Method.

By exclusion of the possibility of reaction with acetic anhydride, it is apparent that formaldehyde reacts with ammonium nitrate or with ammonium nitrate and acetic anhydride to form the by-products soluble in the reaction liquor.

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* End-point (using phenolphthalein) was very uncertain.

It has been mentioned that steam distillation of the reaction liquor sweeps off most of the formaldehyde which has not been consumed in forming R.D.X. This technique was applied to the reaction liquor of runs made by the Reversed Addition Method, in order to see if the larger amounts of by-products formed in this reaction were also readily hydrolyzable.

A preliminary investigation of the efficiency of steam-distillation as a means of removing formaldehyde from solution was made, by steam distilling 1.000 gm. of E.K.paraform (0.965 gm. of formaldehyde) in 100 cc. of water for one and for four hours. The formaldehyde in the distillate and in the residual liquid was determined by the volumetric method of Romijn (109), as modified by Signer (110). It was found that after steam-distillation for one hour 69.3% of the formaldehyde was in the distillate; after distillation for four hours, 97.1% was in the distillate. It is evident that a prolonged distillation is necessary to effect complete removal of the formaldehyde.

The diluted reaction mixtures of three runs made by the Reversed Addition Method were steam distilled for six hours,and the distillate was analysed by the Romijn-Signer method for formaldehyde. The details of the reaction conditions during the runs have been given previously.

Table 41

Formaldehyde Balance in Runs Made by the Reversed Addition Method

Run No.	Conditions of Reaction	Reactant: Paraform Wt. gms.	Reactant: CH_2O Wt. gms.	Product: R.D.X. Wt. gms.	Product: CH_2O in R.D.X. gms.	Product: CH_2O in liquor gms.	Total CH_2O accounted for gms.	Total CH_2O accounted for %
1	Run 1,Table 15,page 56	12.5	12.0	4.8	1.95	8.83	10.8	90.0
2	" 3, " 16, 56	12.5	12.0	8.3	3.4	7.92	11.3	94.3
3	" 4, " 16, 56	12.5	12.0	8.9	3.6	6.84	10.4	86.8

From these results it follows that all except about 10% of the formaldehyde forms either R.D.X. or hydrolyzable by-products. It consequently appears that the same by-products are formed in runs made by the Reversed Addition Method as in those by the Continuous Addition Method: the increased amount of them formed being due to the excess of paraform during the greater part of the reaction.

3. Attempts to Titrate Directly the Formaldehyde in the Reaction Liquor.

Previous work in this laboratory had shown that ammonium nitrate interferes with the determination of formaldehyde by the method of Walker (105). It was for that reason that steam-distillation was resorted to. This treatment removes the formaldehyde and some of the acetic acid from the diluted reaction liquor, but leaves the ammonium nitrate behind.

As has been mentioned, treatment as drastic as steam-distillation would hydrolyze many compounds, and so this method does not show if any free formaldehyde is present in the reaction liquors. An attempt was made to discover this by titrating directly the diluted reaction liquor,using the Romijn-Signer method. The value so obtained should correspond to the formaldehyde free or in the form of very easily hydrolyzable compounds in the reaction liquor.

The values, however, were too high. It was found that although acetic acid does not interfere in this titration, ammonium nitrate does. This is shown in Table 42.

Effect of Ammonium Nitrate on Formaldehyde Determinations by the Romijn Method.

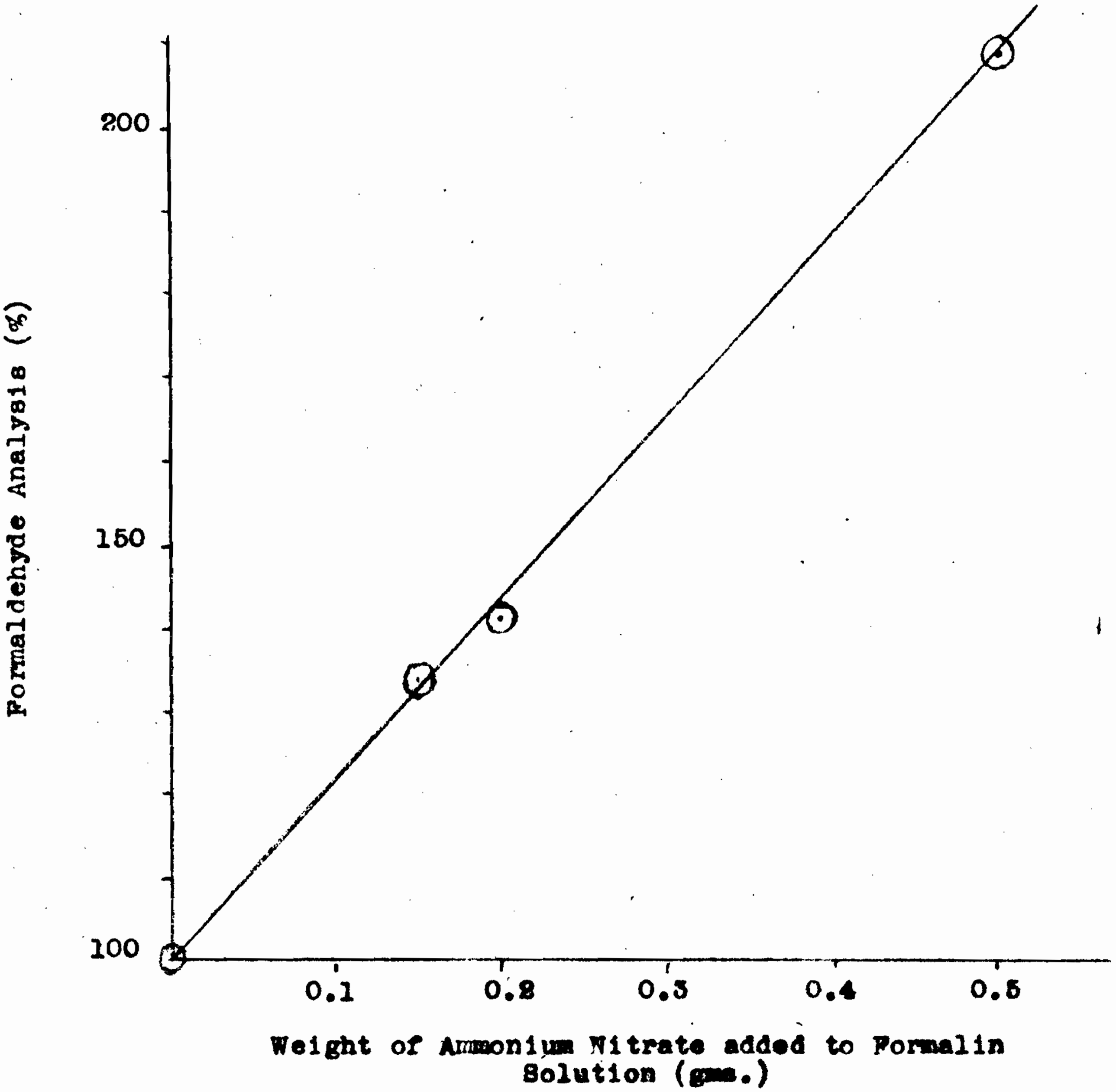


Figure 8

Table 42

Effect of Ammonium Nitrate on the Analysis for Formaldehyde by the Romijn-Signer Method.

Amount NH_4NO_3 added to 25 ml. of formalin soln.	CH_2O analysis	
gms.	gms.	%
-	0.0239	100
0.15	0.0320	134
0.2	0.0336	141
0.5	0.0500	209

These results are represented graphically in Fig. 3.

IX. Thermal Phenomena of the McGill Process

A. The Relation Between Evolution of Heat and Formation of R.D.X.

When a mixture of ammonium nitrate and paraform is added to hot stirred acetic anhydride, as in the Continuous Addition **Method**, it is noted that the evolution of heat commences a certain time after the beginning of addition and continues for some time after addition is complete. This period of the reaction is known as the Heating Period of H.P.

The time between the beginning of addition and the start of the H.P. is known as the First No-Heating Period, or N.H.P.(1); the period after the H.P. is known as the Second No-Heating Period or N.H.P.(2).

The H.P. as so determined does not correspond to the true period of evolution of heat during the reaction, but is somewhat smaller. Owing to the crudeness of the method employed (see page 46), it is impossible to know when the evolution of heat begins. The time when external cooling rather than heating is required to maintain the temperature of the reaction mixture at the desired level is regarded as the start of the H.P. The reaction is most exothermic in the early part of the H.P.; it then becomes progressively less exothermic so that the change from H.P. to N.H.P.(2) is by no means sharp.

The heat of reaction in the McGill Process has been determined in this laboratory (111); and an exhaustive study of the rate of the reaction and the factors affecting it, especially at low temperatures, has been made by A. Gillies (112). The work to be described is a study of the relationship between the two phenomena.

1. Effect of Types of Reactants upon Thermal Phenomena.

It was found that in runs made at 70° with E.K. paraform and Type O acetic anhydride, the N.H.P.(1) was 6 mins.; with E.K. paraform and Type N anhydride, 9 mins.; and with R. & H. paraform and Type N anhydride, 3½-4 mins.

Throughout the work in this chapter, R. & H. paraform and Type N acetic anhydride were used.

2. Thermal Phenomena and Rate of Reaction at 70°.

The rate of the reaction at 70° was investigated in a series of runs using 12.5 gms. (0.42 mole) of paraform, 40.0 gms. (0.50 mole) of ammonium nitrate, and 100 cc. (1.06 mole) of acetic anhydride. These were carried out by the Continuous Addition Method. To ensure as uniform as possible a rate of addition of the mixture of paraform and ammonium nitrate, it was divided into ten equal portions. Each portion was added over a period of one minute.

In all runs it was found that the N.H.P.(1) was 3½-4 mins.; the N.H.P.(1) + H.P. was 12 mins.

At a given time the reaction was stopped by the addition of a mixture of ice and water sufficient to give a 50% acetic acid concentration. When the run had proceeded for more than 6 mins., this caused a smooth hydrolysis of the acetic anhydride. The mixture was then boiled, following the Shawinigan Method of purification.

When the reaction had not been allowed to proceed for 6 mins., addition of the ice and water caused the separation of a lower layer of acetic anhydride, and a sharp drop in temperature. After standing some time this mixture suddenly heated up violently, and unless it was energetically cooled material was lost by frothing.

This sudden heating up undoubtedly came from the hydrolysis of acetic anhydride. The hydrolysis of acetic anhydride at room temperature is slow, but is tremendously accelerated by the presence of acetic acid. Thus in rough tests it was found that while the time of hydrolysis of 25 cc. of acetic anhydride in 200 cc. of water at room temperature was 60 seconds, the time of hydrolysis of 20 cc. of anhydride and 5 cc. of acid was 45 seconds, and the hydrolysis of 25 cc. of anhydride and 25 cc. of acid was practically instantaneous.

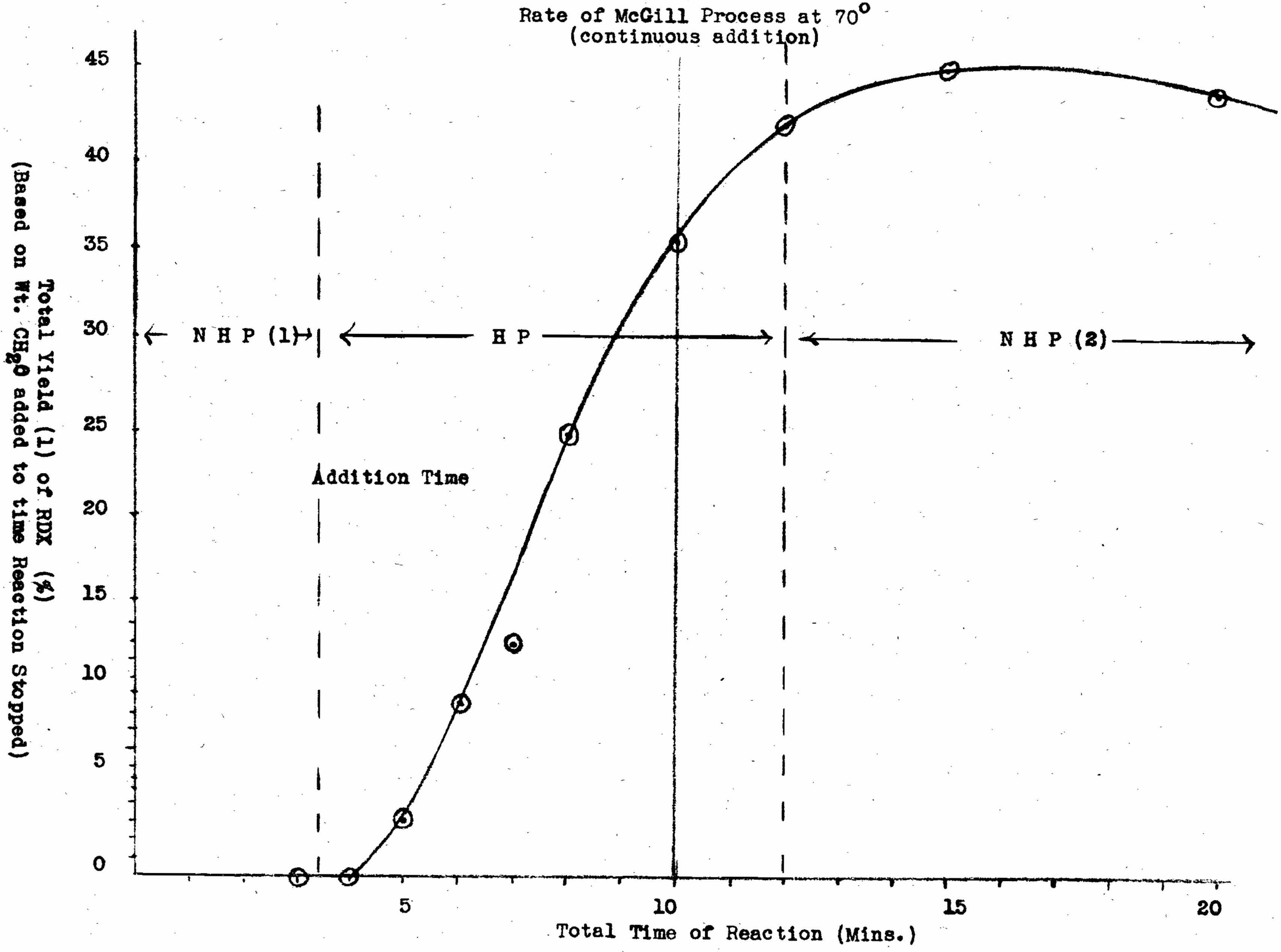
It is apparent that until the sixth minute very little acetic acid has been formed. This may well be related to the induction period existing until about that time, in view of the marked effect of small amounts of acetic acid upon the solubility of ammonium nitrate in acetic anhydride (page 93).

The results of these runs at 70° are recorded in Table 43 and shown graphically in Fig. 4. From them one may conclude that

1. The existence of an induction period at 70° (See page 40) is confirmed;

2. This induction period is made up of the N.H.P.(1) and the early part of the H.P.; i.e. the start of the H.P. does not coincide with the beginning of the formation of R.D.X.; and

3. The McGill Process is complete in 15 mins. at 70°.



Rate of McGill Process at 70°
(continuous addition)

Figure 4

Table 43

Rate of Formation of R.D.X. at 70°

	Time		$(CH_2O)_x$	First Crop				Second Crop				Total	Total
Run No.	Addition mins.	Total mins.	added gms.	Wt. gms.	M.P. °C	Yield (1) %	Yield (2) %	Wt. gms.	M.P. °C	Yield (1) %	Yield (2) %	Yield (1) %	Yield (2) %
1	3	3	3.75	-	-	-	-	-	-	-	-	-	-
2	4	4	5.00	-	-	-	-	-	-	-	-	-	-
3	5	5	6.25	-	-	-	-	0.5	189-194	3.2	1.6	3.2	1.6
4	6	6	7.50	0.3	194-200	1.6	0.9	1.5	183-188	8.1	4.9	9.7	5.8
5	7	7	8.75	2.0	194.198	9.3	6.5	0.8	187-194	3.7	2.6	13.0	9.1
6	8	8	10.00	4.7	192-199	19.0	15.3	1.4	180-188	5.7	4.5	24.7	19.8
7	10	10	12.50	9.2	188-195	29.8	-	1.7	180-188	5.5	-	35.3	-
8	10	12	12.50	12.5	189-195	40.5	-	0.4	180-185	1.3	-	41.8	-
9	10	15	12.50	13.5	190-195	43.8	-	0.3	169-174	1.0	-	44.8	-
10	10	20	12.50	13.4	189-194	43.5	-	-	-	-	-	43.5	-

Yield (1) is based on the amount of formaldehyde which was added before the reaction was stopped.

Yield (2) is based on the amount of formaldehyde added in 10 mins.

3. Thermal Phenomena and Rate of Reaction at 50°.

The necessity for the use of the Continuous Addition Method at 70° makes the interpretation of the results difficult. Hence a series of runs was made to 50° using the same quantities of reactants but conducted by the Total Addition Method. The anhydride was first heated to 55-58°, so that on addition of the cold solids a temperature of about 50° was immediately established. The product was worked up by the Shawinigan Method of purification. The results are recorded in Table 44, and shown graphically in Fig. 5.

Table 44

Rate of Formation of R.D.X. at 50°

	Time			H.P.	First Crop			Second Crop			Total
Run No.	Total mins.	N.H.P.(1) mins.	H.P. mins.	N.H.P.(1) mins.	Wt. gms	Yield %	M.P. °C	Wt. gms.	Yield %	M.P. °C	Yield %
1	5	-	-	-	-	-	-	-	-	-	-
2	10	-	-	-	-	-	-	-	-	-	-
3	20	14	-	-	-	-	-	-	-	-	-
4	25	16	-	-	-	-	-	trace	-	-	-
5	30	4½(1)	-	-	-	-	-	1.3	4.2	187-192	4.2
6	35	16	-	-	1.5	4.9	190-195	1.7	5.5	187-192	10.4
7	40	14	24	38	4.0	13	189-196	1.2	3.9	183-188	17
8	50	10(1)	27	37	8.0	26	187-191	1.0	3.3	181-185	29
9	60	9	26	35	8.2	27	188-191	2.0	6.5	181-186	33
10	70	10(1)	30	40	9.7	31	188-193	0.7	2.3	179-184	34
11	105	4½	30½	35	9.3	30	188-193	0.9	2.9	178-183	33

---

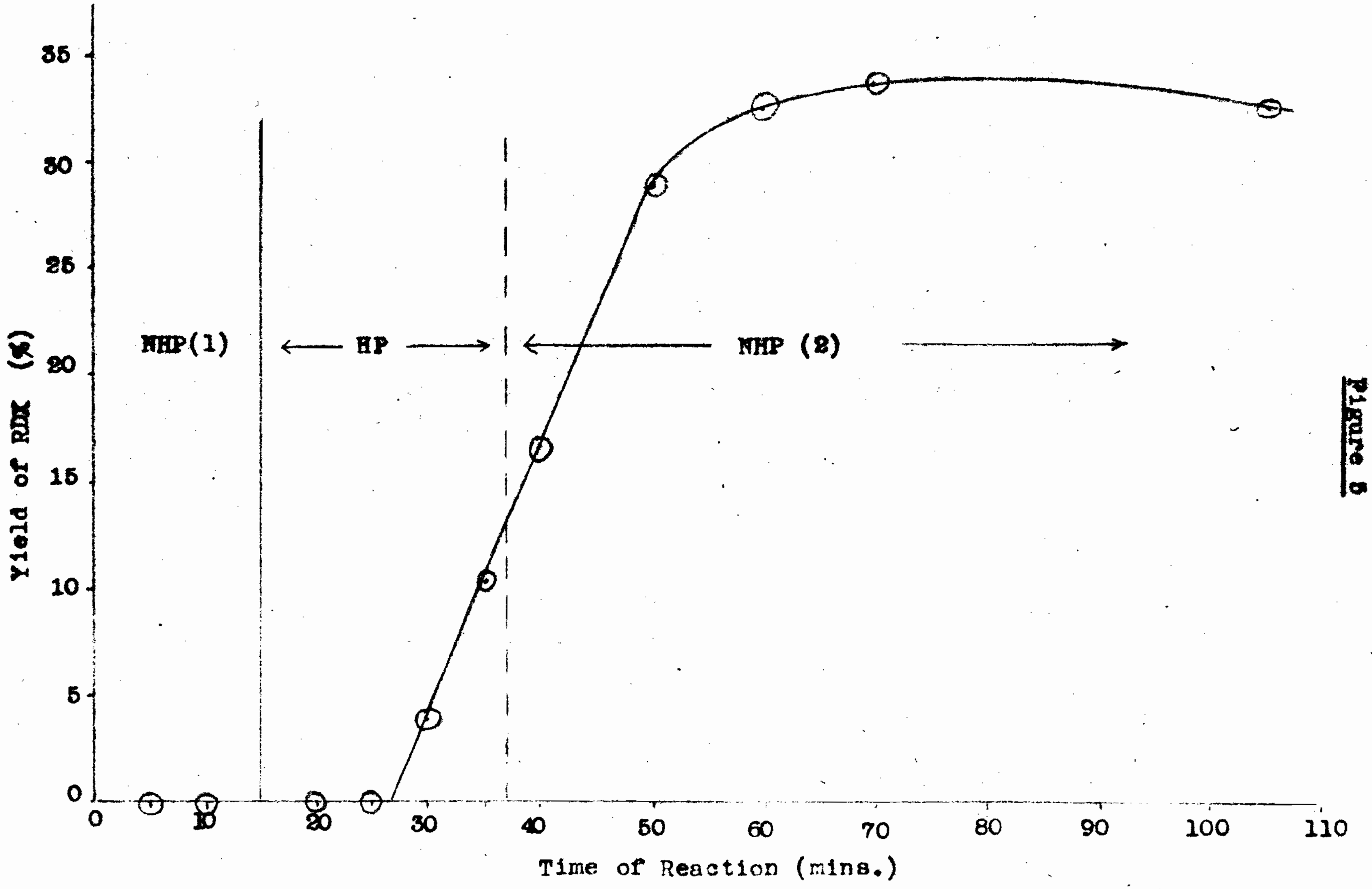
(1) In these runs the mixture of ammonium nitrate and paraform had been allowed to stand for some time before using.

At this temperature the distinction between the N.H.P. (about 15 mins.) and the induction period (27 mins.) is very noticeable.

A feature worthy of note is the manner in which the N.H.P.(1) varied, without appreciably affecting the yield, as evidenced by the smoothness of the curve. The time from the start of the reaction to the end of the H.P. is much more constant.

Figure 5

Rate of the McGill Process at 50°



The decrease in the N.H.P.(1) appeared to be proportional to the length of time the ammonium nitrate and paraform were allowed to remain in contact before being added to the acetic anhydride, although no quantitative study was made of this phenomenon. It may be related to the decreased yield resulting when the mixture is allowed to stand for 24 hours before use: it was noted in that case that the H.P. commenced immediately on addition of acetic anhydride to the mixture (page 41).

4. Thermal Phenomena at 60°.

A run was made at 60° by the Total Addition Method using the same quantities of reactants as before. The N.H.P.(1) lasted for 7 mins. During the first 8 mins. of the H.P. frequent cooling with a water-bath was needed; for the next 3½ mins. air-cooling was sufficient; and for the last 11½ mins. external heating was necessary (the N.H.P.(2)).

The reaction was then stopped (30 mins. after the beginning) by addition of ice and water.

First Crop	9.5 gms.	(31% yield),	m.p. 191-196°
Second Crop	1.0 "	(3.2% "),	" 183-188°.

The effect of temperature upon the N.H.P.(1) is thus very great: it is about 3½ mins. at 70°, 7 mins. at 60°, and 14 mins. at 50°.

B. The Kick-Off.

Unless the reaction flask is cooled frequently during the H.P. the temperature rises rapidly until a "kick-off" occurs with violent frothing of the reaction mixture.

It was believed at first that the frothing was due to the oxidation of formaldehyde to carbon dioxide. This would account for the lower yields of R.D.X. which result whenever a kick-off occurs. It was noted by Ross (113), however, that the amount of gas evolved was relatively small; furthermore, that the gas was evolved <u>after</u> the most vigorous frothing had occurred. The frothing was explained by the rapid boiling of acetic acid ($B.P._{760}=118^{\circ}$) which is altogether reasonable in view of the fact that the kick-off occurs at temperatures between 110 and 120°.

1. Source of Heat causing the Kick-Off.

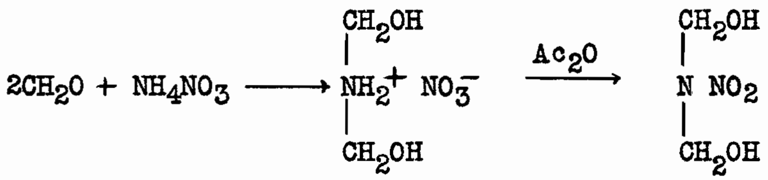
The source of the heat producing the kick-off is obscure. The condensation of formaldehyde with ammonia to give hexamine and with formamide to give methylenediformamide is vigorously exothermic, in the latter case leading to an energetic frothing analogous to the kick-off (page 85). However, on heating formaldehyde and ammonium nitrate together in acetic acid to 90°, there is no noticeable heat evolved.

A mixture of ammonium nitrate and acetic anhydride when heated to 100° reacts in mildly exothermic fashion:

$$NH_4NO_3 + 2Ac_2O \longrightarrow N_2O + 4AcOH$$

The reaction is far less energetic than the "kick-off", however, and at 70° there is no detectible reaction at all (page 93).

A more likely source of heat is the dehydration of secondary amine nitrates formed by condensation of formaldehyde with ammonium nitrate during the reaction:



$$2CH_2O + NH_4NO_3 \longrightarrow \overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{NH_2^+}}\ NO_3^- \xrightarrow{Ac_2O} \overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{N}}\ NO_2$$

The exothermic nature of this reaction was noted by Bamberger (56), who found that once the reaction between piperidine nitrate and acetic anhydride had been initiated by heating, it was necessary to cool occasionally to prevent the reaction from becoming too violent. There is no report of the temperature at which the reaction becomes vigorous.

2. The Gases Evolved during the Kick-Off.

A mixture of 0.5 gm. (0.016 mole) of paraform, 2.7 gms. (0.033 mole) of ammonium nitrate, and 7 cc. (0.066 mole) of acetic anhydride was placed in a test-tube fitted with a thermometer and a delivery tube. The delivery tube led to a graduated cylinder filled with chloroform standing in a trough of this liquid.

The mixture was heated to 70°. A reaction became evident, and the temperature rose to 110-120°. Vigorous frothing occurred. The reaction yielded 70 cc. of gas. When some 40% NaOH solution was floated to the top of the chloroform in the cylinder, no diminution in volume occurred. This proved the absence of appreciable amounts of carbon dioxide.

The gas in the cylinder extinguished a burning splint. Nitrous oxide, prepared by the thermal decomposition of ammonium nitrate and collected in the same way, caused a burning splint to flare up. Hence the gas must have contained little if any nitrous oxide, and must have been mostly nitrogen.

A possible source of the nitrogen is the reduction of ammonium nitrate by formaldehyde (114):

$$NH_4NO_3 + CH_2O \longrightarrow NH_2NO_2 + HCOOH$$

$$NH_2NO_2 + 2Ac_2O \longrightarrow N_2 + 4AcOH$$

It appears likely that such a reaction occurs on fusing ammonium nitrate and paraform together, for about 29% of the formaldehyde appears as formic acid on distillation of the melt (115).

The amount of gas collected , however, corresponds to a consumption of only about 0.09 gm. of paraform and 0.23 gm. of ammonium nitrate, i.e. to less than 10% of the reactants. This confirms Ross's observation that the evolution of gas is only a minor feature of the kick-off, which is primarily a thermal effect. When other aldehydes, however, showing less tendency to condense with ammonium nitrate are substituted for paraform in the McGill Process, this oxidation may become predominant. This would explain the kick-offs obtained (page 81). This point could easily be settled by a reinvestigation of these reactions with special attention to the evolution of gas.

X. The Condensation of Formaldehyde with Ammonium Acetate and Acetamide.

The research to be described in this chapter is the earliest work of the author on the McGill Process. The repeated failure of attempts to verify the "nitramide" hypothesis for the formation of R.D.X. (pages 3, 5) had lead to a belief that the acetic anhydride was acting as an acetylating rather than as a dehydrating agent (c.f. 116). It consequently seemed possible that intermediates might be formed by the condensation of formaldehyde with ammonium acetate or acetamide, which on nitrolysis would yield R.D.X.

It has already been shown that such compounds are not formed by the interaction of ammonium nitrate and acetic anhydride at 70° (page 92). In view of the fact that their formation would involve the displacement of nitric acid by acetic acid in ammonium nitrate, or the acetylation of the ammonium ion (117), this result is not surprising.

A. Condensation with Ammonium Acetate.

An attempt was made to condense formaldehyde with ammonium acetate in acetic anhydride. A mixture of 0.75 gms. (0.025 mole) of paraform, 1.92 gms. (0.025 mole) of ammonium acetate, and 6.25 cc. (0.066 mole) of acetic anhydride was heated to 90° for 10 mins. with stirring. The solids dissolved to form a clear yellow solution. However, no product came out of solution on dilution with water or with ether even after the latter mixture had stood in the refrigerator for 48 hours.

Condensation accordingly was accomplished by fusing the solids together. Forty-five gms. (1.5 mole) of paraform and 115 gms. (1.5 mole) of ammonium acetate were heated together for 40 mins. at 120-130° (compare preparation of N-methylolacetamide, page 9). A clear syrupy liquid formed, which set to a mush on cooling in the refrigerator. The mush redissolved on warming to 40°. Fifty cc. of absolute ethanol was added, and the solution was again cooled. Crystals were formed (m.p.63-66°) which were filtered off. By evaporating ethanol and acetic acid from the filtrate at room temperature under reduced pressure, several crops of white solid were obtained. These all melted either about 250° (with decomposition), or below 66°. The total yield was 40% of the weight of reagents used.

The low-melting solid appeared to have a melting point of 65-66°: usually the melting points of the crops obtained were lower because of impurities. It was very hygroscopic. It was soluble in water, ethanol, acetic acid, acetone, and pyridine; insoluble in ligroin, chloroform, and toluene. It could not be purified, however, because of its instability. On crystallization from absolute ethanol, several crops were obtained, some low-melting and some high-melting: repeated crystallization led to a complete conversion to the high melting compound. This change was irreversible: the high melting compound on repeated recrystallization was recovered unchanged.

The high-melting solid was identified as hexamine (reported m.p.230-270°) by formation of a derivative with mercuric chloride (118), m.p.230°. The derivative from an authentic sample of hexamine melted at 226°, and the mixed m.p. was 230°.

On crystallization of the low-melting compound from ethanol, acetic acid was given off and could be detected by its odour. Similarly, on heating the dry compound on a spatula, it melted, gave off an odour of acetic acid, and then solidified to give a high-melting compound, presumably hexamine in this case also. From its physical properties and its instability, it seems likely that the low-melting solid was methylolamine acetate (LXIX). The formation of hexamine on fusing ammonium acetate and paraform would then be represented thus:

$$\mathrm{CH_2O} + \mathrm{NH_4OAc} \longrightarrow \underset{\text{LXIX}}{\mathrm{CH_2OH{-}NH_3OAc}}$$

$$\mathrm{6CH_2OH{-}NH_3OAc} \longrightarrow \mathrm{(CH_2)_6N_4} + \mathrm{2NH_4OAc} + \mathrm{4AcOH} + \mathrm{6H_2O}$$

To verify this formula for the low-melting compound an attempt was made to form a derivative*. It was treated with benzoyl chloride in pyridine. It did not dissolve completely: but it appeared to react and change over into another compound. This compound, a white solid, was shown to be ammonium chloride by

1. Its physical properties: it was very soluble in water, and had a melting-point above 300°.

2. Its analysis for chlorine by the standard gravimetric procedure using silver nitrate.

Calcd. for NH_4Cl : Cl, 66.4. Found : 65.1.

A control run with an authentic sample of NH_4Cl gave a chloride analysis of

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* This derivative was prepared by R.W.Schiessler and Dr.J.H.Ross.

66.2%: the product formed by the action of benzoyl chloride is evidently slightly impure.

The failure to form a benzoate is not surprising in view of the lack of success of Einhorn and coworkers in forming such derivatives of the methylolamides (page 12).

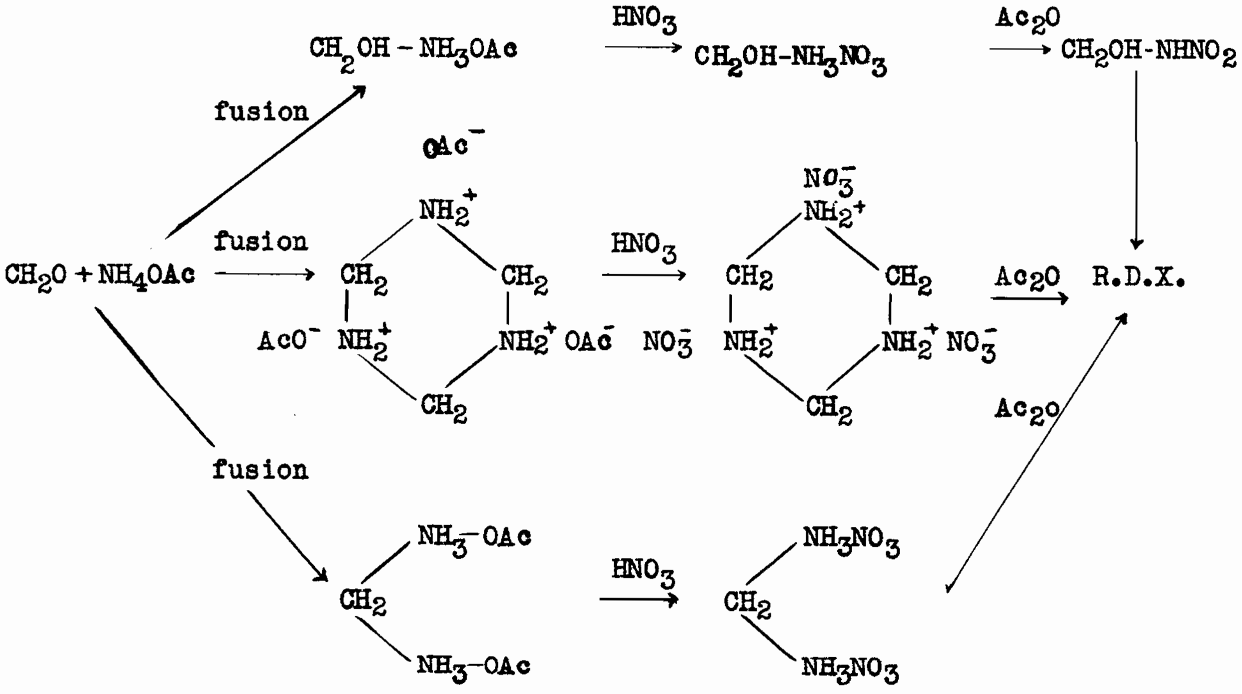
1. Formation of R.D.X. from the Condensation Product.

Because of the impossibility of obtaining the low-melting compound pure, the following work was done on the crude product furnished by the fusion of equimolecular amounts of paraform and ammonium acetate.

Treatment of this product with 85% nitric acid and at 0°C gave a sticky solid which could not be characterized. It was dried by standing in a desiccator over P_2O_5, or by heating to 110° in a Fischer pistol under reduced pressure (25-40 mm.). Even when this latter treatment was prolonged to 20 hours, no water-insoluble material (R.D.X.) was formed. Instead, the solid so obtained was still pasty. It melted at 132-137° (decomposition). It was soluble in water, but insoluble or nearly so in acetone, ether, benzene, chloroform, glacial acetic acid, ligroin, and ethanol. When treated with concentrated NaOH solution, it gave an odour of ammonia. On addition of acetone to an aqueous solution of it, a white solid m.p.176-182°, was obtained. It thus appears likely that the solid was a mixture of compounds.

The "nitrated" solid, on treatment with acetic anhydride at various temperatures, followed by dilution with water, sometimes gave R.D.X. in small amounts (in yields of 1-5%), but more often did not. The reason for this erratic behaviour is not known, but indicates that some important variable was being consistently overlooked in the preparation of the condensation or of the nitration product. The treatment of the nitrated solid with other dehydrating agents (phosphoric acid, glycerol) failed to give R.D.X.

Because of the failure to isolate definite intermediates in this process, the mechanism of the formation of R.D.X. is not known. A few of the possible modes of formation are given:



B. <u>Condensation with Acetamide</u>

An attempt was made to prepare N-methylolacetamide (m.p.50-52°) by the condensation of paraform and acetamide (13; see page 9). Thirty gms. (1 mole) of paraform and 59 gms. (1 mole) of acetamide were fused together at 120-130° for 40 mins. On cooling, a clear liquid with a slight amount of insoluble material was obtained. Chloroform was added, but failed to precipitate any solid. The mixture was filtered, and the excess of chloroform evaporated off. On cooling, a solid was obtained, m.p.90-175°. Chloroform was evaporated from the filtrate again. A large amount of solid, m.p. 189-194° was obtained. The m.p.of methylenediacetamide is 196°. It seems likely that the prolonged heating with chloroform caused a conversation of the N-methylolacetamide to methylenediacetamide.

When another attempt was made to prepare N-methylolacetamide, under the same conditions as above but not diluting with chloroform, a thick syrupy liquid was obtained. Crystallization could not be unduced, even after scraping the sides of the container for 30 mins.,while cooling to -10°C. In the light of later knowledge, it appears likely that this was a solution of N-methylolacetamide, the crystallization of which can often be accomplished only with great difficulty.

N-methylolacetamide was prepared by the method of Einhorn and coworkers (14; see page 10). Crystallization of the compound from methanol solution required several days' standing in the refrigerator. The crops obtained melted at or slightly below 50-52°. The yields in two runs were 8% and 33%.

This compound was shown to be unstable on standing in the dry state. After one week in the refrigerator, the m.p. was 50-52°, indicating that no appreciable decomposition had occurred; after six months at room temperature, however, it had decomposed to give a syrup and crystals of two different materials, melting at 51-54° (impure N-methylolacetamide) and 65-81° (impure acetamide).

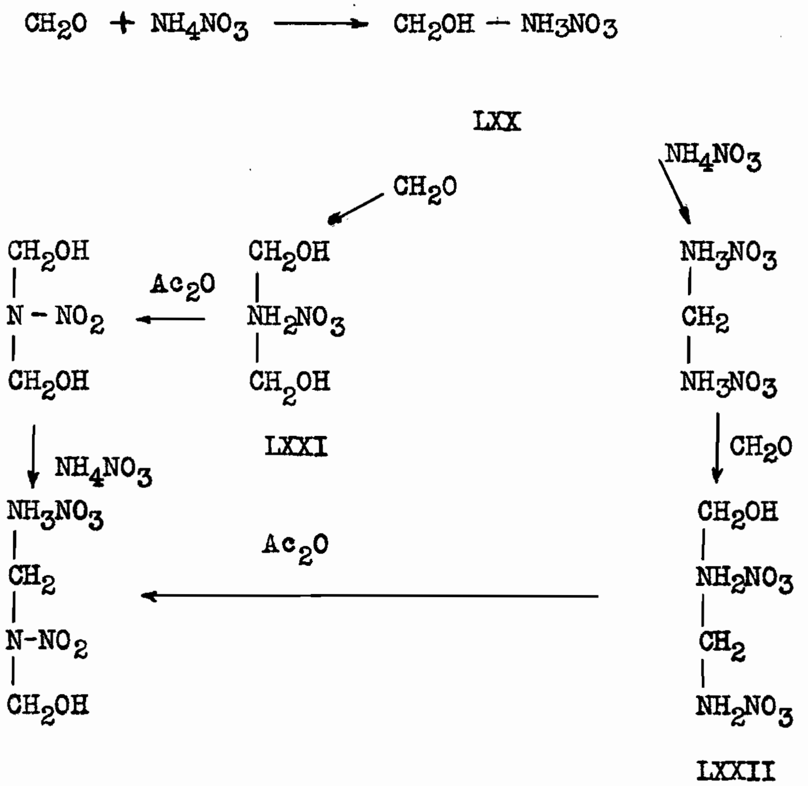
The investigation of this compound as a possible intermediate in the formation of R.D.X. was not carried further by the author. It was found (119) that on being heated with ammonium nitrate in acetic anhydride, and on treatment with 95% nitric acid in chloroform, acetic anhydride, and water, it failed to yield R.D.X.

XI. Discussion of Possible Mechanisms of the McGill Process

In view of the fact that no products except R.D.X. and H.M.X. have been isolated from the reaction mixture of the McGill Process, any discussion of its mechanism must necessarily remain speculative. Hypotheses of the mechanism, if they are to be of any value, must not only account for the experimental facts, but must predict more facts capable of verification. The mechanisms so far advanced for this reaction (120) fail to meet one or the other of these requirements. Since they have been adequately discussed elsewhere, they will not be considered here.

The mechanism proposed in this chapter postulates the formation of R.D.X. and H.M.X. by a polycondensation of formaldehyde and ammonium nitrate, rather than by a polymerization of methylenenitramine. Such a mechanism has been envisaged by other workers (120), but the steps through which the reaction passes have not been considered in detail, and the possible by-products have not been predicted.

According to this mechanism, the first step in the reaction is the condensation of formaldehyde and ammonium nitrate to give methylolamine nitrate (LXX) (page 18). This compound then condenses further with formaldehyde and with ammonium nitrate to build up chains of carbon and nitrogen atoms alternately linked:

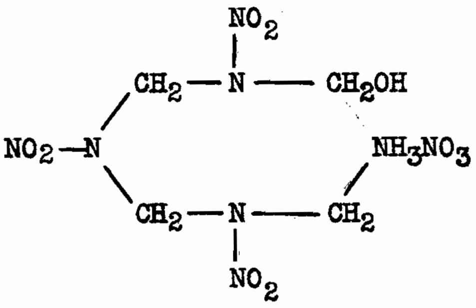


It is assumed that when the ammonium nitrate has by condensation with formaldehyde become a secondary amine nitrate (e.g.LXXI,LXXII) it is dehydrated by the acetic anhydride to form a nitramine group. This view is supported by the ease of dehydration of secondary as compared with primary amine nitrates (page 29).

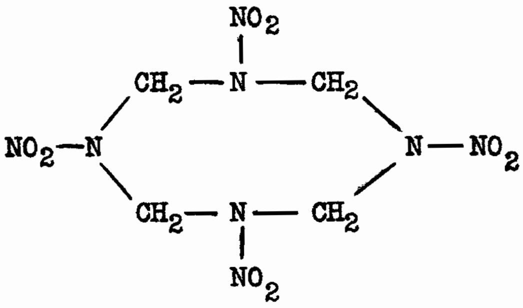
The growth of these chains can be halted in three ways:

1. <u>Cyclization by reaction of the ends of the chains with each other</u>.

When the terminal groups on the chain are different (e.g.LXXIII), cyclization leads to the formation of cyclopolymethylenepolynitramines (LXXIV):



LXXII



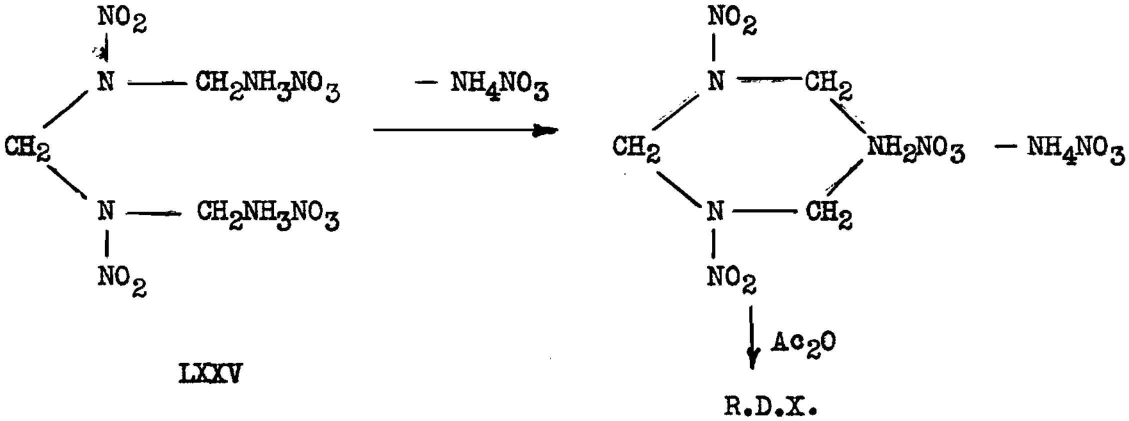
LXXIV (H.M.X.)

So far, only the six- and eight-membered rings of this series of compounds have been identified among the reaction products of the McGill Process. If they are formed by a polycondensation as outlined above, one might expect the formation of a four-membered ring also, by analogy with the condensations of formaldehyde with sulphonamides (page 6) and urethane (page 13).

The larger rings with ten and more members, have no analogues among the condensation products of formaldehyde with amides or amines. They can be formed with the Fischer-Hirschfelder atomic models, and so are sterically possible. However, the probability of ring closure decreases rapidly with the increasing length of a molecule (121), and so if formed they would be present in very small amount.

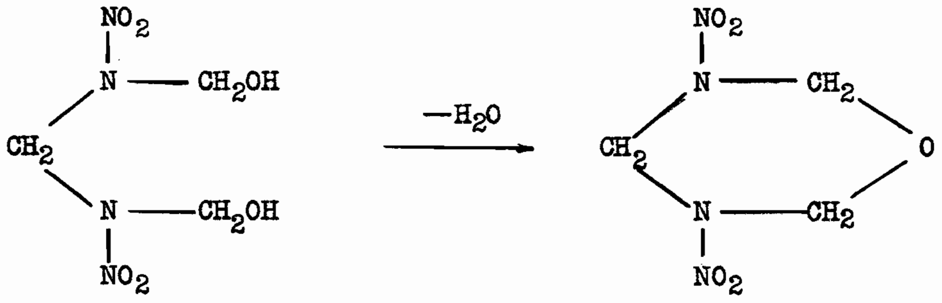
The discovery of cyclopolymethylenepolynitramines with other than six or eight members would be of fundamental importance in demonstrating the validity of this proposed mechanism. If they were shown to be present in the crude product from the McGill Process, and to be absent in the crude product obtained by the nitrolysis of hexamine, the mechanism postulating the formation of R.D.X. and H.M.X. by a partial rather than total degradation of the hexamine molecule during nitrolysis would be strengthened (see pages 21,26).

Ring closure might also be accomplished by reaction between the ends of the chain when it is terminated by similar groups. When the chain ends in amine nitrate groups (LXXV), such a reaction would also lead to the formation of cyclopolymethylenepolynitramines.



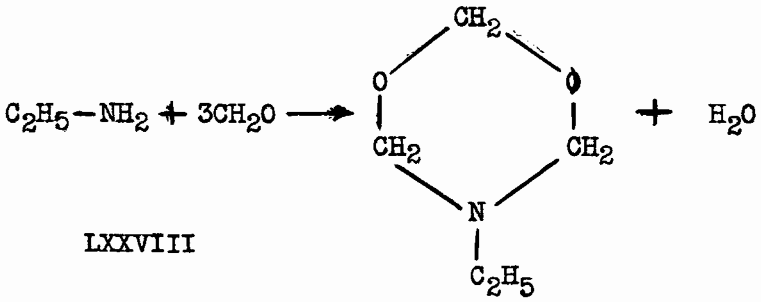
The possibility of such a reaction is supported by the behaviour of the simplest member of the series of chains terminated by amine nitrate groups, methylenediamine dinitrate. It has been shown that this compound in acetic anhydride breaks down to ammonium nitrate and R.D.X. (page 88). It seems probable, however, that longer chains would not exhibit this instability. Ethylenediamine dinitrate appears, unlike methylenediamine dinitrate, to be a perfectly stable compound (122).

The third type of chain which might undergo ring closure is that terminated by methylol groups (LXXVI).



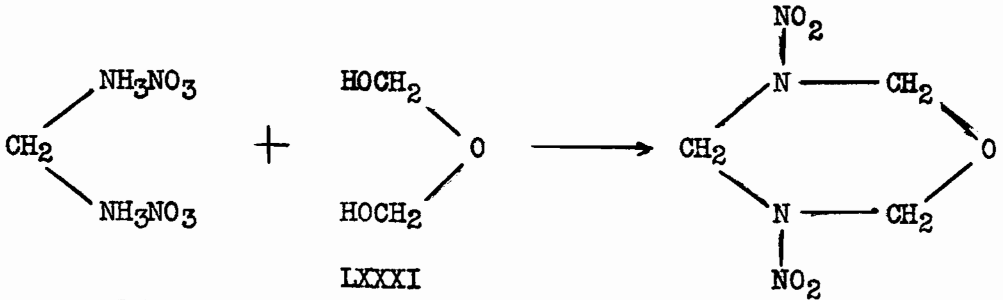
LXXVI LXXVII

Such a reaction would give rise to rings in which some methylene groups are separated by oxygen and others by nitrogen. Compounds of this type are already known: cyclonite oxide (LXXVII) (123) is a by-product in the nitrolysis of hexamine; and the condensation of ethylamine (LXXVIII) with formaldehyde at ice-bath temperature yields a "mixed" ring containing two oxygen members (LXXIX) (124)



LXXVIII LXXIX

These "mixed" rings (e.g.LXXVII) might also be formed by the condensation of diamine dinitrates (LXXX) with incompletely depolymerized paraform fragments (LXXXI)

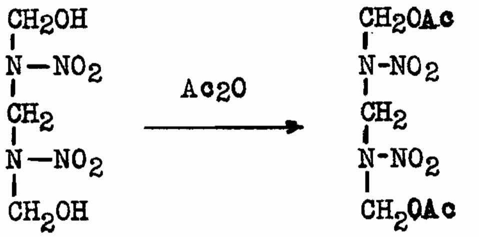


LXXX LXXXI LXXVII

These compounds, by analogy with cyclonite oxide and trioxane, would be soluble in water and resistant to hydrolysis. Their formation would be favoured by a high concentration of methylol-terminated chains, and a high concentration of paraform fragmens: i.e. by an excess of paraform. It has already been shown (pages 38, 54, 99) that the formation of water-soluble by-products is favoured by an excess of formaldehyde, and furthermore, that under these conditions the by-products, like the "mixed" rings, are made up of more formaldehyde than of ammonium nitrate molecules (page 99). On the other hand, the greater part of the by-products is made up of hydrolyzable compounds (page 100). This fact merits reinvestigation; but, for the moment it may be assumed that the "mixed" rings make up only the 10% of the by-products which cannot be hydrolyzed to give formaldehyde.

2. Acetylation of the ends of the chains.

For reasons already given (117;page 92),acetylation of terminal amine nitrate groups is considered unlikely. The acetylation of terminal methylol groups (e.g.in LXXVII) on the other hand, is considered more probable (page 12). It is known to be very slow for O-methylol groups (125) but the rate has never been investigated for N-methylol groups.

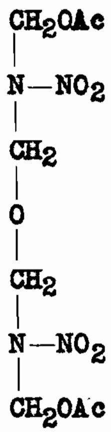


LXXVII LXXVIII

The formation of these compounds would, like that of the "mixed" rings, be favoured by an excess of paraform; and, like them, would explain the higher molar proportion of formaldehyde than of ammonium nitrate in the by-products when this condition obtains.

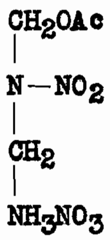
Unlike the mixed rings, however, they would also satisfy the requirement that the by-products must be hydrolyzable, so that almost all the acetic acid (126; page 66) and most of the formaldehyde can be accounted for on analysis of the boiled, diluted reaction liquor.

Acetylation may also stabilize various "mixed" compounds (e.g.LXXIX), and compounds with a terminal amine nitrate group (LXXX). Such compounds would be of the same general properties as LXXVII.



$\mathrm{CH_2OAc{-}N(NO_2){-}CH_2{-}O{-}CH_2{-}N(NO_2){-}CH_2OAc}$

LXXIX



$\mathrm{CH_2OAc{-}N(NO_2){-}CH_2{-}NH_3NO_3}$

LXXX

3. <u>Exhaustion of the Reactants.</u>

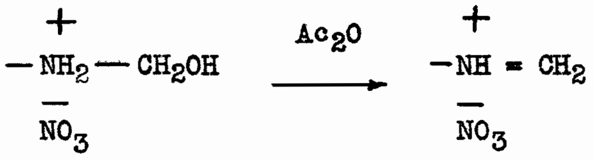
An excess of formaldehyde in the reaction mixture favours the formation of chains terminated by methylol groups; an excess of ammonium nitrate favours the formation of chains terminated by amine nitrate groups.

The chains terminated with methylol groups can form by-products by acetylation or by loss of water to form an ether linkage, as described above. The chains terminated by amine nitrate groups may possibly decompose, but more probably remain unchanged in the reaction liquor (page 127). They are not, like the derivatives of methylol-terminated chains, by-products, but unused intermediates. The reaction has ceased because there is no formaldehyde left to react with them.

The formation of such compounds would explain why a large excess of ammonium nitrate in the Continuous Addition Method causes a decreased yield of R.D.X. (page 47). In the Total Addition Method it has no such deleterious effect (page 37), probably because at high enough temperatures they are unstable, as the first member of the series, methylenediamine dinitrate, is at a lower temperature. The fact that an excess of ammonium nitrate gives "by-products" (or unused intermediates) containing more of this compound than of formaldehyde (page 99) would be explained by their formation.

This mechanism is in agreement with most of the facts known about the McGill Process. The results of the analytical work so far done on this process (Chapter VIII) are explicable in terms of the side-reactions postulated. The lengthy induction period, during part of which reaction is taking place as shown by the evolution of heat, indicates a mechanism involving many intermediate steps. And the indispensable nature of the acetic anhydride (pages 78,88, 121) is shown to be related to its function in converting the amine nitrate to a nitramine group.

At the same time, cognizance must be taken of some of the weaknesses of the mechanism. It does not take into account the possibility of dehydration of methylolamine (LXXXI) to methyleneimine (LXXXII) groups.



$$\underset{\overline{NO_3}}{\overset{+}{-NH_2}}-CH_2OH \xrightarrow{Ac_2O} \underset{\overline{NO_3}}{\overset{+}{-NH}}=CH_2$$

LXXXI LXXXII

It does not explain why the formation of H.M.X. is favoured by the Reversed Addition Method. (127) It does not explain the effects of catalysis and dilution (Chapter VI), and of many more experimental facts.

The mechanism has, however, the virtue of predicting the formation of certain types of as-yet unidentified by-products. Its verification will depend on their isolation. The other method of proof, that of attempting to form the intermediates by condensation of formaldehyde with ammonium nitrate in acetic acid, has so far proved unsuccessful (128). In view of the ease of decomposition of such compounds if formed (pages 10, 88) this result is readily understandable.

Summary

The effect of reaction conditions upon the yield of R.D.X. from the McGill Process has been studied with special attention to such variables as proportions of reactants, temperature and time of reaction, and mode of addition of reactants. An improved method of conducting the reaction, designated the Continuous Addition Method, is presented. This method enables the reaction to be controlled when run on a large scale, and under optimum conditions gives a yield of about 50%.

Methods of purification of this product have been investigated. It has been shown that there is no method of obtaining a product meeting the British Specifications for melting point without a large loss of the crude material.

The effect on the yield of R.D.X. caused by the addition of various compounds to the reaction mixture has been investigated.

An attempt has been made to elucidate the mechanism of the reaction by finding analogous reactions and by investigating the kinetics and the by-products of the reaction. On the basis of the chief characteristics of the reaction, a mechanism is proposed. This predicts the formation of several by-products as yet not isolated.

The author is aware of the unfinished character in many places of the work done. It cannot be judged by normal academic standards, however. Especially in the earlier period of development of the McGill Process, the work was oriented along industrial lines, and many avenues of research which appeared more of theoretical than of practical importance were not followed up.

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