WAR RESEARCH

THE MECHANISM OF THE DIRECT NITROLYSIS OF HEXAMINE

A Thesis

by

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FOREWORD

The investigations of the direct nitrolysis of hexamine prior to this research by the author were chiefly of a practical, rather than theoretical, nature. They involved mainly a search for the optimum conditions for reaction and suitable processes for the recovery of nitric acid and formaldehyde.

Towards the end of 1942, when the author's investigations were started, research on the direct nitrolysis of hexamine had ceased entirely in North America and had dwindled considerably in England.

The results of the research presented in this thesis caused a certain stimulus of interest in the nitrolysis reaction, promoting further investigations by other workers. However, these investigations were so interlocked with the author's work that any review of them prior to presentation of this work would be more or less incomprehensible.

To avoid this confusion, it was considered preferable to review in the historical introduction only the relevant work performed before research by the author was begun, reserving the subsequent work for later discussion.

Ph.D. Department of Chemistry

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THE MECHANISM OF THE DIRECT NITROLYSIS OF HEXAMINE

A kinetic study of RDX formation by the direct nitrolysis of hexamine indicates strongly that nitracidium ion is the active nitrolyzing agent. The rate of nitrolysis increases rapidly as the molar ratio of nitric acid to hexamine is increased, and continues to do so after the molar ratio is raised above that required for maximum yields. An upper limit to the initial rate exists at extremely high molar ratios.

Maximum yields of RDX are obtainable with nitric acid of all concentrations down to 88 per cent if sufficient nitric acid is used.

The main reason for the large excess of nitric acid required is apparently to maintain the concentration of nitracidium ion, which is lowered during nitrolysis by the production of water and nitrate ion.

An intermediate (PCX) in the nitrolysis of hexamine has been isolated. Its conversion to RDX probably represents the rate controlling step. Kinetic studies of the disappearance of hexamine dinitrate and of RDX producibility during nitrolysis have enabled an estimation of the rates of formation and decomposition of PCX. Other kinetic studies of the decomposition of PCX and of its conversion to RDX have been made.

A mechanism for RDX formation is postulated.

HISTORICAL INTRODUCTION

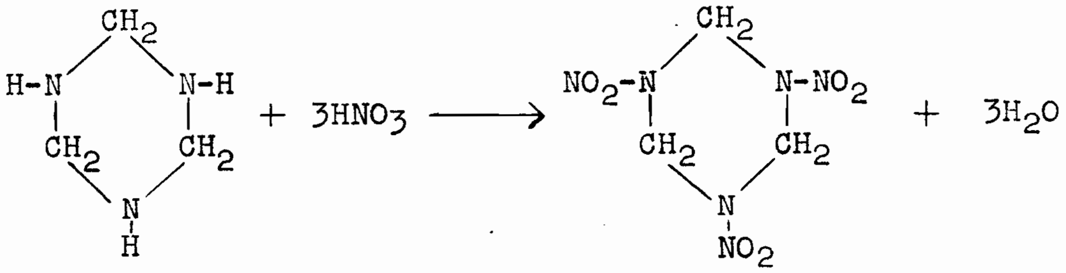
The nitrolysis of hexamethylene tetramine, now commonly referred to as hexamine, has been studied intermittently by a number of investigators ever since the discovery by Henning in 1899 (1) that the reaction of the nitric acid salt of hexamine with a large excess of cold, very concentrated nitric acid gave a substance having excellent explosive properties. Henning called this material Hexonite and took out a German patent for its preparation. More recently it has been called Hexogen by the Germans, French and Swiss, T_4 by the Italians, and Cyclonite or RDX by the British and Americans.

Henning first tried adding hexamine to 100 per cent nitric acid but found that violent decomposition to formaldehyde and ammonia interfered with nitration. He then prepared hexamine dinitrate by adding an aqueous solution of hexamine to concentrated nitric acid and added one part of the well-dried salt slowly to five parts (21 mols. per mol. of hexamine dinitrate) of 100 per cent nitric acid at -5°C. The mixture was left to react for 30 minutes and then poured into cold water to precipitate the RDX. This procedure gave 63 per cent of the theoretical yield, assuming that one mole of hexamine dinitrate can yield one mole of RDX.

The high cost of hexamine, whose preparation involved formaldehyde from methanol, resulted in comparatively little interest being shown in the new explosive until synthetic methanol was developed. Then between 1919 and 1922, Herz (2) took out German, British, Swiss and American patents covering the preparation and use of RDX as an explosive. Herz accomplished what Henning had found impossible to do, i.e., nitrate hexamine to RDX without first obtaining the nitric acid salt. He added dry hexamine, in small portions, with stirring to 7.1 parts of 100 per cent nitric acid at 20 to 30°C. After all the hexamine had dissolved, the temperature was raised to 55°C. for five minutes. The mixture was then cooled to about 20°C. and diluted with four volumes of water to precipitate the RDX. The yield was not reported.

Henning did not propose any structure for his explosive, but merely concluded, from an elemental analysis, that the empirical formula was $C_3H_6O_6N_6$. Herz, however, called his product cyclotrimethylenetrinitramine and was the first to postulate any kind of a mechanism for its formation. He suggested that the hexamine was converted first to the hypothetical cyclotrimethylenetriamine and the explosive was obtained by the action of nitric acid on this intermediate.

Thus



No proof for the structure of the nitramine or for the postulated mechanism was given.

The next published work in this field was that of Hale in 1925 (3) who found difficulty in repeating the procedure of Herz without the occurrence of a violent and uncontrollable oxidation or fume-off. In the light of later work it appears that this may have been due to insufficient stirring accompanied by too rapid addition of the hexamine, the result being local over-heating. Another possibility is that the nitric acid contained too much nitrogen tetroxide.

Increasing the quantity of nitric acid to 11 parts per part of hexamine and cooling with ice enabled Hale to carry out the reaction smoothly without fume-offs using 92 per cent nitric acid, but the use of 100 per cent nitric acid necessitated working at -20°C. Eleven parts of 92 per cent nitric acid at 0°C. gave yields of RDX up to 68 per cent, while the same quantity of 100 per cent acid at -20°C. gave a maximum yield of 74.4 per cent. These yields were calculated on the basis that 1 mole of RDX is produced from 1 mole of hexamine. Eighty per cent nitric acid gave only a trace of RDX and 70 per cent none at all. Hale found that there was no advantage in increasing the proportion of nitric acid above 11 parts to 1 part of hexamine, but this represents a very large excess, being 25.4 mols. per mol. of hexamine for 100 per cent nitric acid.

Hale also investigated the nitrolysis of hexamine dinitrate using several concentrations of nitric acid at different temperatures. His maximum yield of 49 per cent was obtained at 30°C. with 95 per cent acid, the highest concentration studied. He considered the nitrolysis of hexamine dinitrate to be a reaction quite different from the nitrolysis of hexamine itself and apparently did not realize the effect of the molar ratio of nitric acid to hexamine dinitrate upon the yield of RDX. His relatively low yields are at least partially explained by the fact that he used consistently a 5 to 1 weight ratio of nitric acid to hexamine dinitrate with nitric acid concentrations of only 80 to 95 per cent. This represents a molar ratio of acid to hexamine dinitrate of 17 to 20, depending on the acid concentrations.

In an attempt to discover the fate of the remainder of the hexamine which did not go to RDX, Hale analyzed the nitration mixture for formaldehyde, carbon dioxide, carbon monoxide, methylamine, ammonia and, after neutralization, for hexamine. He concluded that approximately 15 per cent of the original hexamine was left after the reaction and suggested that this had not been nitrated because it had first been converted to hexamine dinitrate. This view is untenable after considering more recent work (22) and will be discussed later.

The first industrial RDX plant mentioned in the literature was operated by the Nobel Dinamite Co. at Avigliana, Italy (4). The process, which involved the preliminary isolation of hexamine dinitrate, was patented in several countries including France and Britian in 1932 and 1933. Formaldehyde was produced from methanol formed by the oxidation of water gas and was then converted to hexamine which was either dried and treated with dilute nitric acid or preferably precipitated from acid solution as the dinitrate.

One part of hexamine dinitrate was then added to 6 or 7 parts of very concentrated nitric acid, cooled below 15°C. during the addition. Later the temperature was allowed to rise to 30°C. where it was held for one hour.

Cooling the solution to $0^{o}C$. precipitated 60 per cent of the RDX. The mother liquor from this was distilled under vacuum at a temperature not exceeding $40^{o}C$. The recovered nitric acid was used again. The residue was cooled, more RDX recovered, and the mother liquor again distilled under vacuum. The solution was finally diluted to 45 per cent nitric acid to precipitate the remainder of the RDX. Formaldehyde was recovered from this mother liquor by distillation after neutralizing the acid with chalk. In this way the consumption of formaldehyde was halved. Other technical details were described in a paper by Grottanelli.(5)

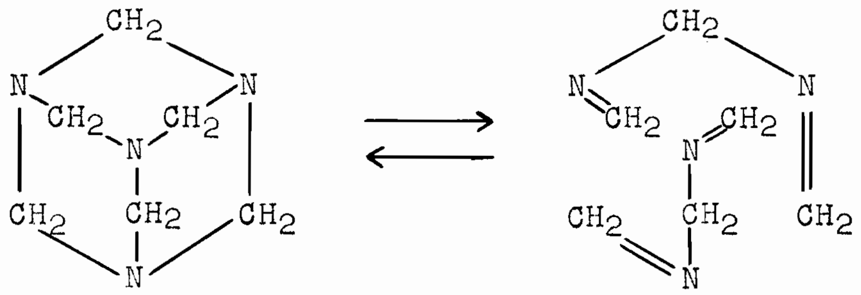
The only other material published in the open literature dealing with the subject describes miscellaneous studies of minor importance. Desvergnes (6) determined the solubility of RDX in twelve different organic solvents and reported a melting point of $203.5^{o}C$., dec., after acetone recrystallization. Previously the highest melting point reported by several workers had been $202^{o}C$. Desvergnes also attempted to nitrate hexamine with sulphuric acid - sodium nitrate and sulphuric acid - nitric acid mixtures without success. Desvergnes and Sollazzo (7) both reported low yields of 30 and 38.5 per cent, respectively, from the nitrolysis of hexamine.

The Research Department of the Royal Arsenal, Woolwich, has studied the direct nitrolysis of hexamine during the past decade but, for purposes of secrecy, none of the work has been published in the open literature. After the start of World War II, a series of reports on this work was circulated through official channels to the various laboratories engaged in war research on RDX. The remainder of the Historical Introduction deals with secret reports of this nature.

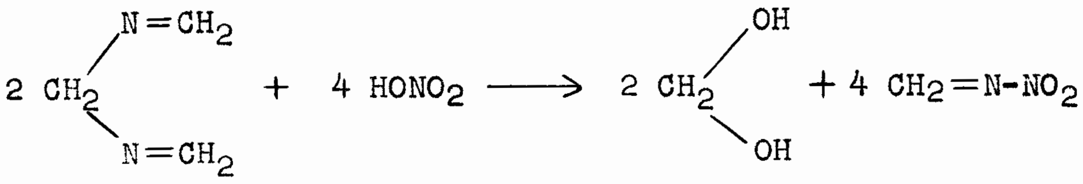
A major development of the Research Department was a continuous process for the industrial manufacture of RDX(8). Hexamine was nitrated continuously at 25-30°C. with 97 per cent nitric acid, the potential formaldehyde not used in the formation of RDX being converted simultaneously to unstable nitrated derivatives. The nitration mixture was diluted hot with a "controlled fume-off" in which the unstable formaldehyde derivatives were oxidized by nitric acid. The RDX was precipitated in a granular crystalline form and after cooling was separated by filtration. The mother liquor was 55 per cent nitric acid. This, along with the oxides of nitrogen evolved during the fume-off, was mixed with sulphuric acid and converted to 97-98 per cent nitric acid in Pauling towers. The RDX was washed and purified by passing steam into its aqueous suspension.

In developing this process, the Research Department made extensive analyses of the nitration system before and after the fume-off (9,10,11), and studied the effect of the formaldehyde nitration products, designated P_1 and P_2, on the stability of the system (9,16). Other investigations included attempts at stabilization by adding urea and hydrogen peroxide (12,14,15), and a large number of miscellaneous attempts to synthesize RDX by other methods, all of which were unsuccessful(17).

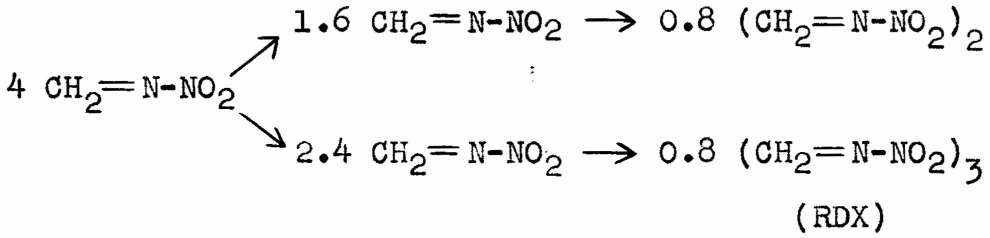
The original mechanism postulated by the Research Department for the nitrolysis of hexamine (10,18) was designed to account for all the experimental facts previously found. The initial reaction occurring when the hexamine dissolved in the nitric acid was assumed to be a depolymerization of the hexamine molecule to "hemihexamine", involving the fission of four bonds:



This intermediate was then attacked by the pseudo form of nitric acid as follows:



The monomeric methylene nitramide so formed may be viewed as a condensation product of formaldehyde and nitramide. A subsequent polymerization of this compound was postulated, giving a dimer and trimer in equal proportions:



$$4\ CH_2{=}N{-}NO_2 \begin{cases} \nearrow 1.6\ CH_2{=}N{-}NO_2 \longrightarrow 0.8\ (CH_2{=}N{-}NO_2)_2 \\ \searrow 2.4\ CH_2{=}N{-}NO_2 \longrightarrow 0.8\ (CH_2{=}N{-}NO_2)_3\ \text{(RDX)} \end{cases}$$

The trimer is RDX. The dimer was assumed to be stable in the concentrated nitric acid but to hydrolyze on dilution with water to formaldehyde and nitramide:

$$(CH_2{=}\ N{-}NO_2)_2 + 2\ H_2O \longrightarrow 2\ CH_2O + 2\ NH_2NO_2$$

Nitramide is known to decompose on warming:

$$NH_2NO_2 \longrightarrow N_2O + H_2O$$

This agreed with the known fact that at 70-90°C. a brisk evolution of nitrous oxide occurred from nitrolysis mixtures.

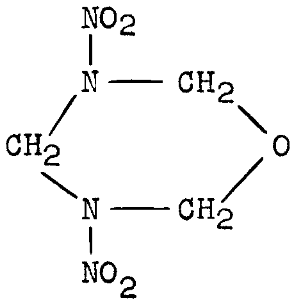
Hale (3) had observed that a small amount of nitrogen was given off from the reaction mixture at 20°C. This was attributed by the Research Department to:

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

or $$CH_2O + N_2O \longrightarrow HCOOH + N_2$$

the nitrous oxide in this case being considered capable of oxidizing the liberated formaldehyde.

By evaporating a large bulk of nitrolysis mixture after fume-off, the Research Department workers (10,18) were able to isolate a compound having the structure:



This compound was named cyclonite oxide by Wright (22,27) who found it to be an impurity in the hexamine from his formaldehyde recovery process described later. It was soluble in acids and water but apparently not easily hydrolyzed. Its formation was represented as occurring through the condensation of formaldehyde with the dimer of methylene nitramide.

Previous work (9) by the Research Department had also shown that P_1 and P_2, formaldehyde nitration products, were present in the nitrolysis mixture and could be at least partially extracted with chloroform. The occurrence of these compounds was accounted for by a nitration of the formaldehyde liberated during the initial reaction of nitric acid with the depolymerized hexamine.

The susceptibility of the nitrolysis mixture on dilution or heating to the violent decomposition, or fume-off, was attributed to a series of reactions involving:

(a) hydrolysis of the dimer of methylene nitramide to formaldehyde and nitramide,

(b) decomposition of nitramide to nitrous oxide and water,

(c) hydrolysis of P_1 and P_2 to formaldehyde, nitric and nitrous acids,

(d) oxidation of formaldehyde by nitric acid to carbon dioxide, nitrogen tetroxide and water,

(e) oxidation of formaldehyde by nitrous oxide to carbon dioxide, water and nitrogen.

Reaction (d) is catalyzed by nitrogen tetroxide or nitrous acid. It is therefore autocatalytic and initiated by reaction (c).

Detailed balanced equations of the above reactions were worked out by the Research Department on the basis of their experimental data. Although the postulated mechanism accounted for the known facts, there was no conclusive evidence or proof that it was the correct one. Indeed, the theory received much criticism, as will be seen later.

The Research Department was the first to attempt nitrolyzing hexamine isothermally to study the effect of temperature on the rate of reaction(13). The procedure was as follows:- 10 g. of hexamine was added during 2 minutes to 110 g. of 98 per cent nitric acid at a temperature slightly below that selected for the particular experiment. Solid carbon dioxide, added alternatively with hexamine, was used to control the temperature. The mixture was kept at the specified temperature for various lengths of time, and then poured onto ice.

Insufficient points in the early stage of reaction were obtained to draw complete reaction-time curves. The trend of the results is illustrated in the table below.

Reaction Temperature (°C.)	Time	Yield (%)
- 25	2 min.	5.91
"	5 hrs.	44.23
- 15	2 min.	22.15
"	6 hrs.	73.62
0	2 min.	49.65
"	2 hrs.	81.85
10	2 min.	56.13
"	30 "	80.97
20	2 min.	71.80
"	10 "	80.67
30	2 min.	78.50
"	10 "	80.17
40	2 min.	77.31
"	20 "	80.24

The reaction times indicated for yields greater than 80 per cent correspond roughly to the minimum time for complete reaction. Where the higher yield at any given temperature is below 80 per cent, the reaction was still incomplete.

At the higher temperatures the maximum yield was considerably below 80 per cent, varying from 72 per cent at 50°C. to 51 per cent at 70°C. The rate of reaction at these temperatures was extremely high, the maximum yield being obtained within 2 minutes.

It was observed that the initial addition of a small quantity of hexamine to concentrated nitric acid in a nitrolysis experiment produced a very marked rise in temperature. Towards the end of the hexamine addition the temperature did not rise so rapidly and was easier to control. It was concluded that the dilution of the acid, by nitrolysis of the initial hexamine added, had a marked effect on the respective velocities of the reactions involved.

The same report (13) by the Research Department describes experiments in which ammonium nitrate, equal in weight to the hexamine used, was added to the nitrolysis reaction. Adding the ammonium nitrate before the hexamine, decreased the yield from a reaction at 20°C., but increased the yield at 50°C. almost to 80 per cent. Adding the ammonium nitrate after the nitrolysis was complete at 20°C., followed by warming to 50°C. for 30 minutes increased the yield of RDX to 84.5 per cent; warming to 60°C. for 30 minutes increased the yield to 85.7 per cent. Longer periods of heating at 50 to 60°C. resulted in degradation of RDX. These experiments indicated a synthesis of RDX at high temperatures and are of interest with regard to work referred to later.

Two attempts (13) to synthesize RDX by nitration of paraformaldehyde with a 20:75 weight ratio of ammonium nitrate : nitric acid were unsuccessful as, on warming, decomposition began before any RDX had been formed.

In 1940, G.F. Wright in Canada and F.C. Whitmore in the United States began independent investigations of the nitrolysis of hexamine. Their findings were substantially in agreement with those of the Research Department.

Following Hale's procedure Wright found (19) that decreased yields were caused by local overheating during the initial mixing of hexamine and nitric acid. By adding the hexamine mixed with solid carbon dioxide, he was able to increase the yield from 75 per cent, the best reported by Hale, to 82 per cent. Wright usually worked with nitric acid : hexamine molar ratios of 22:1 to 32.5:1 and with nitric acids of 89 to 100 per cent. His yields with the acids in the lower concentration range are not of great significance because it is not clear what ratio of acid to hexamine was used. He, like most other contemporary workers, apparently did not realize the effect of this ratio upon the yield from the less concentrated acids.

From a preliminary nitrolysis of hexamine dinitrate with 22.5 moles of 92 to 93 per cent nitric acid per mole of dinitrate, Wright (20)obtained a 59 per cent yield of RDX. On adding a solution of hexamine in chloroform to concentrated nitric acid during a nitrolysis (21), he observed that a white turbidity, caused by the formation of hexamine dinitrate, occurred as each drop of solution came into contact with the acid. Since the yields from such nitrolyses were almost identical with those in which dry hexamine was added, Wright questioned his low yield, and those of Hale (3), from the nitrolysis of hexamine dinitrate. A subsequent report (22) described an experiment in which hexamine dinitrate was added slowly to 100 per cent nitric acid (amount unspecified) to give an 84 per cent yield of pure RDX, m.p. 203°C. Wright concluded that Hale was in error and that RDX was formed entirely via hexamine dinitrate as intermediate.

Experiments (22) in which 22 equivalents of 99 per cent nitric acid was added to a stirred solution of hexamine in chloroform at 0°C. and at room temperature gave low yields of RDX, even when additional acid was added later to make the acid : hexamine molar ratio 32:1. This indicated the importance of keeping the hexamine in contact with a large excess of pure nitric acid at all times during the reaction.

Whitmore (23) investigated the effect of the nitric acid concentration upon the yield of RDX for the ratio of acid : hexamine of 10:1 by weight. The hexamine was added over a period of 30 minutes to the stirred nitric acid below 0°C. and the mixture was allowed to stand another 30 minutes, apparently without further cooling, before dilution. He found an almost linear relation between yield and acid concentration for concentrations of 87 to 99 per cent nitric acid, the yield from the former concentration being zero, and from the latter, about 90 per cent. There was no indication, however, that sufficient time had been allowed for complete reaction with the lower concentrations of nitric acid. The high yield of 90 per cent from 99 per cent nitric acid has not been confirmed by work in other laboratories. No indication of the purity of this product was given.

Using approximately the same nitration technique, Whitmore studied the effect of varying the ratio of nitric acid to hexamine, but only with 98 per cent nitric acid. The results, which are essentially in agreement with those of Hale(3) and the Research Department (10), indicate that about eleven parts of 98 per cent nitric acid to one part of hexamine is necessary for the maximum yield; increasing the nitric acid to twenty parts gave no improvement. Below eleven parts of acid, the yield decreased linearly to 64 per cent with eight parts.

Whitmore also studied the effect of the initial temperature upon the yield of RDX. For this series of experiments, ten parts of 98 per cent nitric acid was maintained at the selected temperature for 40 to 60 minutes while one part of hexamine was added slowly. The mixture was allowed to stand another 60 minutes at room temperature before diluting. He varied the initial reaction temperature from -40°C. to 52°C. and found the yield to be unaffected by temperature below 5°C. Above this point, however, the yield decreased sharply to 53 per cent at 52°C. The yields begin to decrease at a lower temperature and fall off more rapidly than those recorded by the Research Department (13), presumably owing to the minor difference in procedure.

Whitmore designed two continuous reactors for the nitrolysis of hexamine. One of these was of glass and produced RDX in 80 per cent yield at the rate of 0.8 pound per hour. The other was constructed of aluminum and produced RDX in 72 per cent yield at the rate of two pounds per hour.

Two methods of purification were used by Whitmore. In the first the product was poured with stirring into three or four parts of water, filtered, washed with water and dried overnight at 90°C. The product so obtained was finely-divided, fluffy, and held water tenaciously. Crystallization could be carried out from 70 per cent nitric acid, acetone, or 1-nitropropane. The second and better method was to use a "controlled fume-off" similar to that used by the Research Department in their continuous process (8). This gave a nicely crystalline product, free from contaminants, and decomposed only a small fraction of the RDX.

The effect of adding solvents and other compounds was studied at this time by both Wright and Whitmore. No increase in yield, but usually a decrease, was observed. Chloroform (19,22) and nitromethane (24), were the only solvents which did not affect the reaction appreciably. Acetic acid (6,19,25) and acetic anhydride (12) were both shown to have harmful effects. Sulphuric acid (19,23) decreased the yield and gave an impure product.

Whitmore (23) studied the effects of a large number of inorganic salts. His normal procedure without addition of a salt gave a yield of 70 per cent. When potassium nitrate formed 33 per cent of the nitration mixture only a ten per cent yield of RDX was obtained. Smaller amounts had proportionate effects. Potassium bisulphate reduced the yield to 53 per cent when five per cent was added, and caused a fume-off when sixteen per cent was added.

The effect of ammonium nitrate as observed by the Research Department has been mentioned previously. Whitmore reported that the yield was lowered to 65 per cent by the presence of five percent ammonium nitrate and to 39 per cent by the presence of sixteen per cent. Wright (19) recorded a yield of only nine per cent following the saturation of 90 to 93 per cent nitric acid with ammonium nitrate. Without the ammonium nitrate, this acid gave a 55 per cent yield.

The presence of appreciable amounts of nitrous acid or nitrogen tetroxide in the nitric acid was shown to increase the susceptibility of the nitration mixture to fume-off (23), but neither Whitmore nor Wright (19) observed any decrease in yield when sodium nitrite was added in amounts of 1.5 and 3 per cent, respectively. However, recent and more accurate work (26) by the Armament Research Department (formerly the Research Department) has indicated that for each 0.1 per cent nitrous acid in the nitric, the yield decreases by 1.3 and 1.8 per cent with the acid:hexamine weight ratios of 15:1 and 10:1, respectively. The velocity of the side reaction involving nitrous acid appeared to be slow compared with the normal velocity of nitrolysis to RDX. Assuming that a decrease in the amount of nitric acid would not affect the reaction of nitrous acid but would retard the nitrolysis, the greater loss in yield when using less nitric acid is to be expected.

The two major weaknesses of the preparation of RDX by the direct nitrolysis of hexamine are (a) the loss of half of the potential formaldehyde in the hexamine, and (b) the relatively large amount of very concentrated nitric acid required. The recovery of unused formaldehyde, the most valuable raw material, has been the object of many investigations. In the Italian process for manufacturing RDX previously described, most of the nitric acid was distilled under vacuum from the undiluted reaction liquor, then the residue was diluted, neutralized with chalk, and formaldehyde was distilled off. A disadvantage of this method was the danger of explosion of the unstable liquor during distillation.

The Research Department developed a formaldehyde recovery process (15) in which the nitration liquor was diluted with water, containing a little hydrogen peroxide as stabilizer, to give a concentration of 40 per cent nitric acid. After cooling, the RDX, was filtered off. The mother liquor was diluted to 20 per cent nitric acid and fed continuously through a fractionating system. In this way formaldehyde was removed without neutralization. This process was successful on a laboratory scale but has not been used on a plant scale.

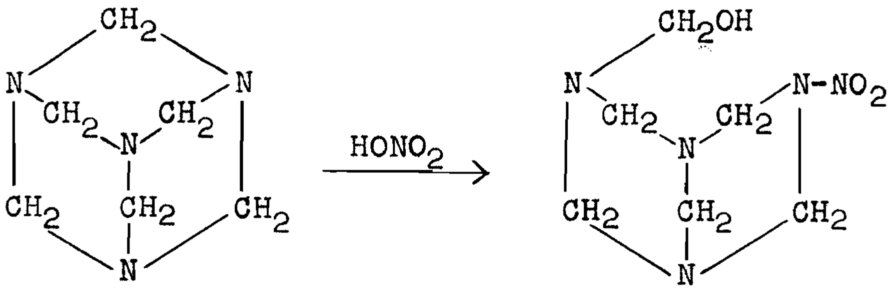
Wright (27) discovered that it was unnecessary to separate the formaldehyde by distillation. Instead, he neutralized the undiluted reaction liquor with aqueous ammonia, converting the nitric acid to ammonium nitrate and the potential formaldehyde to hexamine. The precipitated RDX was filtered off and the hexamine extracted from the filtrate with chloroform. Ammonium nitrate was recovered by evaporation of the aqueous layer, and hexamine by evaporation of the chloroform extract. This process was operated on a continuous pilot plant scale in conjunction with a continuous nitrator for hexamine which gave 78 to 79 per cent yields of RDX. Whereas exhaustive laboratory extractions had shown that about 95 per cent of the re-formed hexamine could be recovered (28), the continuous extractor gave approximately 70 per cent hexamine recovery only. This lower efficiency was attributed to insufficient length of the extraction column.

In October, 1941, a monograph on the chemistry of RDX by R.P. Linstead (29) was circulated. This was a comprehensive review of the available literature to date with some accompanying theoretical discussion of reaction mechanisms. Besides the direct nitrolysis of hexamine and properties of RDX, the paper dealt with other preparative methods for RDX just previously discovered. These were the McGill Process, involving the reaction of paraformaldehyde with ammonium nitrate in the presence of acetic anhydride at 70°C., and the Bachmann or Combination Process which permits hexamine to react with nitric acid and ammonium nitrate in the presence of acetic anhydride and acetic acid at 70°C.

Linstead's discussion of the mechanism of the reaction between hexamine and nitric acid is interesting and original. He criticized the mechanism postulated by the Research Department involving a depolymerization of the hexamine molecule and formation of the monomeric methylene nitramide.

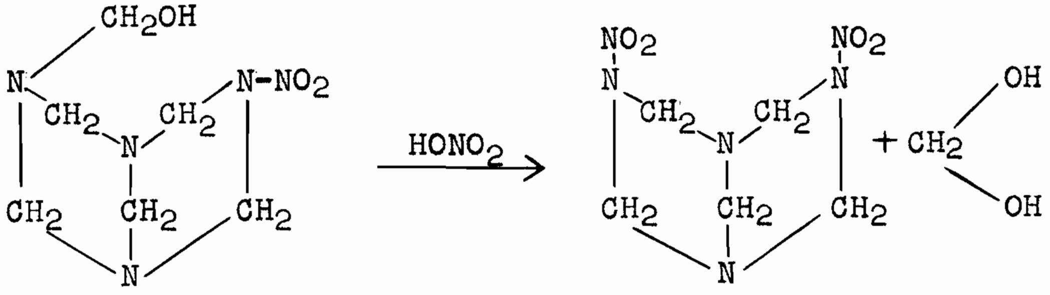
He pointed out that there was a considerable bulk of evidence that formaldehyde does not condense with nitramide to give RDX. Unless formaldehyde completely fails to condense with nitramide, the possibility that methylene nitramide is an intermediate to RDX seems unlikely. Linstead also suggested that the mechanism failed to account satisfactorily for the evolution of nitrogen, and that the initial depolymerization was open to objection on general grounds.

The following mechanism involving the preservation of a six-membered ring was then postulated by Linstead. The initial attack of nitric acid on hexamine was presumed to be a nitrolysis of a C - N bond, and as all such bonds of the hexamine molecule are identical, the initial fission must be



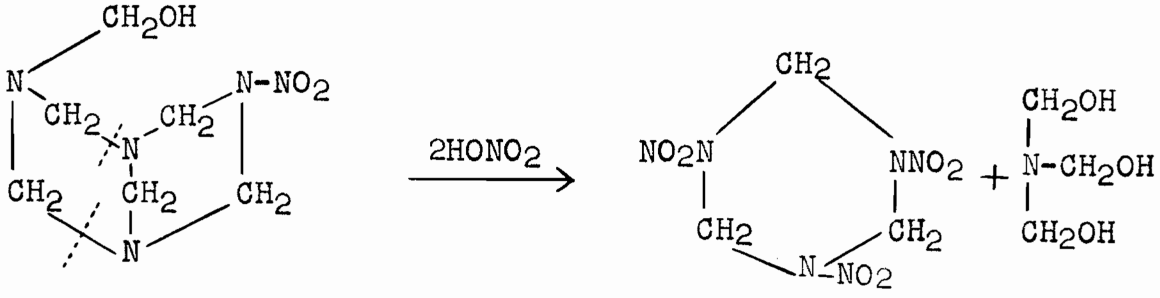
The central point of the hypothesis was that if such an unsymmetrical intermediate were formed, a rapid stepwise crumbling of the molecule would occur until the stable stage of RDX was reached.

The second step was considered to be one of several possible reactions. One of these was the following:



The dinitropentamethylenetetramine so postulated, however, was later isolated (30) as the product of other reactions and was shown to react with 98 per cent nitric acid to give no RDX but a 34 per cent yield of HMX, the eight-membered ring compound analogous to RDX. This precludes the possibility of the above reaction occurring, since only a trace of HMX is found with the RDX from the direct nitrolysis of hexamine.

One of the alternative possibilities for the second step of the mechanism was another nitrolysis, similar to the first, followed quickly by a third. This would liberate a trimethylolamine fragment:



Linstead pointed out, however, that there was no evidence for the existence of such a fragment in the nitrolysis liquor, and that it seemed more likely that after each nitrolysis the methylol group was hydrolyzed off as formaldehyde. The formaldehyde would then be converted to its nitration products, P_1 and P_2, and the nitrogen atom, if liberated as ammonia, would be fixed as ammonium nitrate.

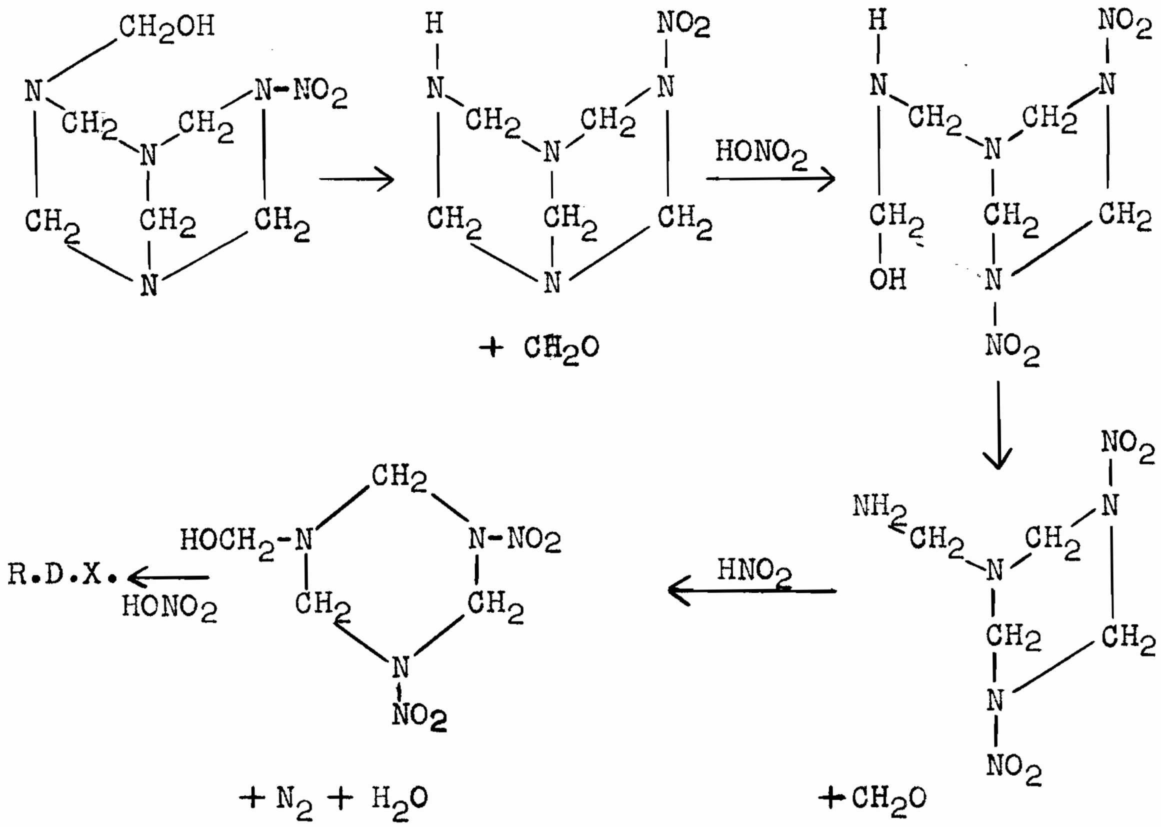
Linstead recognized the plausibility of Hale's suggestion (3) that the evolution of nitrogen occurring during the nitration at room temperature was caused by the decomposition of ammonium nitrite. This might be formed by a reaction of the liberated ammonia with nitrous acid either present in the original acid or formed from side reactions.

According to Linstead's ring hypothesis, however, it was not essential that ammonia be liberated to account for the nitrogen evolution. Instead it might be explained by the formation and decomposition of a primary amine nitrite. According to the Research Department mechanism nitrogen comes from the side reactions (10,18):

$$CH_2{=}N\text{-}NO_2 \longrightarrow NH_2NO_2 \longrightarrow N_2O \longrightarrow N_2$$

Linstead was dubious about the supposed reduction of nitrous oxide to nitrogen by formaldehyde. He pointed out that the Research Department had shown (17) that nitramide dissolved in formalin with the formation of nitrous oxide, not nitrogen.

Linstead's ring hypothesis assumed the formation of nitrogen to be an integral part of the main reaction:



The formation of water was ascribed solely to side reactions such as the esterification of methylol groups and the nitration of formaldehyde. It was presumed that the water liberated was partly used in the hydrolysis of hexamine to formaldehyde and ammonia. Thus more water would be formed from the nitration of this formaldehyde. Linstead believed this cycle of reactions to be responsible for the fact that the maximum yield was only of the order of 80 per cent.

Contrary to the suggestion of Wright (22), Linstead did not regard hexamine dinitrate as an intermediate, but found it preferable to assume (a) that in the nitric acid the hexamine was in equilibrium with the dinitrate, the composition of any mixture depending upon the concentration of nitric acid and of water; (b) that the nitration probably involved an attack on hexamine itself; (c) that the equilibrium was then displaced and more hexamine was formed from the dinitrate. Thus there should be no difference between the behaviour of hexamine and its dinitrate in the nitrolysis reaction.

KINETICS OF RDX FORMATION

The object of the kinetic investigations was to obtain more information about the mechanism of the nitrolysis of hexamine, with a view to understanding better the function of the large excess of very concentrated nitric acid required for good yields of RDX. When these investigations were started, there was little experimental evidence to indicate the probable course of the reactions responsible for the conversion of hexamine or hexamine dinitrate to RDX. The mechanism postulated by Linstead, in which the six-membered ring was preserved, accounted for all the known experimental data practically as well as that postulated by the Research Department involving a break-down to a one-carbon intermediate.

The nitrolysis of hexamine had been studied isothermally only by the Research Department (13), and of the three variables, acid concentration, acid : hexamine ratio, and temperature, only the influence of the latter had been investigated under isothermal conditions.

The reaction kinetics had not been studied previously under any conditions, possibly because of the difficulty of maintaining constant temperature when the reactants were mixed, owing to the highly exothermic reaction of hexamine with nitric acid to form hexamine dinitrate. A rapid rise in temperature accompanies rapid addition of hexamine to nitric acid despite vigorous shaking of the reaction mixture in a constant-temperature bath. On the other hand if the hexamine is added slowly, both the rate of reaction and the final yield of RDX are altered.

These difficulties were overcome in the present work by using hexamine dinitrate and by adding it to nitric acid at -40°C., where reaction is negligible in acids of concentrations below 95 per cent. To start the reaction, the flask containing the reaction mixture was immersed, and shaken, in a constant-temperature water bath at 0°C.

The use of hexamine dinitrate instead of hexamine is justified since there is ample evidence from results to be presented later, and from independent investigations, that hexamine dinitrate is intermediate in the formation of RDX from hexamine, and is formed extremely rapidly. For example, Wright observed (22) that hexamine dinitrate was momentarily precipitated when a chloroform solution of hexamine came into contact with nitric acid during a nitrolysis reaction giving the full yield of RDX.

Additional confirmation that hexamine dinitrate is an intermediate in the reaction is furnished by the work of Gilpin and Winkler (31) who showed that the heat of formation of hexamine dinitrate from hexamine plus the heat of nitrolysis of hexamine dinitrate to RDX is equal to the heat of nitrolysis of hexamine to RDX. The advantage in using hexamine dinitrate for the kinetic study is evident from the fact that the heat of nitrolysis of hexamine dinitrate to RDX is only 41.7 Kcal. per mole, whereas the heat of nitrolysis of hexamine to RDX is 88.0 Kcal. per mole.

Experimental Procedure

In calculating the molar ratio of nitric acid to hexamine, the two molecules of nitric acid in combination with hexamine as the dinitrate were included with the value for free nitric acid used in the nitrolysis. Thus the same molar ratios, and all results, should apply to the use of hexamine as well as hexamine dinitrate.

All the reactions except one (Table VI) have been studied in a constant-temperature bath at 0°C., and this temperature is to be assumed unless otherwise stated.

The nitric acid generally used was light yellow in colour, but the results agreed within the experimental error with those obtained with colourless nitric acid. Acids of the desired concentrations were obtained by diluting 97-98 per cent nitric acid with water or colourless 70 per cent nitric acid, keeping the temperature below 10°C. during the dilution. The acid concentrations were checked by titration with standard sodium hydroxide solution.

Nitric acid of the proper concentration and amount was cooled in 125-ml. Erlenmeyer flasks to about -40°C. by immersion in a solid carbon dioxide - acetone bath. A 1.90 gm. sample of hexamine dinitrate was added to each flask which was then immediately immersed in a bath containing chopped ice and water at 0°C., and shaken mechanically. Each flask was stoppered with a paraffin-coated cork fitted with a glass tube leading outside the bath. This permitted the escape of evolved gases and prevented moisture from entering and diluting the reaction mixture.

It was found experimentally that one minute was required for the reaction mixture, made at -40°C., to warm up to the reaction temperature (0°C.) and allowance has been made for this in the reaction times as tabulated.

The reactions were quenched after various intervals by diluting with cold distilled water to ten times the original volume of the liquor. Final, or end-point, yields were obtained by allowing the reaction to proceed at 0°C. for approximately 20 hours before diluting. The diluted liquors were allowed to stand overnight for complete precipitation of the RDX, then filtered through weighed sintered-glass Gooch crucibles, washed with water, and dried at 90°C. for 12 hours.

The solubility of RDX in the diluted liquors was determined by dissolving one gram samples of RDX in the concentrated acid, then diluting and filtering under the same conditions as described above for a nitrolysis experiment. For molar ratios of nitric acid : hexamine less than 25:1, the correction for solubility loss was negligible, but for ratios of 100:1 and higher, the correction amounted to several per cent of the theoretical yield of RDX. All the yields as tabulated have been corrected for the appropriate loss of RDX by solubility in the diluted liquors.

Unless otherwise stated all percentage yields have been calculated on the basis of the theoretical assumption that one mole of RDX is produced from one mole of hexamine or hexamine dinitrate. Thus, from 1.90 gm. of hexamine dinitrate the theoretical yield of RDX is 1.585 gm. For one graph the yield of RDX has been calculated on the nitric acid basis and plotted against the molar ratio of hexamine to nitric acid. This calculation is based on the assumption that one mole of RDX is produced from three moles of nitric acid.

Initial rates of RDX formation were estimated by drawing tangents to the rate curves at zero time and reading the slope in per cent of theoretical yield per minute.

Results

Effect of Nitric Acid : Hexamine Ratio upon Rate of RDX Formation

The rate of RDX formation at $0^{o}C$. has been studied with various molar ratios of reactants, for nitric acid concentrations of 97,94,91 and 88 per cent, respectively. The results of these experiments are given in Tables 1 to 4 and are shown graphically in Figures 1 to 4. In Figure 4 a comparative curve is given for the use of hexamine instead of hexamine dinitrate, and it is seen that for the same molar ratio of nitric acid to hexamine, the rate curves for hexamine and for hexamine dinitrate coincide exactly. This is evidence that hexamine is converted extremely rapidly to hexamine dinitrate under these conditions.

The similarity of the rates of RDX formation with nitric acids of different concentrations when an appropriate molar ratio of reactants is used is evident from a survey of these families of curves (Figures 1-4). To

TABLE I

Kinetics of RDX Formation with 97% Nitric Acid

Hexamine dinitrate = 1.90 gm. (0.0071 mole)
Temperature of reaction = 0°C.

Molar Ratio[*] HNO_3/Hexamine	Time (min.)	RDX (gms.)	Yield (%)
100	3	1.280	80.8
"	6	1.312	82.8
"	10	1.324	83.7
"	20	1.349	85.2
26	5	0.566	35.7
"	10	0.867	54.7
"	16	0.966	60.9
"	43	1.184	74.7
"	120	1.290	81.6
22	7	0.465	29.3
"	14.5	0.636	40.1
"	45	0.921	58.1
"	120	1.126	71.2
18	15	0.365	23.0
"	30	0.436	27.5
"	62	0.585	36.9
"	120	0.745	47.0

---

[*] Includes the 2 mols. of HNO_3 in hexamine dinitrate.

TABLE II

Kinetics of RDX Formation with 94% Nitric Acid

Hexamine dinitrate = 1.90 gm. (0.0071 mole)
Temperature of reaction = 0°C.

Molar Ratio* HNO_3/Hexamine	Time (min.)	RDX (gms.)	Yield (%)
35	8	0.636	40.1
"	25	1.011	63.7
"	60	1.167	73.6
"	120	1.228	77.6
28	15	0.544	34.3
"	30	0.728	45.9
"	60	0.924	58.2
"	120	1.037	65.6
22	15	0.235	14.8
"	30	0.359	22.7
"	60	0.502	31.7
"	120	0.598	37.7
18	15	0.096	6.0
"	30	0.124	7.8
"	60	0.179	11.3
"	120	0.261	16.5

---

* Including the 2 mols. of HNO_3 in hexamine dinitrate.

TABLE III

Kinetics of RDX Formation with 91% Nitric Acid

Hexamine dinitrate = 1.90 gm. (0.0071 mole)
Temperature of reaction = 0°C.

Molar Ratio[*] HNO_3/Hexamine	Time (min.)	RDX (gms.)	Yield (%)
45	14	0.604	38.1
"	30	0.859	54.2
"	60	1.029	65.0
"	120	1.145	72.4
30	10.5	0.213	13.4
"	21	0.370	23.3
"	33	0.447	28.2
"	60	0.587	37.0
"	120	0.709	44.6
26	14	0.125	7.9
"	18	0.159	10.0
"	31	0.252	15.9
"	60	0.407	25.7
"	120	0.459	28.9
22	10	0.046	2.9
"	30	0.127	8.0
"	60	0.182	11.5
"	120	0.247	15.6

---

[*] Including the 2 mols. of HNO_3 in hexamine dinitrate.

TABLE IV

Kinetics of RDX Formation with 88% Nitric Acid

Hexamine dinitrate = 1.90 gm. (0.0071 mole)
Temperature of reaction = 0°C.

Molar Ratio[✱] HNO_3/Hexamine	Time (min.)	RDX (gms.)	Yield (%)
110	15	0.586	37.0
"	36	0.853	53.9
"	66	1.063	67.2
"	120	1.155	73.0
60	15	0.257	16.2
"	30	0.457	28.8
"	62	0.649	40.9
"	120	0.799	50.4
26	44	0.068	4.3
"	82	0.082	5.2
"	140	0.114	7.2
26[*]	47	0.063	4.0
"	72	0.082	5.2
"	107	0.101	6.4
"	150	0.122	7.7

[✱] Including the 2 mols. of HNO_3 in hexamine dinitrate.
[*] 1.00 gm. samples of hexamine used instead of hexamine dinitrate for this series.

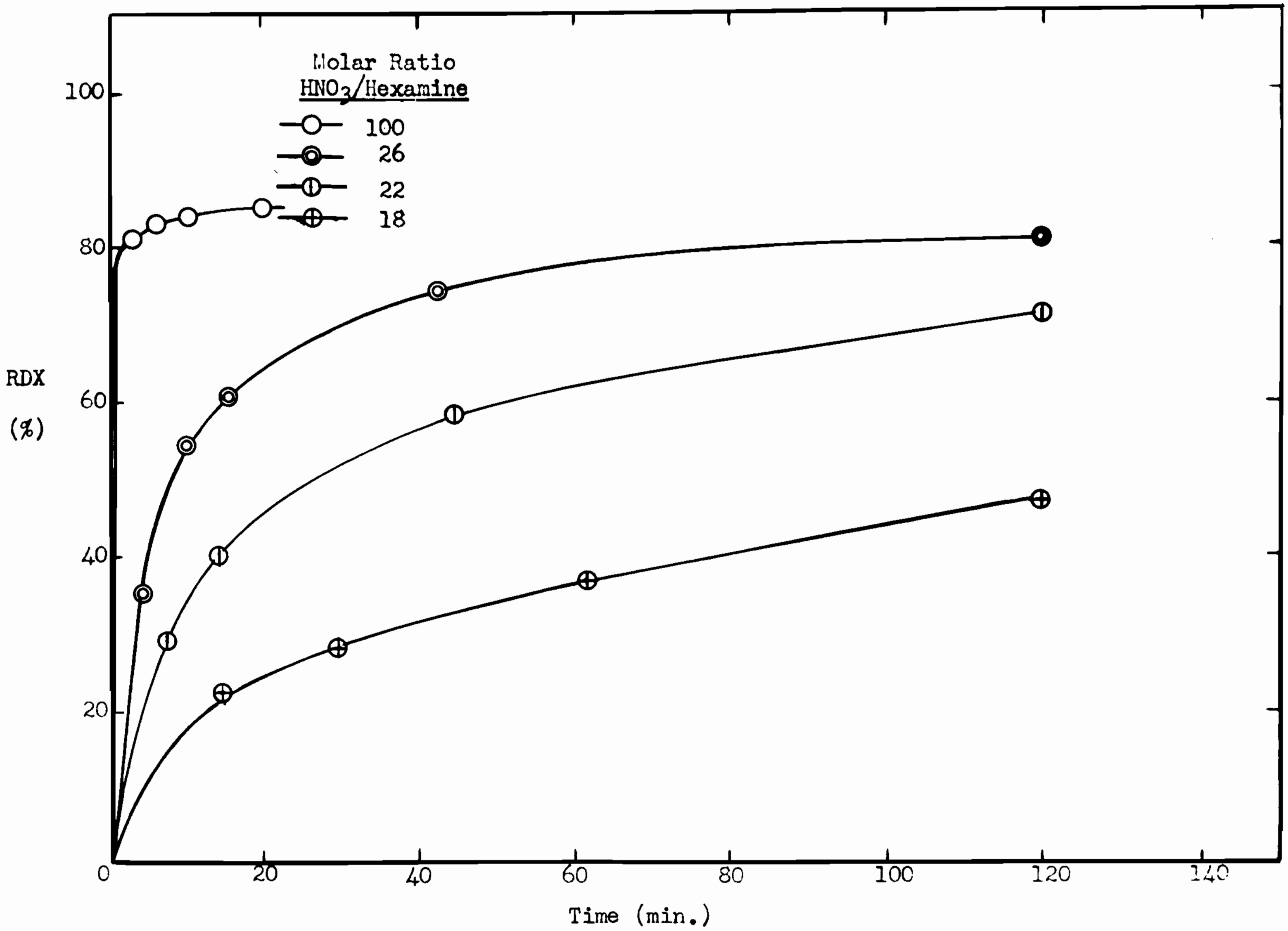


Fig. 1. Rate of RDX Formation with 97% Nitric Acid at 0°C.

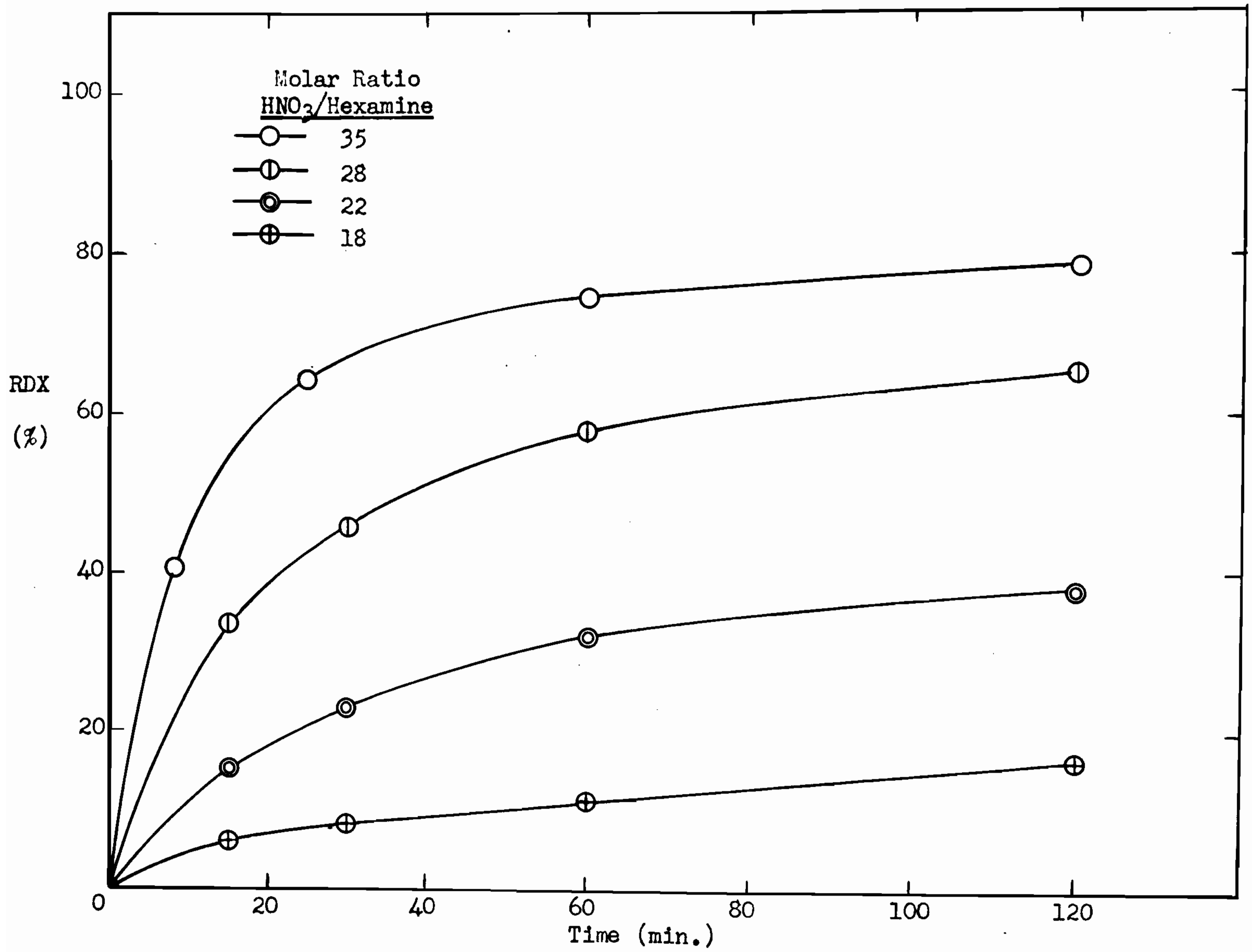


Fig. 2. Rate of RDX Formation with 94% Nitric Acid at 0°C.

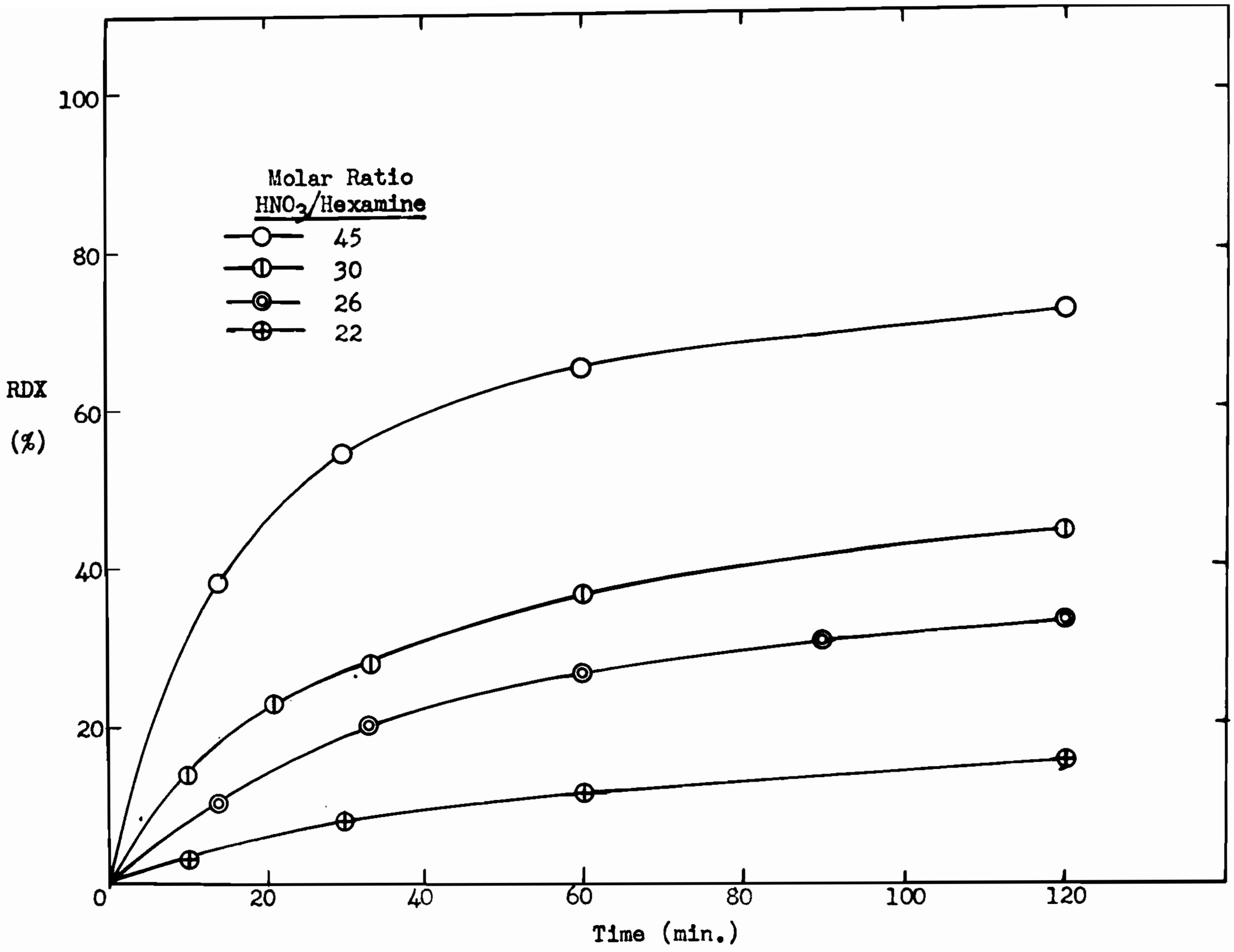


Fig. 3. Rate of RDX Formation with 91% Nitric Acid at 0°C.

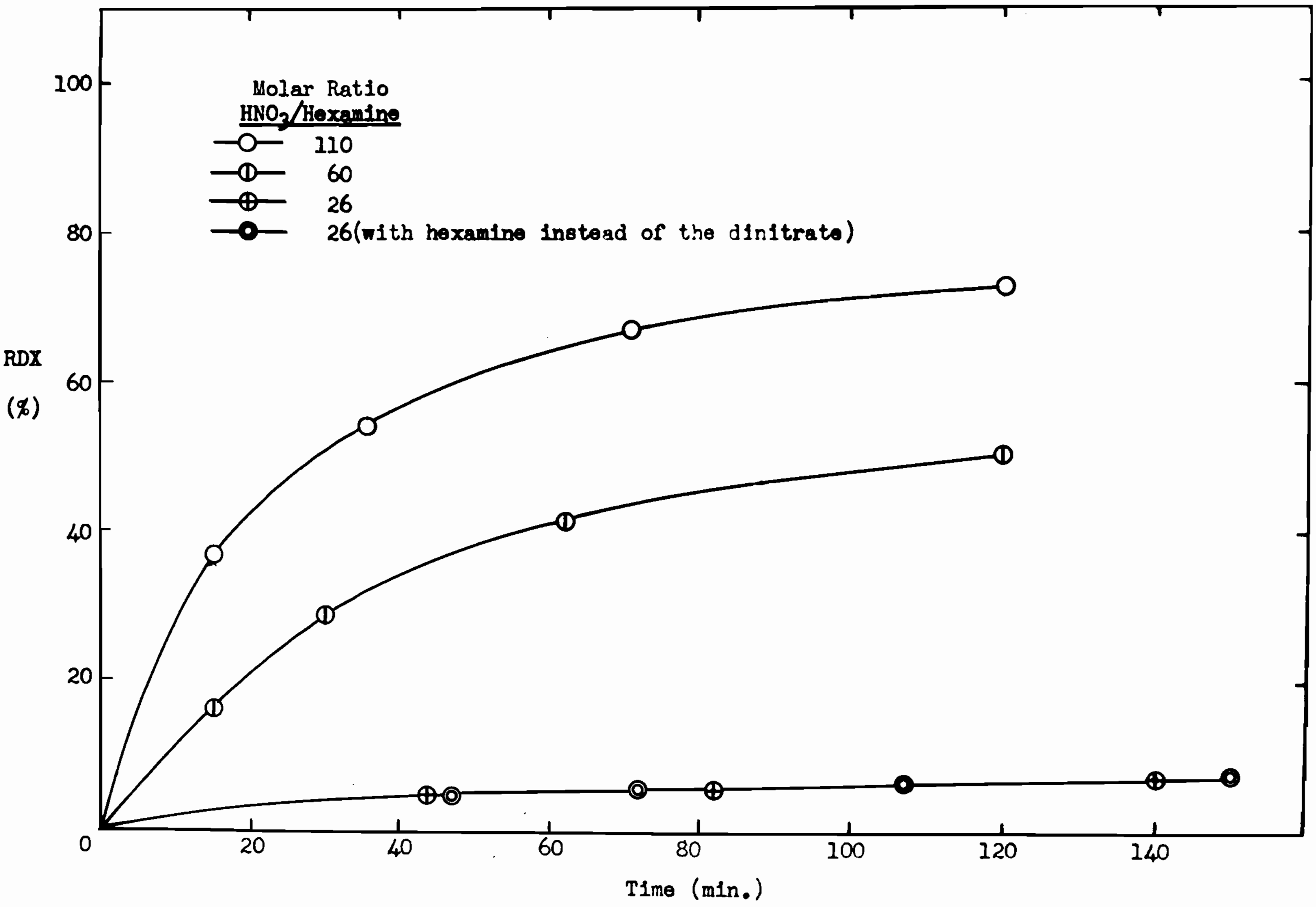


Fig. 4. Rate of RDX Formation with 88% Nitric Acid at 0°C.

emphasize this fact the curves for molar ratios which lead to maximum yields of 80 per cent in approximately two hours have been plotted together in Figure 5. Also included for comparison are other sets of curves for reactions giving lower yields. It is evident that almost identical rates of RDX formation result from the use of different concentrations of nitric acid between 88 and 97 per cent when the molar ratio of acid : hexamine is selected so as to give the same yield in two hours at 0^oC.

Effect of Nitric Acid : Hexamine Ratio upon Final Yield of RDX

The data given in Table V and illustrated in Figure 6 show that maximum yields of about 80 per cent are obtainable with nitric acid of all concentrations down to 88 per cent, if sufficient acid is used. With 88 per cent nitric acid a molar ratio of acid : hexamine of 110:1 is required. When the acid concentration is decreased to 85 per cent, however, a molar ratio of 300:1 gives only a 44 per cent yield of RDX. There is no assurance that higher yields would not be obtained if higher molar ratios were used but these were avoided owing to technical difficulties.

TABLE V

Initial Rates of RDX Formation and Final Yields

Hexamine dinitrate = 1.90 gm. (.0071 mole) Reaction Temp.=0°C.

HNO_3 Conc'n. (%)	Molar Ratio* of HNO_3/Hexamine	Initial Rate (% per min.)	Final Yield of RDX Hexamine Basis(%)	Final Yield of RDX HNO_3 Basis(%)
97	26	8.5	82.0	8.2
"	22	5.4	75.4	10.1
"	18	2.2	-	-
"	17	-	50.5	8.9
"	12	-	9.4	2.3
94	35	6.2	79.3	5.9
"	28	4.0	-	-
"	26	-	65.0	7.5
"	22	1.5	-	-
"	18	0.4	21.5	3.6
"	13	-	2.3	0.5
91	45	4.0	80.8	5.3
"	30	1.6	64.0	6.4
"	26	0.9	-	-
"	22	0.3	30.0	4.1
"	15	-	5.0	1.0
88	110	3.4	78.0	2.1
"	60	1.3	56.7	2.8
"	26	0.15	12.0	1.4
85	300	-	44.0	0.4

* Including the 2 mols. of HNO_3 in hexamine dinitrate.

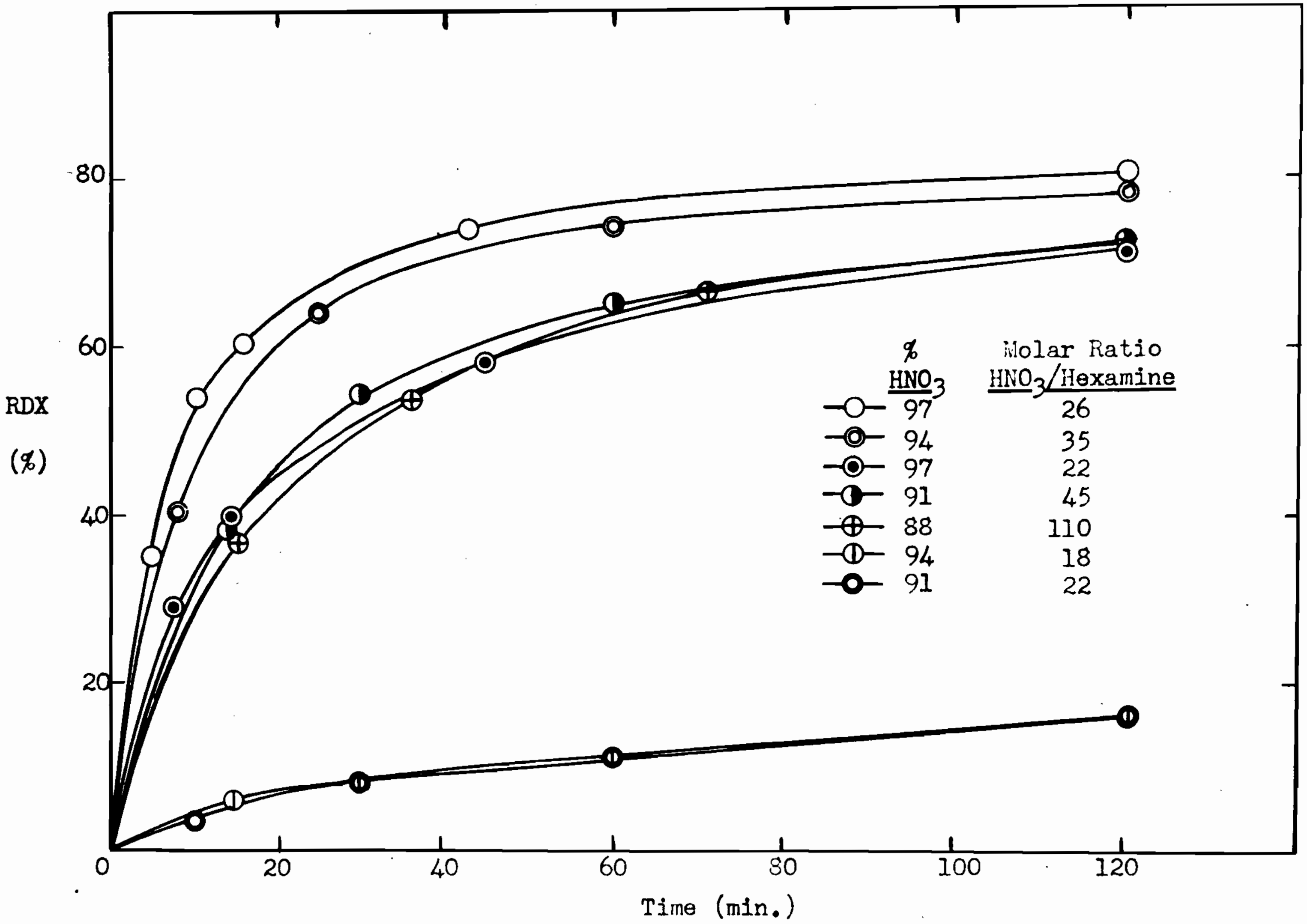


Fig. 5. Rate of RDX Formation with Various Concentrations of Nitric Acid at 0°C.

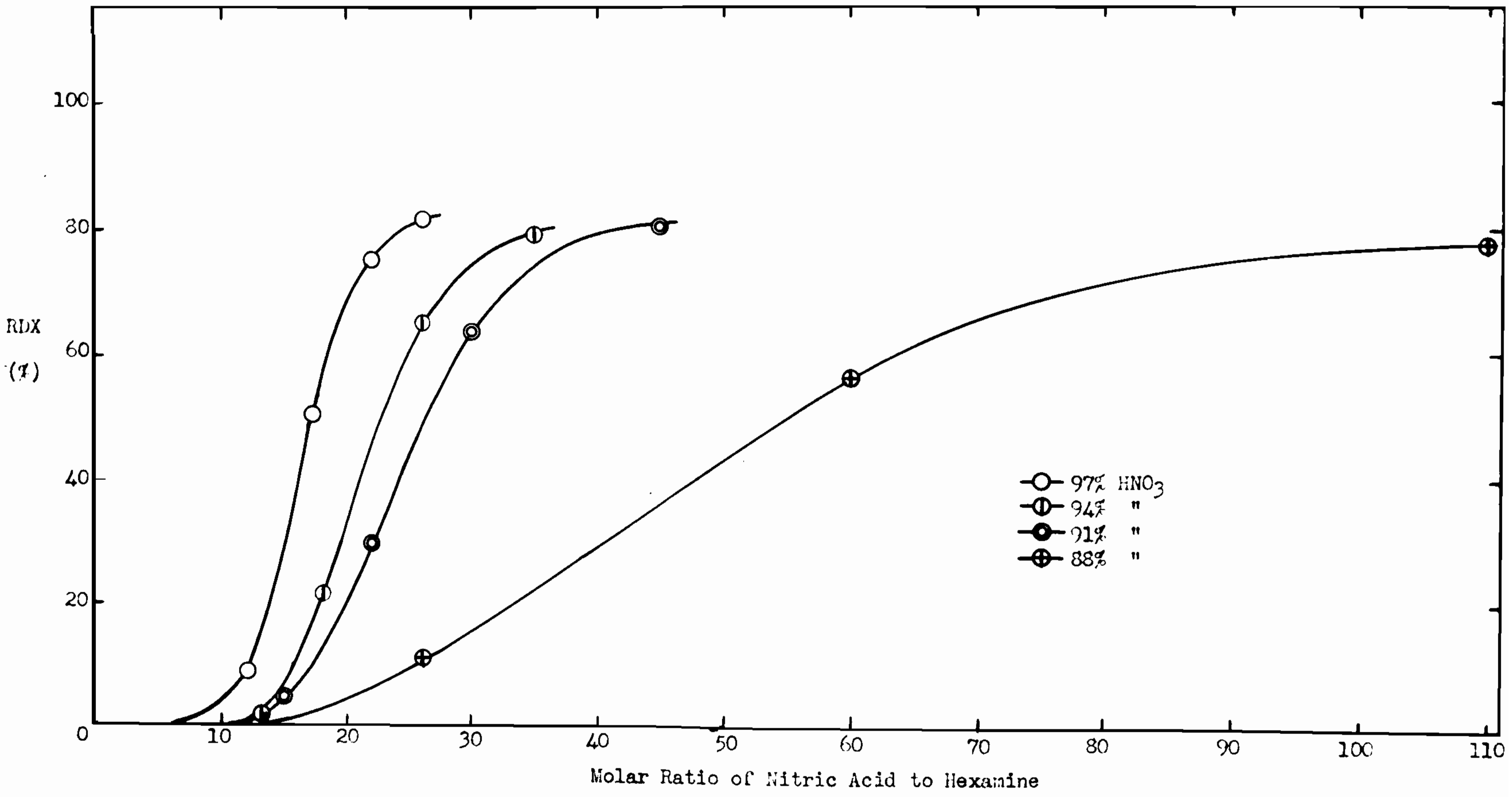


Fig. 6. Effect of Nitric Acid : Hexamine Ratio on Final Yield of RDX.

Effect of Nitric Acid : Hexamine Ratio upon Initial Rate

Table V also gives data plotted in Figure 7a showing that the initial rate of RDX formation for various concentrations of nitric acid bears a linear relation to the molar ratio of nitric acid to hexamine. The increase in initial rate with increased nitric acid : hexamine ratio continues with molar ratios greater than the minimum required for maximum yields. It appeared at first that there was no limit to the initial rate when increasing amounts of acid were used. With 100 moles of 97 per cent nitric acid per mole of hexamine, the yield of RDX after three minutes at 0°C. was 80.8 per cent (Table I).

As the existence of an upper limit to the initial rate is a point of considerable theoretical significance, an effort was made to find it. A series of experiments was made at -20°C. using 97 per cent nitric acid and molar ratios of acid : hexamine up to 400:1. The yield of RDX produced in one minute was determined, corrections being made for the solubility loss of RDX in the diluted liquors. The figures are given in Table VI.

The resulting curve, plotted in Figure 7b, shows that the increase in initial rate starts to fall off at about 50:1 molar ratio, and that from 200:1 to 400:1 there is little increase in initial rate. Admittedly, the yield

TABLE VI

Determination of Upper Limit of Initial Rate

Concentration of nitric acid = 97 per cent
Hexamine dinitrate = 1.90 gm. (0.0071 mole)
Temperature of reaction = -20°C.
Duration of reaction = 1 min.

Molar Ratio[*] of HNO_3/Hexamine	RDX (actual wt.) (gms.)	Solubility Correction (gms.)	Yield of RDX (corr. for sol'y.) (gms.)	(%)
25	0.101	0.008	0.109	6.9
50	0.367	0.023	0.390	24.6
100	0.426	0.056	0.482	30.4
150	0.510	0.087	0.597	37.7
200	0.567	0.120	0.687	43.3
400	0.389	0.329	0.718	45.3

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[*] Including the 2 mols. of HNO_3 in hexamine dinitrate.

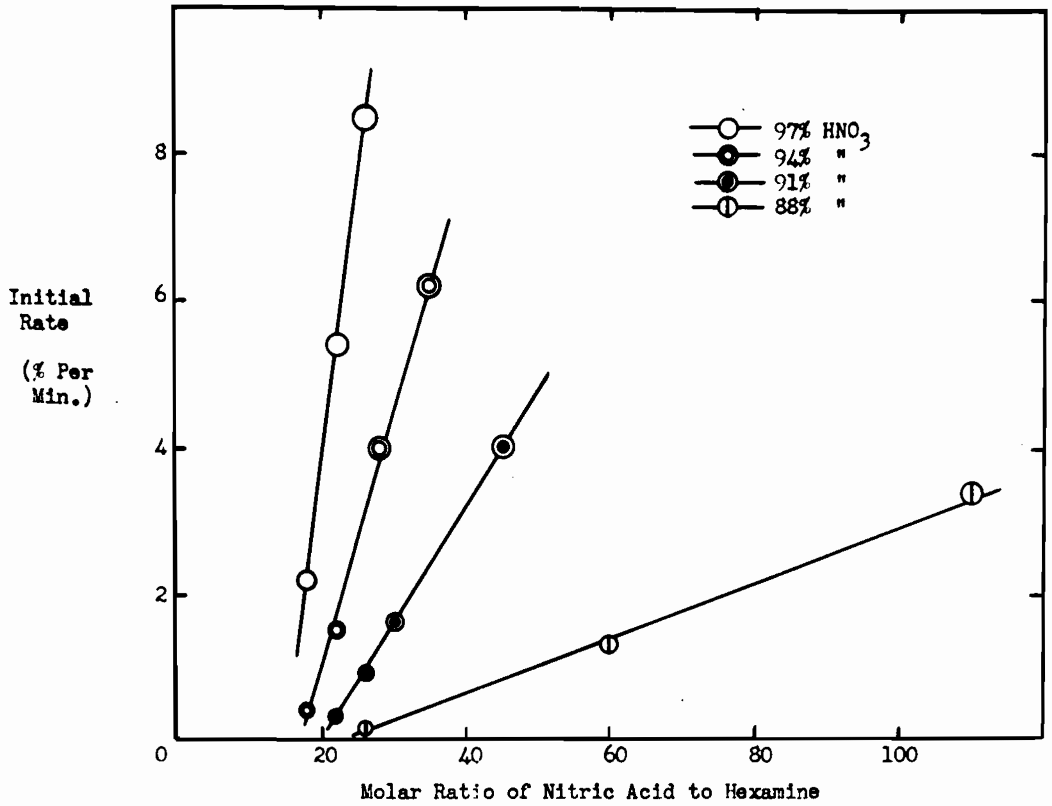


Fig. 7a. Effect of Nitric Acid : Hexamine Ratio on Initial Rate of RDX Formation at 0°C.

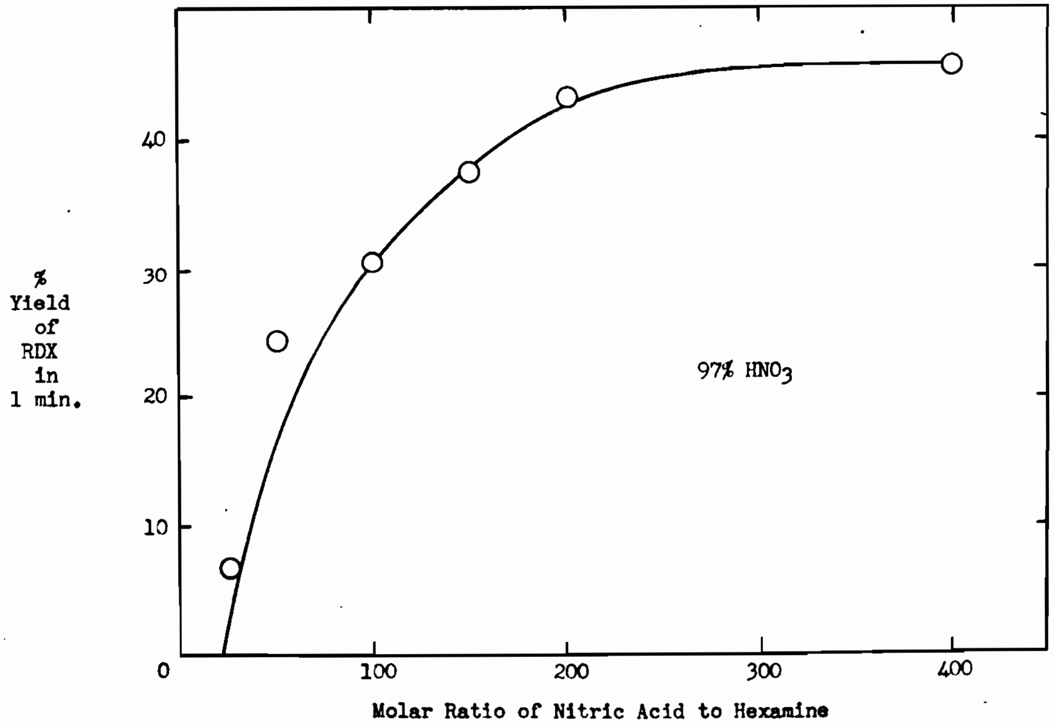


Fig. 7b. Effect of Nitric Acid : Hexamine Ratio on Initial Rate of RDX Formation at -20°C.

after one minute may not be an accurate measure of the initial rate but it should be a sufficiently close approximation to infer from the shape of the curve that an upper limit does exist.

Attention is drawn to the first two points on this curve which appear to be high. These two products were relatively impure, melting at 193° - 200°C., corr., whereas the products corresponding to all the other points on the curve had much higher melting points, 201° - 202.5°C., corr. This difference in purity was attributed to the greater rise in temperature when the nitrolysis liquors containing the larger amounts of acid were diluted. In some cases a fume-off was narrowly escaped, and it is quite possible that under these conditions an impurity would be destroyed.

As the impure products resulted from the use of acids which gave pure RDX under normal nitrolysis conditions, it seemed quite possible that the impurity was an intermediate which had not reacted owing to the low temperature and short time of reaction. Further investigations of this phenomenon are described in the next section.

Discussion

The nitrolysis of hexamine to RDX undoubtedly involves several consecutive reaction steps having different rates and it was originally a matter of speculation which step was represented by the rate curves for RDX formation. The slowest step should control the rate of RDX formation, while if there were two or more slow steps of comparable rates, an induction period should be observed in the formation of RDX.

The fact that no induction period exists in any of the rate curves as determined indicates that there is only one rate controlling step in the nitrolysis of hexamine and that all other steps are at least one hundred times faster. There was no conclusive evidence, at this point in the work, to indicate whether the rate controlling step was one of the initial or final steps in the overall reaction. The indication of the presence of an intermediate in the product from reactions at -20°C. would suggest, however, that the initial steps are very rapid and that one of the final steps is rate controlling.

The large excess of nitric acid present during the reaction might be expected to make the rate controlling step appear to be first order unless by-products, formed simultaneously with the RDX, interfered. Figure 8 shows that log (a-x) bears a linear relation to time, "t", over the major part of reaction, when "a" is defined as a yield slightly below the values found for final yields, and "x" is the yield at time, "t". This behaviour, characteristic of first order reactions, is confirmed by later work of the Armament Research Department (32), who obtained the yields for infinite reaction time by extrapolating the plot of yield against rate of RDX production to zero rate. Taking these final values as "a", and plotting log (a-x) against time, gave good straight lines.

The necessity for taking a value for "a" slightly below the final yield of RDX as determined by the author is not readily explicable. It may indicate the presence of an impurity in the products obtained from long reaction times. The Armament Research Department reported (33) that products from reactions at 0°C. for 5 to 6 hours were impure, melting at about 180°C. The final yields of RDX as recovered by the author's procedure melted at 197 - 200°C. (corr.) or higher, but the products for reaction times up to two hours melted at about 201 - 202°C. (corr.).

An alternative possibility is that of a slow resynthesis of hexamine fragments yielding a small amount of

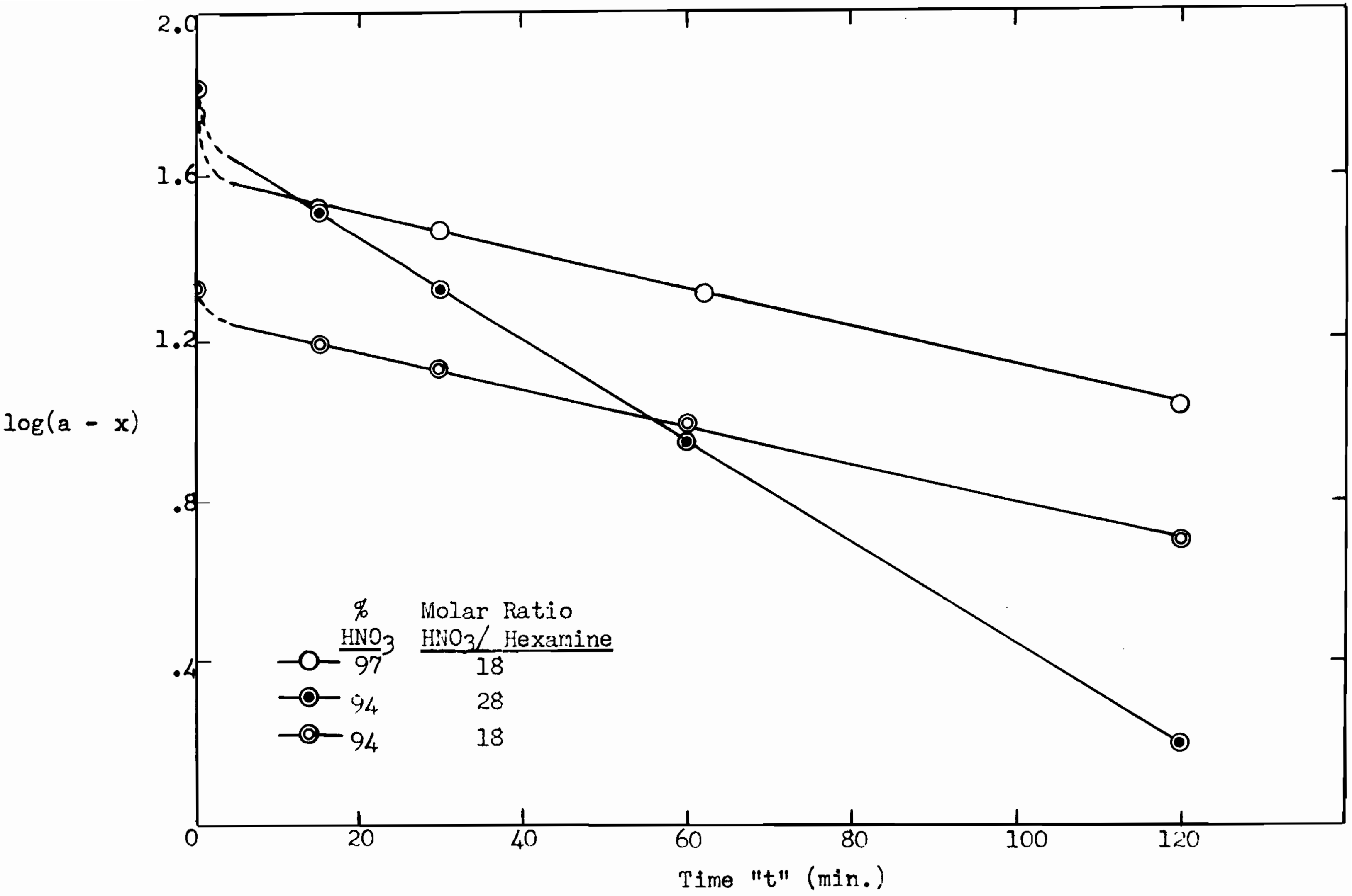


Fig. 8. Typical Curves Indicating Apparent First Order Behavior of Nitrolysis of Hexamine.

RDX. Two other indications of such a re-synthesis have been obtained, and will be discussed later.

The change of slope of the lines in Figure 8 during the first few minutes of reaction, corresponding to a decrease in the rate constant, is evidence that a marked change occurs in the nitrating medium during this period. This is probably due to the formation of water or other by-products which decrease the concentration of the agent responsible for the nitrolysis reaction.

The behaviour of the initial rate of RDX formation on varying the ratio of nitric acid to hexamine makes it appear that only a small percentage of the nitric acid is in a form capable of converting hexamine or an intermediate to RDX. Also, the concentration of this active factor apparently decreases very rapidly as the concentration of nitric acid falls from 97 to 85 per cent, so that below 85 per cent it is present in only extremely small concentration.

The literature on nitric acid and nitrating agents was studied with a view to finding evidence for a possible form of nitric acid which might explain some of the behaviour observed during the nitrolysis of hexamine. A review of nitrating agents by Bennett and Williams (34) was particularly helpful. Considerable evidence was found to indicate that the active factor in the rate controlling step of the nitrolysis is probably a nitric acid cation which exists to a small extent in very concentrated nitric acid. Hantsch (35, 36) referred to this cation as nitronium, or preferably nitracidium, ion.

It is an established fact (37, 38) that nitric acid acts as a base, or proton acceptor, towards strong acids. Hantsch (35) isolated and identified the crystalline salts of nitracidium perchlorate, $NO(OH)_2^+\ ClO_4^-$ and $N(OH)_3^{++}\ (ClO_4)_2^-$, from mixtures of nitric and perchloric acids. The compound, $N_2O_5 \cdot 4SO_3 \cdot 3H_2O$, isolated by Weber in 1871 (39), was also cited and written as nitracidium pyrosulphate, $N(OH)_3^{++}\ S_2O_7^{--}$. It was shown that the two perchlorates were binary and ternary electrolytes, respectively, in nitromethane solution, and that nitric acid accumulated at the cathode when the solutions were electrolyzed.

Strong evidence exists (34) to indicate that the corresponding nitracidium sulphates are formed when nitric acid is dissolved in absolute sulphuric acid, and to the nitracidium ion, or its dehydrated form, NO_2^+, is attributed the powerful nitrating action of the mixed acids.

In Raman spectra the $\Delta\nu$ 1400 cm.$^{-1}$ line is attributed to a nitric acid cation (34). This line is given by nitric acid in sulphuric acid, more weakly by 100 per cent nitric acid, by solid nitrogen pentoxide (quite faintly,- due presumably to traces of moisture on the surface of the crystals), but not by nitrogen pentoxide in carbon tetrachloride, chloroform, or phosphoryl chloride.

The electrical conductivity and the absorption spectrum of nitric acid both support the view that in high concentrations some of the nitric acid is present as nitracidium nitrate. By these means, Hantsch (36)estimated that 98.6 per cent nitric acid was composed of 20 per cent nitracidium nitrate and 80 per cent pseudo-nitric acid, $NO_2.OH$. The addition of water affects this ionic equilibrium greatly since H_2O is a much better proton acceptor than $NO_2.OH$; i.e. $NO_2.OH$ is more acidic. A proton transfer such as the following probably occurs:

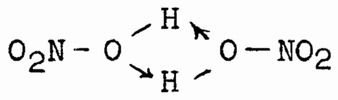
$$NO(OH)_2^+ + H_2O \longrightarrow NO_2.OH + H_3O^+ \qquad (1)$$

As a result of the formation of oxonium ion, the following equilibrium would then shift to form more pseudo-nitric acid:

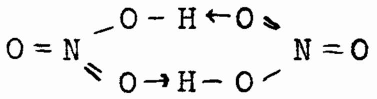
$$\overset{+}{H_3O} \quad \overset{-}{ONO_2} \longrightarrow HONO_2 + H_2O \qquad (2)$$

Hantsch observed that after the addition of one molecular equivalent of water (corresponding to 77.8 per cent nitric acid), the nitracidium ion had disappeared entirely. He also estimated that the concentration of pseudo-nitric acid was at a maximum at about the same point.

W.N. Hartley (40) inferred from observations on absorption spectra that anhydrous nitric acid was probably bimolecular. Hantsch's theory of the association of oxygen acids (41) states that acids such as nitric are generally associated in the pure liquid state as for example,

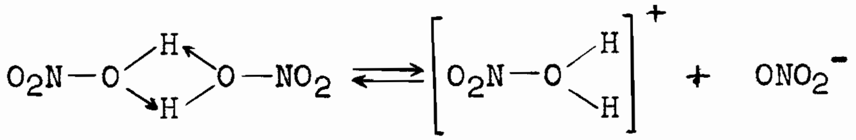


Dalmon and Freymann (42) have recently studied the infra-red absorption spectrum of liquid nitric acid in the concentrations of 80 to 100 per cent. With 100 per cent nitric acid they observed an intense band at 1.017 which they attributed quite definitely to molecules of nitric acid associated either in the above manner or in the following:

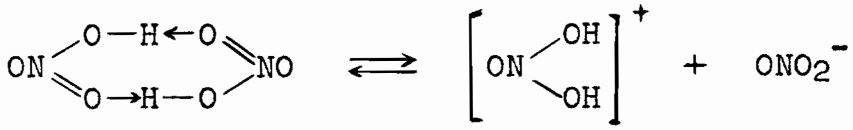


On diluting the nitric acid with water, the intensity of this band decreased rapidly until it had almost disappeared when the acid concentration was 80 per cent. The intensity of another band at about 0.97 , attributed to molecules of pseudo-nitric acid, $NO_2 \cdot OH$, behaved in a directly opposite manner, increasing from almost zero intensity with 100 per cent nitric acid to quite a high value with 80 per cent acid.

Reconciling this evidence for bimolecular nitric acid with the exactly similar behaviour of nitracidium ion observed by Hantsch would suggest that nitracidium ion arises from the ionization of bimolecular nitric acid in one of two postulated forms:



(3)



(4)

To agree with Hantsch's estimate of 20 per cent nitracidium nitrate and 80 per cent undissociated acid in 98.6 per cent nitric acid, the ionization constant of bimolecular nitric acid should be in the order of 0.25.

Additional evidence that nitracidium ion is a most powerful nitrating agent is furnished by Bennett and Williams (34) who point out that the mixed acid compositions, determined by Chédin, (43), at which the Raman line $\Delta\nu$1400 cm.$^{-1}$ disappears, lie close to the limiting acid compositions given by Hetherington and Masson (44) as incapable of nitrating nitrobenzene. The line of maximum vapour pressure, indicating maximum $NO_2 \cdot OH$ content, lies in the same region of acid compositions. The implication is that pseudo-nitric acid does not nitrate nitrobenzene, and that the true nitrating agent is really nitracidium ion. It is also noted (34) that the electronic theory of aromatic reactivity points to a positive ion as the molecular species most likely to be active in nitration.

The lower limit of nitric acid concentration capable of forming RDX has long been known to lie in the vicinity of 80 per cent nitric acid. This also is approximately the concentration at which nitracidium ion disappears and is the concentration estimated by Hantsch (36) at which the pseudo-nitric acid content is at a maximum. As before, the implication is that nitracidium ion, not pseudo-nitric acid, is the nitrating agent in this reaction.

Furthermore, by introducing the concept of nitracidium ion as the active factor in the rate controlling step of the nitrolysis of hexamine, the results of the kinetic studies can be explained, and these results in turn are additional evidence for the above theories.

The evidence for any particular form of nitracidium ion is so slight that discussion of this point would seem of little purpose. The form indicated in equation 3

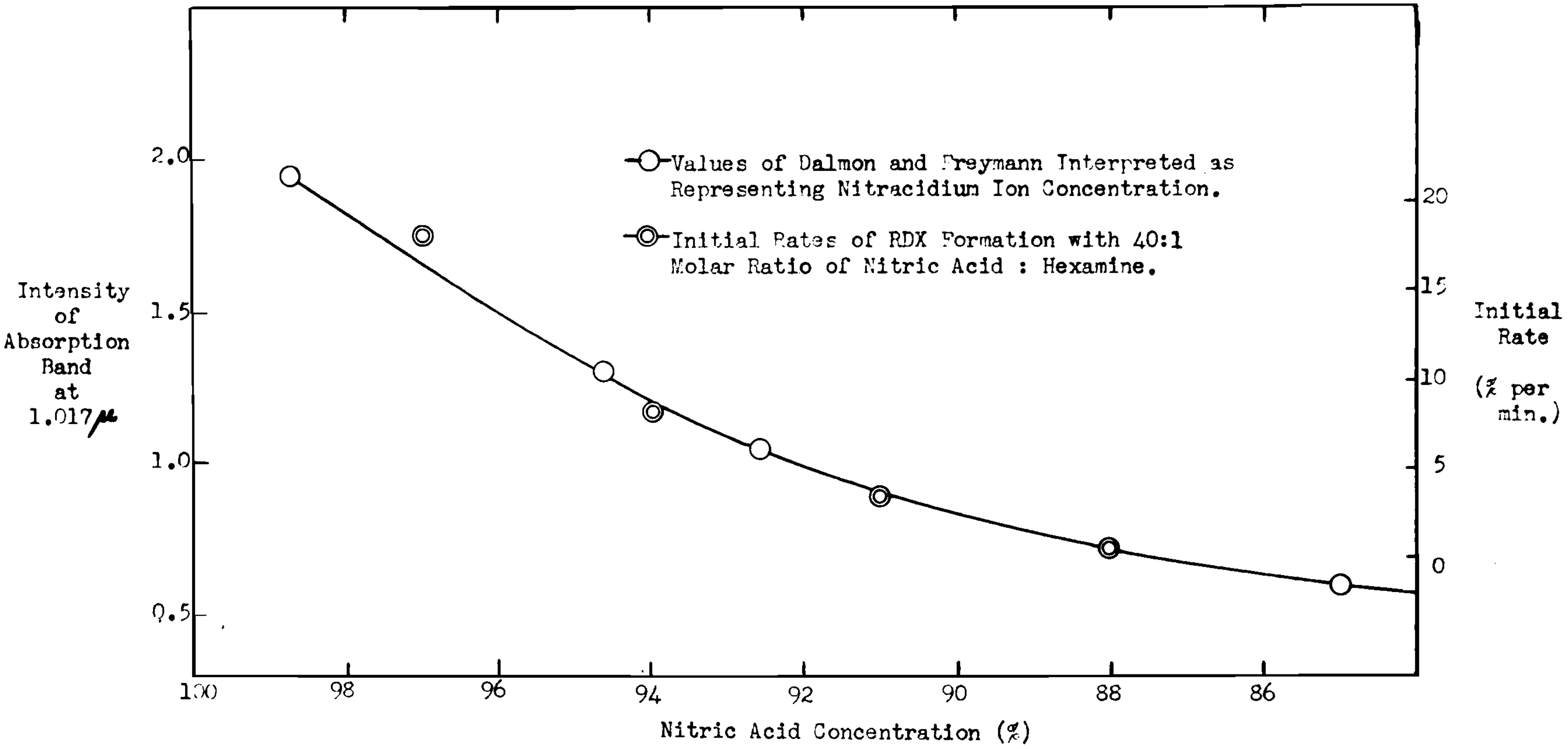


Fig. 9. Comparison of Nitracidium Ion Concentration with Initial Rate for Various Nitric Acid Concentrations.

above may change to that in equation 4 by a tautomeric shift of a proton. As already mentioned, the form $N(OH)_3^{++}$ appears to be present in mixtures of nitric with stronger acids. Also, there is some indication (34) of a dehydrated form, NO_2^+, analogous to the NO^+ of nitrosyl sulphuric acid, in sulphuric acid and other strongly dehydrating media.

Initial Rate as a Function of Nitracidium Ion Concentration

If the above hypothesis holds true, the initial rate of RDX formation should be directly proportional to the nitracidium ion concentration existing in the nitrolysis liquor, at any given temperature. In Figure 9 a curve is reproduced from the data of Dalmon and Freymann representing the change in concentration of bimolecular nitric acid with variation in the water content of the acid. Values for the absorption coefficient of the 1.017 μ band are plotted as ordinates. Assuming that bimolecular nitric acid ionizes to nitracidium nitrate, as previously postulated, this curve also represents, then the change in nitracidium ion concentration with variation in the water content of the acid.

On the same graph there is plotted a series of values showing the change in initial rate of RDX formation at $0^{\circ}C$. with variation in the initial water content of the acid. The initial rates plotted represent reactions in which the molar ratio of nitric acid to hexamine was 40 to 1, and were taken from Figure 7a. The value of 18 per cent per minute for 97 per cent nitric acid was obtained by extrapolation and may not be as accurate as the other values.

The fact that the plot of these initial rates coincides so well with the curve of Dalmon and Freymann is taken as strong evidence that nitracidium ion is the nitrating agent for the rate controlling step of the nitrolysis of hexamine. With increasing molar ratios of acid to hexamine the curves become more identical. This is to be expected when it is recalled that hexamine in the presence of nitric acid exists as the dinitrate, an acid salt of hexamine which presumably ionizes to a dihydro-hexamine ion and two nitrate ions. This ionization, and that of any nitrate bodies in the reaction products, should repress the ionization of bimolecular nitric acid (Equation 3 or 4 above) through the common ion effect. This is equivalent to saying that basic hexamine is a better proton acceptor than the pseudo-nitric acid molecule, and like water (Equation 1 above) its addition to very concentrated nitric acid should result in a decrease in the nitracidium ion concentration. As the molar ratio of acid to hexamine is increased, the interference of hexamine dinitrate, or its initial reaction products (possibly including water), should be correspondingly decreased.

If allowance is made for this effective dilution of the acid, the initial rates for the lower molar ratios, are found to correspond very well with the curve of Dalmon and Freymann. By lowering the values for the concentration of nitric acid about three per cent, and replotting the initial rates for the 40:1 molar ratio on the appropriate scale, the agreement is improved. Likewise, a close agreement is found when the initial rates for a 26:1 molar ratio are plotted with the acid concentrations lowered by 4-5 per cent.

It should be made clear that the apparent initial rate of RDX formation, as estimated, is not an accurate value of the true initial rate since the first point on the rate curves is usually several minutes after the start of the reaction. To obtain the true initial rate, points much closer to zero time would be necessary, but this was impossible under the conditions employed since the time required for complete solution of the hexamine dinitrate was appreciable, being almost two minutes in some experiments. Evidence already presented indicates that the rate constant for the rate controlling step decreases considerably during the first few minutes of reaction, corresponding to dilution of the acid or repression of the ionization of nitracidium ion.

The rapid rise of initial rate with increase in the molar ratio of nitric acid to hexamine (Figure 7a) can be explained by a corresponding increase in the concentration of nitracidium ion available for reaction. With comparatively high concentrations of hexamine (low molar ratios), the ionization of the hexamine so represses the ionization of nitracidium nitrate that practically no RDX is formed with 6 moles of 97 per cent nitric acid, and with 10 moles of 94 to 88 per cent acid, per mole of hexamine. Thus the initial rate curves, when extrapolated to zero initial rate, should bend around quite sharply to these values for the molar ratio. As the molar ratio is increased, the ionization of the hexamine dinitrate becomes less effective in repressing the ionization of nitracidium nitrate giving an almost linear relation between initial rate and molar ratio of nitric acid to hexamine over a wide range of molar ratios.

As the molar ratio is still further increased the concentration of nitracidium ion should approach the normal value for nitric acid of the given concentration. The initial rate should no longer increase at the same rate with increasing molar ratio as this point is approached, but rather should tend toward a maximum and constant value. In accordance with this view, the investigations at -20°C. (Figure 7b) indicate that an upper limit to the initial rate does exist at extremely high molar ratios of acid to hexamine.

The slopes of the lines for initial rate vs. molar ratio of nitric acid to hexamine (Figure 7a) are a function of the acid concentration and should be directly proportional to the nitracidium ion concentration if this is the factor responsible for the initial rate. In Figure 10, the slope of the line for each acid concentration is plotted against that value from Dalmon and Freymann's work which is interpreted as representing the nitracidium ion concentration in the corresponding concentration of nitric acid. The remarkably straight line which results is additional strong evidence to support the view that nitracidium ion is the agent responsible for the rate controlling step. In taking the slope of the initial rate curves, one might expect the disturbing influence of ionization repression by hexamine dinitrate and its reaction products to be ruled out. Hence this demonstration should be more accurate than the one in which initial rates, for acid : hexamine ratios where the ionization repression was appreciable, were plotted along with Dalmon and Freymann's values (Fig. 9).

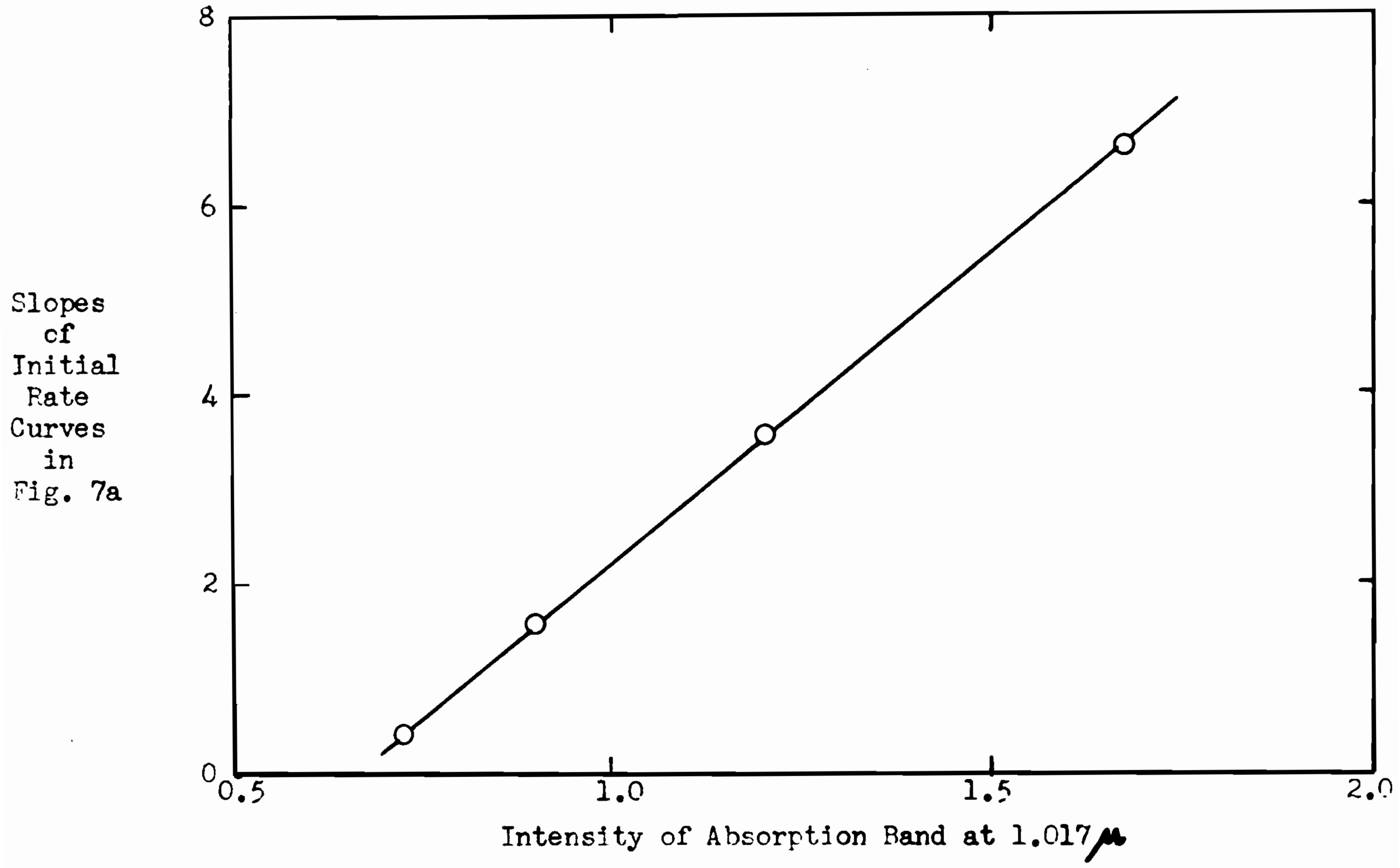


Fig. 10. Change in Initial Rate as a Function of Nitracidium Ion Concentration.

Relation of Initial Rate to Yield of RDX

The yield of RDX obtained in two hours with various concentrations of nitric acid at 0°C. has been plotted against the initial rate of RDX formation in Figure 11. It is evident that the higher the acid concentration, the higher is the initial rate necessary for any given yield of RDX below the maximum. In other words, the rate of RDX formation falls off more rapidly with higher concentrations of nitric acid. This can be explained by assuming that by-products, possibly including water, formed simultaneously with the RDX have a greater effect upon the concentration of nitracidium ion in the higher nitric acid concentrations owing to the lower molar ratios of acid to hexamine used. This effect may also indicate faster decomposition of an intermediate in the acids of higher concentrations.

The slightly higher initial rate with higher acid concentrations is noticeable also in Figure 5, in which are plotted sets of rate curves leading to similar yields of RDX in two hours.

Figure 12 shows a similar set of curves for the final yield of RDX as a function of initial rate. Comparing this with Figure 11, shows that the RDX formation after 2 hours varies greatly as the nitric acid concentration is changed, even though the molar ratio of

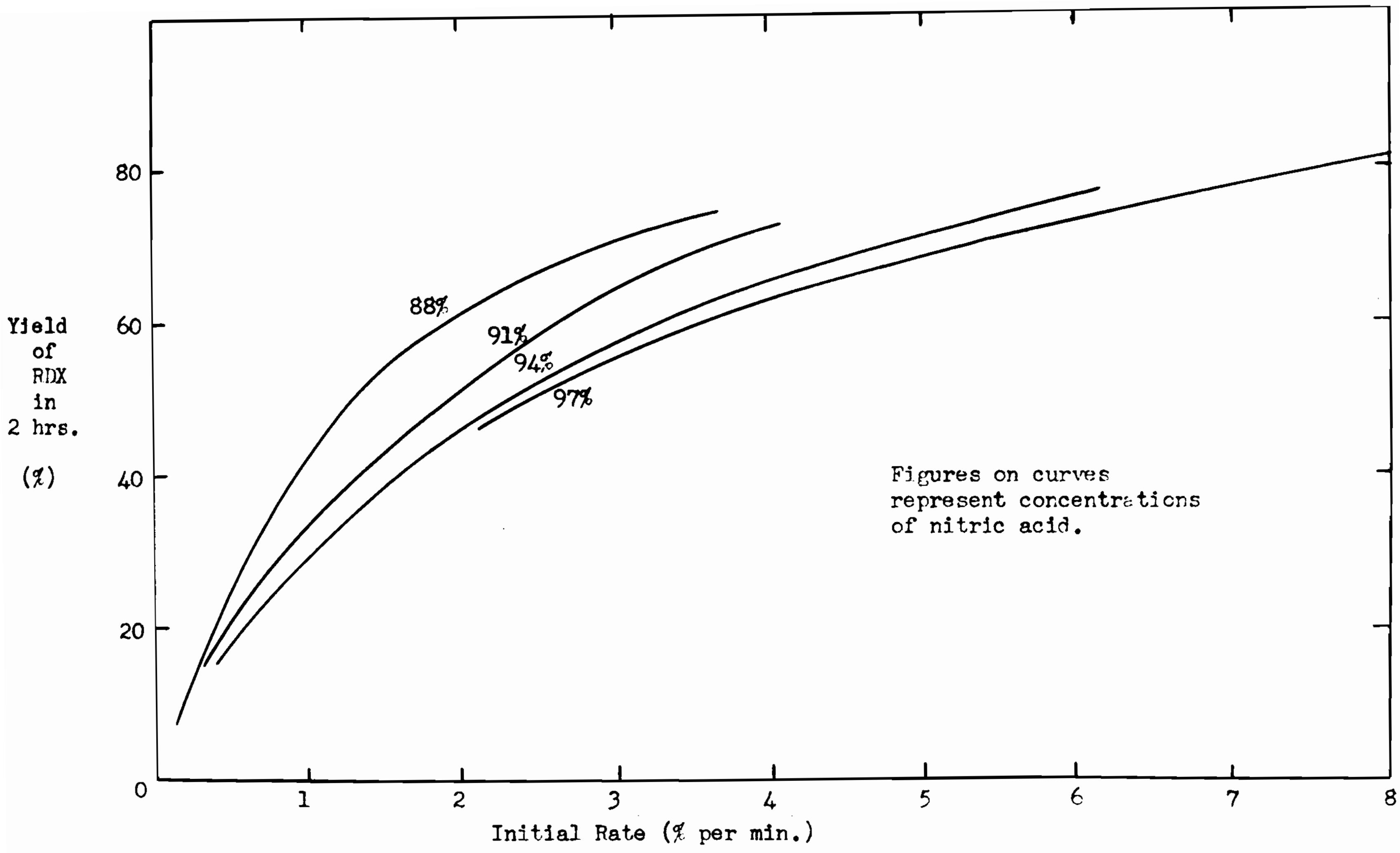


Fig. 11. Relation of Yield of RDX in Two Hours to Initial Rate of Formation.

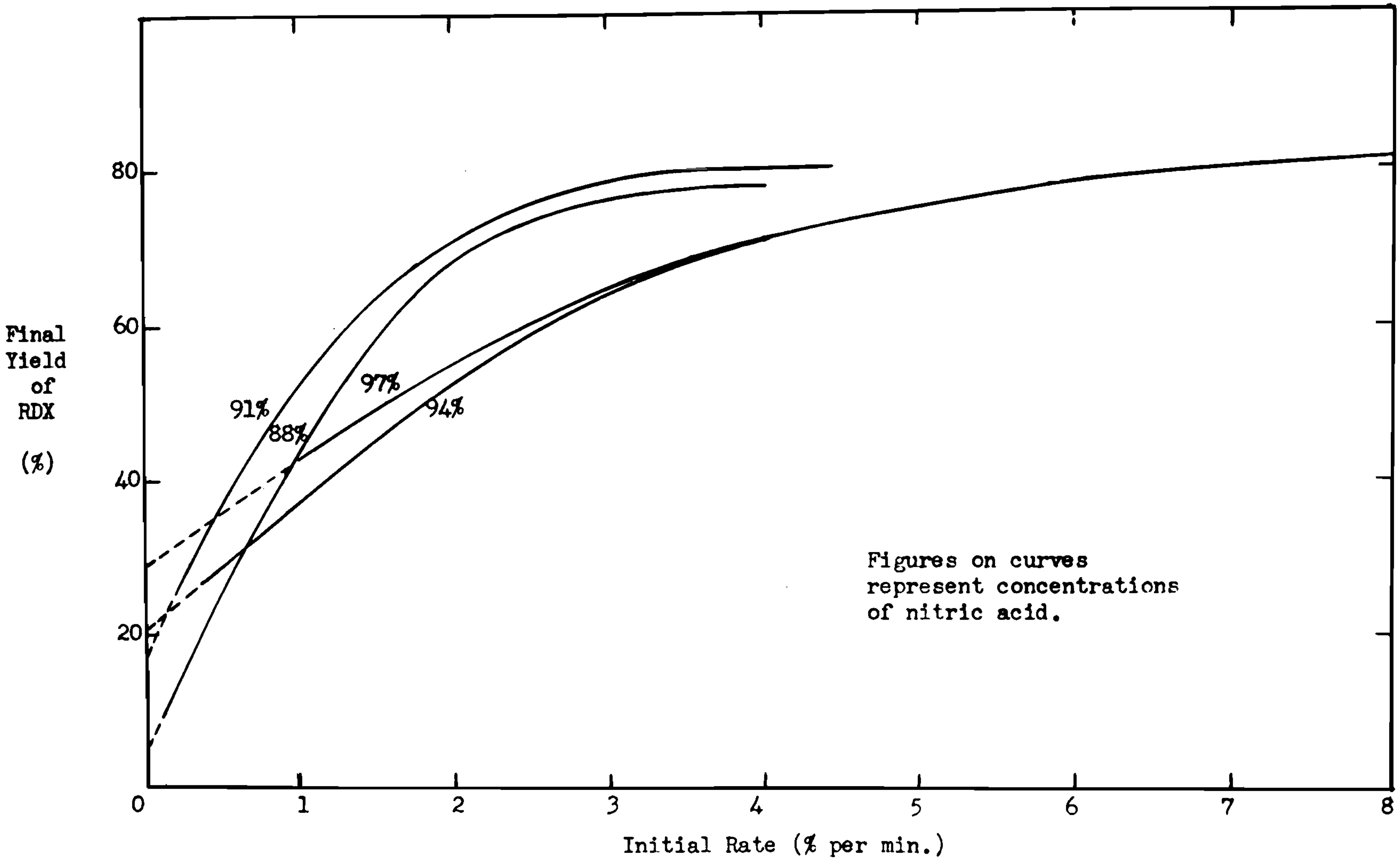


Fig. 12. Relation of Final Yield of RDX to Initial Rate of Formation.

reagents is adjusted to give the same initial rate, i.e., the same nitracidium ion concentration. This suggests, once more, that the latter stage of RDX formation involves another much slower type of reaction, possibly a re-synthesis of hexamine fragments. Since the curve for 91 per cent nitric acid is raised more than those for other acid concentrations, this secondary reaction would appear to proceed most favourably in nitric acid of approximately 91 per cent initial concentration. However, an extrapolation of the curves to zero initial rate indicates that when the molar ratio of acid to hexamine is sufficiently low the yields decrease again in the order of decreasing acid concentrations. The yield of RDX at zero initial rate is apparently due to a reaction other than the one whose initial rate was measured. The change in the relative positions of the curves as the initial rate is increased by increasing the acid : hexamine ratio, suggests a very complex reaction.

Effect of Hexamine : HNO_3 Ratio upon Yield of RDX on Nitric Acid Basis

The final yield of RDX calculated on the nitric acid basis (1 mole of RDX from 3 moles of nitric acid) when plotted against the molar ratio of hexamine to nitric acid gives an interesting graph, Figure 13. It shows that for very low molar ratios of hexamine to nitric acid

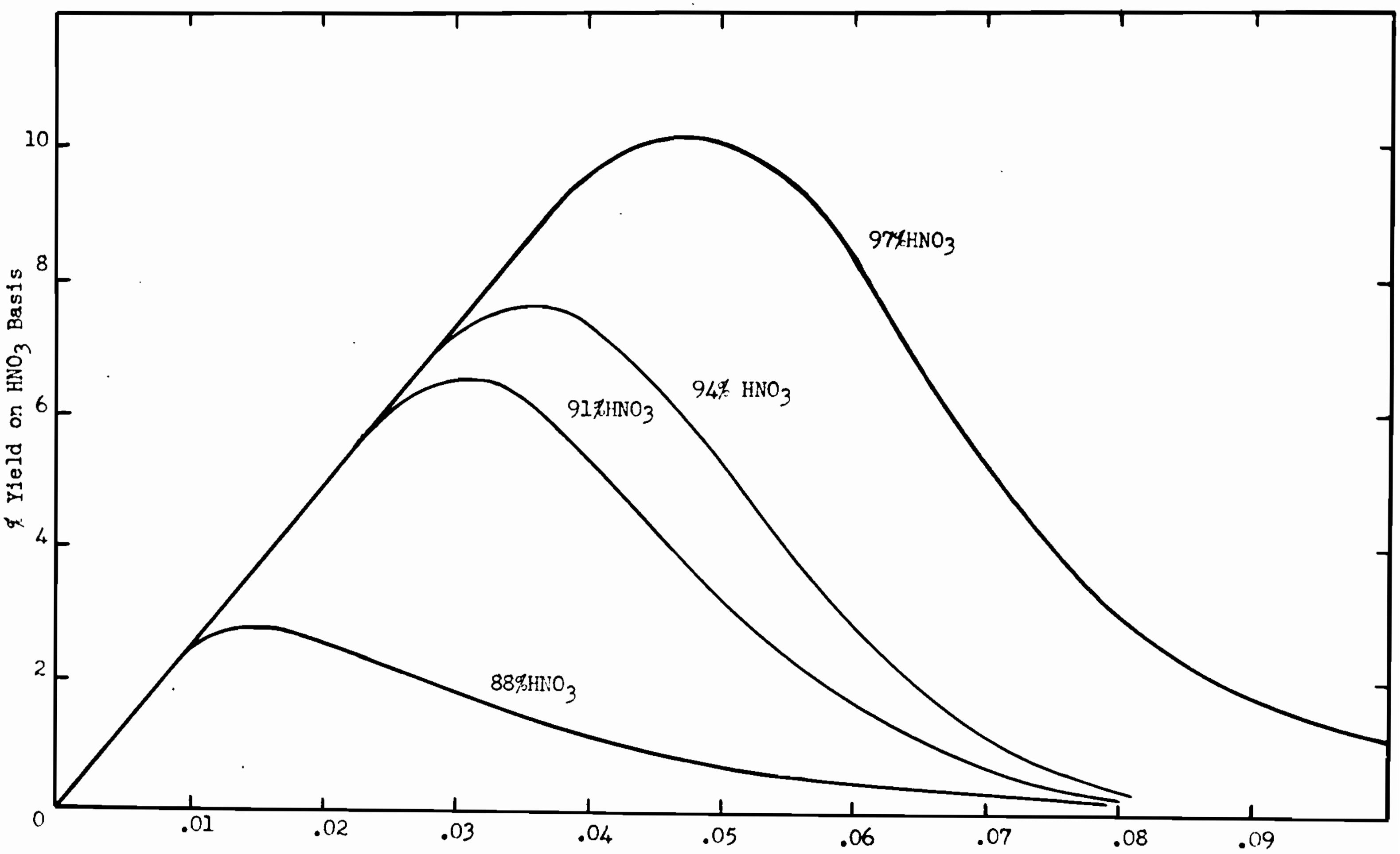


Fig. 13. Effect of Hexamine : Nitric Acid Ratio on Yield of RDX on Nitric Acid Basis.

the yield of RDX on the nitric acid basis is independent of the acid concentration for acids of 88 per cent and over, and is directly proportional to the quantity of hexamine used. This corresponds to the presence of sufficient nitracidium ion for an initial rate great enough to lead to the maximum yield on the hexamine basis.

As increasing quantities of hexamine are added to constant amounts of nitric acid, the weights of RDX obtained increase proportionately until a point is reached where there is insufficient nitracidium ion to give an initial rate capable of leading to maximum RDX yields on the hexamine basis. This point is naturally reached first in those acids having the lowest initial concentrations of nitracidium ion; thus the curve for 88 per cent nitric acid falls off first, and the others in the order of the acid concentrations.

As still larger quantities of hexamine are used, it might be expected that the weight of RDX obtained from a given amount of nitric acid would reach a maximum and constant value, dependent on the concentration of nitracidium ion. It is seen from Figure 13 that this is not true. Here again is strong evidence that hexamine dinitrate, or its reaction products, markedly decreases the concentration of nitracidium ion, so that the addition

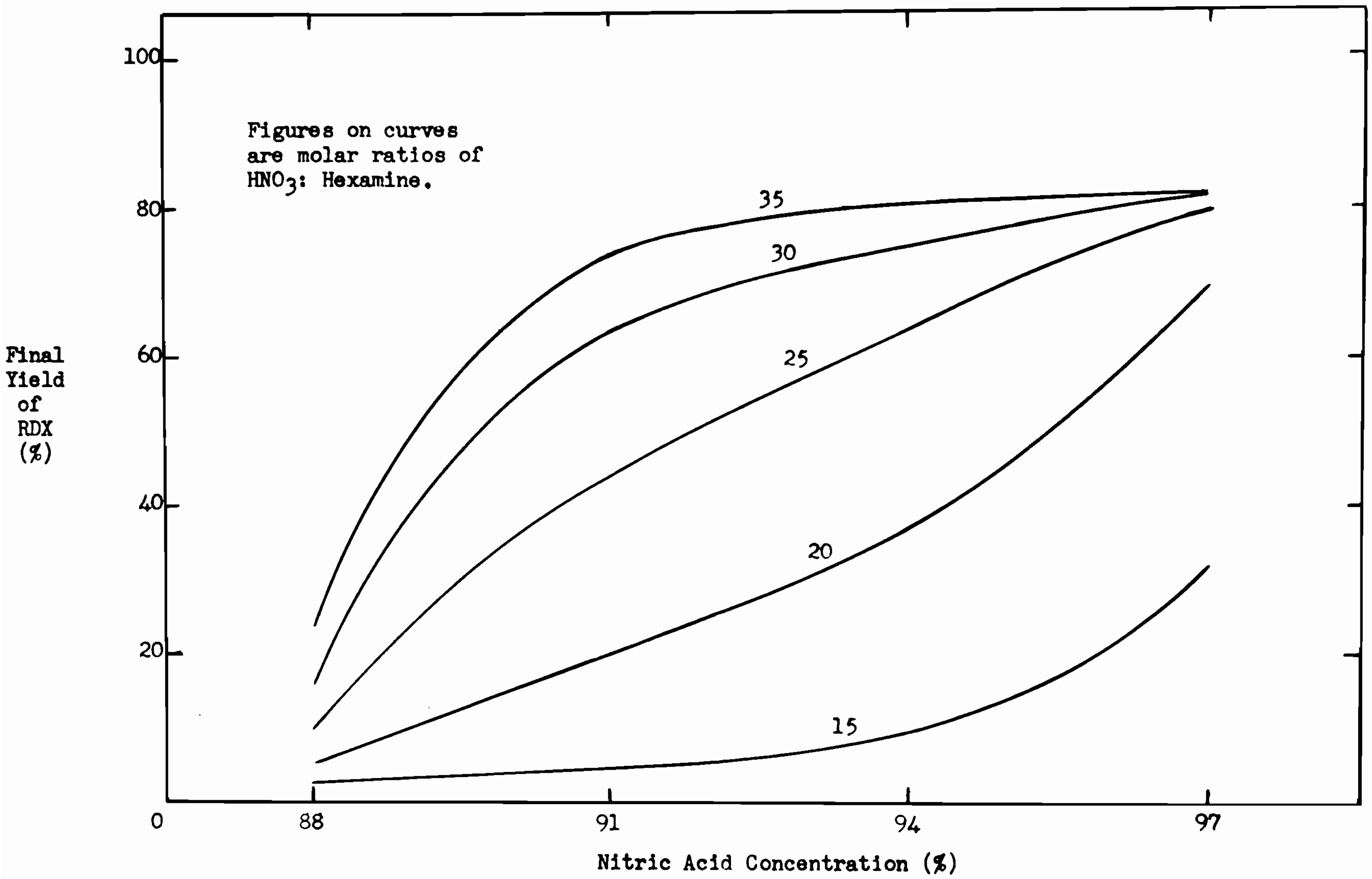


Fig. 14. Effect of Nitric Acid Concentration on Final Yield of RDX.

of further hexamine inhibits the nitrolysis to RDX. The graph shows that the yield of RDX from a given amount of acid begins to decrease again quite rapidly, and that an optimum molar ratio exists.

Effect of Acid Concentration upon Final Yield

Figure 14 shows the effect on final yield of changing the acid concentration keeping the molar ratio of reactants constant. It is seen that for molar ratios of nitric acid : hexamine of less than 25:1, the curves are flattened at the lower acid concentrations. This also is probably due to the increased effect of hexamine dinitrate and its reaction products upon the concentration of nitracidium ion under such conditions.

Some of the results from an early report by the Research Department on the isothermal nitration of hexamine were tabulated in the Historical Introduction. The yield of RDX obtained after 2 min. at $0^{o}C$. is considerably higher than that indicated by the rate curves from the kinetic study of RDX formation (Figure 1). The higher reaction rate is attributed mainly to local overheating arising from the use of hexamine instead of hexamine dinitrate. However, part of the effect may be due to the slower addition of hexamine which required two minutes. Subsequent work of the Armament Research

Department mentioned below, indicated a sensitivity of RDX yield to rate of hexamine addition under certain conditions. The necessity of adding hexamine slower than hexamine dinitrate, for isothermal conditions, may thus account for some of the minor discrepancies between the author's results and those of the Armament Research Department who used hexamine consistently.

The later reports referred to below were not available to the author until the kinetic study of RDX formation had been completed. Most of these independent observations are in general agreement with the results of the above investigations. In comparing curves it must be kept in mind that the Armament Research Department reports acid : hexamine ratios on a weight basis. Reporting a constant acid : hexamine weight ratio represents a molar ratio changing with the acid concentration. Thus the difference in the mode of expressing the ratio causes a difference in the shape of corresponding curves when one of the ordinates is nitric acid concentration.

In December, 1942, the Armament Research Department reported an investigation (33) of the yields of RDX obtained from 12.5:1 and 25:1 weight ratios of nitric acid : hexamine, varying the concentration of nitric acid from 86 to 101 per cent. Using the lower acid : hexamine ratio, the maximum yields of about 80 per cent occurred in the nitric acid concentration range, 96 to 99 per cent. Using the higher ratio, curves of similar shape were obtained but the position of the maximum yield, again about 80 per cent, was shifted to lower nitric acid concentrations and occurred in the range 94 to 96 per cent. This shift of maximum was attributed to the effective concentration of the acid being maintained at a higher level by the greater bulk of acid with the 25:1 ratio than with the 12.5:1 ratio.

With both of the acid : hexamine ratios, the yields of RDX decreased rapidly as the nitric acid concentration was reduced below the range giving the maximum yield. A slight decrease in yield was observed as the nitric acid concentration was increased above this range.

Varying the temperature from 0°C. to 30°C. had no major effect on the yield of RDX, especially at high acid concentrations. At concentrations below 90 per cent nitric acid, the yields at 20°C. were slightly higher than those at other temperatures. It was pointed out, however, that with the low acid concentrations, the reaction may not have been complete in the two hours allowed.

A further study of the nitrolysis of hexamine with

98 per cent nitric acid at 0° and 20°C. was reported by the Armament Research Department in March, 1943 (45). The ratio of nitric acid : hexamine by weight was varied from 4:1 to 65:1, the maximum yield of 79 per cent being obtained with a 12:1 weight ratio. When the acid : hexamine ratio was lower than 20:1, no difference was observed between the yields of RDX at 0° and at 20°C., but with ratios higher than 20:1, the yields at 0°C. were slightly higher than those at 20°C.

Several months later, the Armament Research Department reported more investigations (46, 47) of the variation of RDX yield with variation of the acid concentration and acid : hexamine ratio. From the shape of the curves of yield vs. acid concentration at different acid : hexamine ratios it was estimated that maximum yields of 78-80 per cent could probably be obtained with 100 to 101 per cent nitric acid and a weight ratio of acid : hexamine of only 8:1. When 100 per cent nitric acid is used in higher ratios, the yield is lowered slightly. It was pointed out that, in the region of acid : hexamine ratios where the yield is sensitive to acid concentration, the yield is also sensitive to rate of addition of hexamine. A slower addition of hexamine tended to give a higher yield of RDX. This effect is to be expected from the results of the kinetic study of RDX formation since when the hexamine is added slowly the initial ionization repression and water formation would be less. The result would be a higher initial rate of RDX formation which brings a higher yield of RDX when the yield is below the maximum (the region where yield is sensitive to acid concentration).

ISOLATION OF AN INTERMEDIATE

The results of the investigations of the nitrolysis reaction at -20°C. indicated that the RDX obtained after one minute of reaction contained an impurity in relatively large amount. Furthermore, it appeared quite likely that this impurity was an intermediate between hexamine dinitrate and RDX.

In further investigations the temperature was lowered to -40°C. to retard the formation of RDX still more. Carefully diluting with ice after allowing the reaction to proceed for 45 seconds at this temperature resulted in the precipitation of a practically pure compound, melting at 97-98°C. (corr.), with decomposition. This material was called PCX. The exact procedure used for its isolation is the following:

Eighty millilitres of light yellow 97 per cent nitric acid was mechanically stirred in a 400-ml. beaker immersed in an acetone - solid carbon dioxide bath. When the nitric acid was just slightly solidified, ten grams of hexamine dinitrate free from lumps was added, and after about 45 seconds, finely chopped ice was added to bring the total volume to approximately 250 ml. A fine white precipitate then separated. The cooling bath was removed and the mixture in the beaker was stirred for another five to ten minutes for complete precipitation of the intermediate and for solution of any fine particles of unreacted hexamine dinitrate. The solid in suspension was then separated by suction filtration, being decanted from any lumps of hexamine dinitrate which remained in the bottom of the beaker.

After the solid on the filter had been freed from nitric acid by suction, it was washed three times with cold ether and again sucked dry. The product was placed immediately in a vacuum desiccator and dried overnight. The yield thus obtained was about 5.0 grams. The melting point was 97-98°C.(corr.), with decomposition.

The melting point was raised to 98-99°C.(corr.) by further washing with cold 50 per cent nitric acid and boiling with chloroform, followed by another rinse with ether.

One gram of PCX was converted to approximately 0.9 gm. of pure RDX by allowing it to react with 2.0 ml. of 97 per cent nitric acid at 0°C. for 30 minutes.

It was found that PCX could also be converted to RDX by acetic anhydride alone, but the product was somewhat impure, melting at 197-200°C.(corr.) with decomposition, after boiling. The yield was lower, too, being about 0.7 gm. from 1.0 gm. of PCX. This less efficient action of acetic anhydride was later shown to be due to simultaneous acetylation of the PCX. When one mole of nitric acid per mole of PCX was added to the acetic anhydride, the conversion to RDX was improved greatly, the usual high yield of pure RDX being obtained.

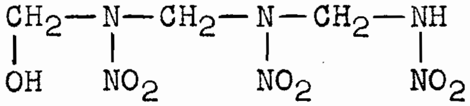
An elemental analysis of PCX gave the following figures:[*]

Carbon $\begin{matrix}15.1\\15.0\end{matrix}$;   Hydrogen $\begin{matrix}3.48\\3.54\end{matrix}$;   Nitrogen $\begin{matrix}34.5\\34.7\end{matrix}$;

This suggested the empirical formula, $C_3H_8N_6O_7$, or $RDX \cdot H_2O$, for which the calculated values are:

Carbon 15.0%;   Hydrogen 3.34%;   Nitrogen 35.0%

Since no test for nitrate ion was obtained at first, the structure of PCX was originally thought to be that of the straight chain compound



$$\begin{array}{ccccccccccc} CH_2 & - & N & - & CH_2 & - & N & - & CH_2 & - & NH \\ | & & | & & & & | & & & & | \\ OH & & NO_2 & & & & NO_2 & & & & NO_2 \end{array}$$

The conversion of PCX to RDX was ascribed to a cyclodehydration reaction. Subsequent work showed, however, that a positive diphenylamine test for nitrate ion was given by solid PCX, and decomposition of PCX in concentrated sulphuric acid, followed by ferrous sulphate titration, showed approximately one mole of nitrate

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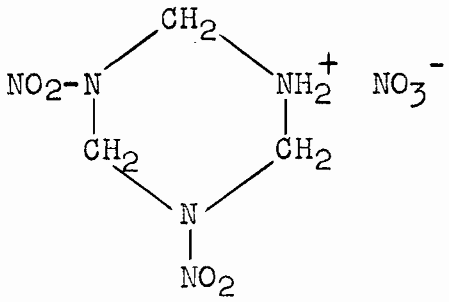
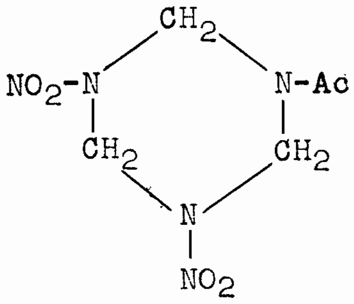
[*] Thanks are due to Dr. G.F. Wright of the University of Toronto for the elemental analysis of PCX. The date of the analysis was March 19th, 1943.

ion per mole of PCX. Estimation of the nitrate ion by hydrolyzing PCX in water and precipitating with nitron reagent according to the method of Cope and Barab (48) showed one mole of nitrate ion per mole of PCX. For this analysis, the absence of nitrite ion in the solution was demonstrated by testing with potassium iodide and starch.

On the basis of the above evidence, a cyclic structure for PCX appears most probable, viz.,



A short time later, Wright (49) isolated a by-product from the Bachmann Reaction which he called TAX and to which he assigned the following structure:



The cyclic structure for PCX was then given support by the conversion of PCX to TAX in the presence of acetic anhydride and sodium acetate(50,52). TAX is undoubtedly the impurity present in the RDX formed by the reaction of PCX and acetic anhydride, alone.

Preparation of PCX

The original procedure for the isolation of PCX was modified later to permit the preparation of large batches of PCX and to eliminate the necessity of first preparing hexamine dinitrate.

Pale yellow 88 per cent nitric acid was obtained by diluting 97-98 per cent acid with 70 per cent, and 280 ml. of this was cooled and mechanically stirred in a beaker immersed in an acetone-solid carbon dioxide bath. When the temperature was between -35° and $-40^{\circ}C.$, 30 gms. of dry hexamine was poured in with vigorous stirring, the addition requiring 10-15 sec. The stirring was continued and the temperature allowed to rise to $0^{\circ}C.$, where it was held carefully for four to five minutes. The reaction mixture was then cooled to about $-25^{\circ}C.$ and poured over chopped ice to give a final volume of about 750 ml. If necessary, cold water was added to complete the dilution, but care was taken to keep the temperature at all times below $0^{\circ}C.$

A method of cooling alternative to immersion of the beaker in an acetone-solid carbon dioxide bath was to add small lumps of solid carbon dioxide directly to the nitric acid. After some experience this method permitted good temperature control.

The diluted liquor was allowed to stand with stirring but without further cooling for five to ten minutes, or until most of the ice had melted. The PCX was separated by suction filtration using a large sintered-glass filter. It was washed on the filter once with cold ethanol (ca 0°C.), then twice with cold ether, and dried in a vacuum desiccator overnight. The yield was approximately 22 gms., and the melting point, 98-99°C.(corr.), with decomposition.

PCX could be obtained in well-defined crystals, with some purification effected, by recrystallizing from nitric acid in the following manner.

Ten grams of PCX was added to 175 gms. of colourless 75 per cent nitric acid at -20°C. and stirred until dissolved. Ice water was then added very slowly with vigorous stirring, keeping the temperature between -20°C. and -15°C. After 85 ml. of water had been added, the temperature was held at -15°C. for another five minutes for complete precipitation, the stirring being continued. The mixture was then filtered with suction, the PCX being washed with cold ethanol and ether as before. The PCX was placed immediately in a vacuum desiccator and allowed to dry overnight.

Samples of PCX were shown to be free from hexamine dinitrate and RDX by the following tests:

About one gram of PCX was shaken with 20-25 ml. of water at 0°C., filtered, and approximately 3 ml. of one normal iodine solution, containing 180 gms. of potassium iodide per litre, was added slowly to the filtrate. The absence of a greenish-black precipitate of hexamine dinitrate tetraiodide indicated no hexamine dinitrate was present. The residual PCX on the filter was added to another 20-25 ml. of water and completely decomposed by boiling for 1-2 minutes. The absence of a precipitate after cooling showed that RDX was not present.

The purity of PCX samples was then estimated by determining the yield of RDX produced from the reaction with very concentrated nitric acid under the following conditions:

Three millilitres of 97-98 per cent nitric acid was cooled in a 125-ml. Erlenmeyer flask to 0°C. by shaking in an ice-water bath, and 1.5 gm. of PCX was added. After shaking for one hour at this temperature, the reaction mixture was diluted to about 50 ml., allowed to stand overnight, then filtered through a weighed sintered-glass crucible, washed with water, and dried in the oven at 100°C. for at least four hours.

The conversion of PCX to RDX under these conditions was assumed to be practically quantitative since yields of RDX approaching 100 per cent of the theoretical were obtained from highly purified PCX. Thus the yield of RDX from any individual sample of PCX was considered to represent the purity of the PCX.

An experiment was made to determine whether acetic acid had any appreciable effect upon the formation of PCX. It has already been shown (6, 19, 25, 29) that it interfered greatly with the formation of RDX under the usual conditions for the direct nitrolysis of hexamine. The substitution of a glacial acetic acid solution of hexamine for solid hexamine in the normal procedure.for preparing PCX failed also to yield PCX. Hexamine dinitrate was formed as usual, but it remained at least partially in suspension in the 88 per cent nitric acid without reacting to PCX. This result, of course, does not mean that PCX cannot be formed by the addition of hexamine in acetic acid to nitric acid under other conditions. Recent investigations of the kinetics of

RDX formation in the presence of acetic acid have been made by Kirsch and Winkler (51) who find that good yields of RDX are obtained if the molar ratio of nitric acid to hexamine is sufficiently increased above the normal value.

A few trial experiments for the continuous preparation of PCX, in which a chloroform solution of hexamine was added to nitric acid under conditions similar to those for the normal preparation, gave promising results.

PCX was found to be relatively insoluble in most of the common inorganic solvents. It is very slightly soluble in ether and chloroform, and is slowly decomposed by alcohols at room temperature. It is hydrolyzed quite readily by water at room temperature, and formaldehyde is evolved. PCX is appreciably soluble in nitromethane. It dissolves slightly in cold reagent quality acetone, but decomposes rapidly on warming, or when added to cold commercial acetone containing a small amount of water. It is slightly hygroscopic and must be kept in a desiccator until used. The purer samples were found to be less hygroscopic and more stable on exposure to the atmosphere.

Explosive Properties of PCX

PCX has been found to have explosive properties approaching those of RDX. Its impact sensitivity is somewhat greater, while its power, as given by ballistic mortar tests, is somewhat less than that of RDX. Tests were made with the kind cooperation of Canadian Industries Limited, Beloeil, Que., on PCX prepared by two different methods: (a) the original method of adding hexamine dinitrate to 97 per cent nitric acid at -40°C., and drowning with ice after 45 sec., and (b) the modified method of adding hexamine to 88 per cent nitric acid and reacting for five minutes at 0°C. Both products gave identical results. The results of the tests were as follows:

Impact sensitivity: 0.02 gm. samples of PCX were used and a 1-kg. weight.

Height for 5 detonations out of 10 = 50 cm.
Equivalent height for RDX = 67 cm.

Ballistic mortar tests: 5.00 gm. samples of PCX were detonated with #6 caps.

Explosive power of PCX = 134% T.N.T.
Explosive power of RDX = 147% T.N.T.

Conversion of these PCX samples to RDX with nitric acid the following day showed them to be only 88 to 90 per cent pure. It is estimated that when the explosive power tests were made, the PCX content of the samples probably was between 90 and 95 per cent. The impurities were neither hexamine dinitrate nor RDX, since tests were made for both of these, but were probably decomposition products of PCX.

X-ray diffraction patterns of PCX, obtained by Canadian Industries Ltd., Beloeil, showed the products prepared by both methods tobe identical in crystalline form.

Reactions of PCX

Reaction of PCX with Nitric Acid

The conversion of PCX to RDX was observed to be complete with relatively small amounts of nitric acid, requiring only five moles of 98 per cent nitric acid, or about eight moles of 94 per cent acid, per mole of PCX. The rate of conversion was found to be much greater than the rate of RDX production from hexamine under similar conditions of nitric acid and temperature. The rate of conversion of PCX to RDX with five moles of 98 per cent nitric acid was greater, even, than the rate of RDX production from 26 moles of 97 per cent acid per mole of hexamine. A separate section of this thesis is devoted to a study of the kinetics of the reaction of PCX to RDX and the decomposition of PCX in nitric acid.

The fast rate of conversion of PCX to RDX appeared originally to be contradictory to the fact that PCX was an isolable intermediate in the direct nitrolysis of hexamine, since this conversion was assumed to be the rate controlling, or slowest, step in the overall reaction. The investigations of the rate of RDX formation from hexamine gave no evidence of an induction period, indicating that only one rate controlling step existed, all other steps being at least 100 times faster.

Since PCX is fully formed in 45 sec. at -40°C., it is evident that all the steps leading to PCX are extremely rapid and these could not include the rate controlling step in the formation of RDX. If PCX is truly an intermediate, then the rate controlling step must be the conversion of PCX to RDX. Yet when PCX is removed from the nitrolysis liquor and mixed with pure nitric acid it is converted to RDX much more rapidly. The question then arose as to what slows up the reaction of PCX to RDX in the normal hexamine nitrolysis.

It was found experimentally that the presence of hexamine dinitrate or its reaction products had a great inhibiting effect on the conversion of PCX to RDX. One gram of hexamine dinitrate was added to 2.5 ml. of 97 per cent nitric acid prior to the addition of one gram of PCX. This lowered the yield of RDX obtained in five minutes at 0^oC. from 0.88 gm. to a few milligrams.

Comparative tests, replacing the hexamine dinitrate by equivalent weights of pyridine nitrate and potassium nitrate, showed similar effects in inhibiting the reaction of PCX to RDX. When pyridine nitrate was used under the above conditions no RDX was formed, and when potassium nitrate was used only 1/8th of the normal yield of pure RDX was obtained.

Substitution of 0.6 gm. of ammonium nitrate for the hexamine dinitrate gave only a small yield of impure RDX, melting at 188^o-200^oC.(corr.) in contrast with the very pure RDX, melting at 203^o-204^oC.(corr.), usually obtained from PCX with nitric acid.

The results of these tests are in accord with the conclusions from the investigations of the formation of RDX from hexamine which suggested that the form of nitric acid active in the rate controlling step is nitracidium ion. Furthermore, these results indicate that the specific function of nitracidium ion in the nitrolysis of hexamine may well be the conversion of PCX to RDX, and that one of the main reasons for the large excess of nitric acid is to maintain the concentration of nitracidium ion in the presence of hexamine dinitrate and its reaction by-products. This would account for the observation that, in the absence of hexamine dinitrate or other ionized nitrates, PCX can be converted to RDX in good yield with comparatively small amounts of nitric acid.

Reaction of PCX with Alkali : Isolation of PCX-A

Samples of finely-divided PCX were swirled with water and titrated with 0.2N sodium hydroxide, using phenolphthalein indicator. Lumps of PCX were avoided since these tended to become coated with a gummy material which interfered with the reaction of the PCX in the interior. Approximately 2.9 moles of alkali per mole of PCX were consumed in the titration. Slightly higher ratios were obtained by allowing the almost neutral solution to stand for several minutes before completing the titration. When a solution was heated just before the end-point was reached, it became alkaline and an odour of ammonia was detected. When PCX was boiled in water until no solid remained and then titrated with sodium hydroxide, the alkali consumption was reduced to 2.07 moles per mole of PCX.

On completion of the cold alkali titration of PCX suspended in water, but not after the titration of PCX which had been decomposed by boiling, the solution was observed to contain a small quantity (approx. 1/20th the weight of PCX used) of a finely divided white solid. This was separated, washed with ether and air-dried. It melted at 133°C.(corr.) with decomposition. Pending an analysis, this compound was referred to as PCX-A. PCX-A, weighing 0.107 gms., was obtained from 2.00 gms. of PCX, and was added to 2.0 ml. of cold 97 per cent nitric acid, allowed to react at room temperature for 15 min., then diluted and filtered. After drying in the oven at 100°C. for four hours, 0.104 gms. of pure RDX was obtained.

When PCX was neutralized with 0.6N sodium hydroxide solution, and the resulting precipitate filtered off and dried in the oven at 90°-100°C., a product, m.p. 178°C. (corr.) with previous softening, was obtained in five to eight per cent yield by weight. There is a possibility that this product may have undergone some change in the oven. One-fifth of a gram of this material was added to 3.0 ml. of 97 per cent nitric acid at 0°C. and allowed to warm to room temperature for 45 min., then diluted, filtered, and the product dried in the oven. Weight, 0.08 gms. M.p. 195°-199°C. No residue remained after boiling the material, m.p. 178°C., in water. The melting point was raised to 183°C.,(corr.) with softening after 173°C., by dissolving in cold 70 per cent nitric acid and re-precipitating with water.

PCX-A was obtained in much better yields by adding the alkali to a suspension of PCX in acetone, rather than in water. Particles of PCX then were not stabilized by the usual gummy coating and a much cleaner reaction ensued. Four grams of PCX was swirled in 10 ml. of cold reagent acetone, and 1.7N sodium hydroxide solution was added with shaking until the reaction mixture was just basic to phenolphthalein. During the addition of alkali the PCX dissolved and then another white precipitate began to appear. Finally, the mixture was diluted with water to about 100 ml. to ensure complete precipitation. The solid was removed by filtration, washed with water, rinsed with a little cold ethanol and ether, and air-dried. The yield of PCX-A was approximately 0.8 gms. or 20 per cent by weight. It melted with decomposition at 134°C.(corr.).

The addition of sufficient alkali to neutralize the PCX was found to be unnecessary and slightly detrimental to the production of PCX-A. The above procedure was followed with the following modifications. Alkali sufficient only to dissolve the PCX (ca 0.4 mole NaOH per mole PCX) was added. Almost immediately on shaking the flask again, a white solid began to crystallize out. The shaking was continued and water added dropwise to precipitate the remainder of the PCX-A. The product prepared by this method was about 24 per cent by weight of the PCX used, and melted with decomposition at 136°C. (corr.). Ethanol can be used instead of acetone in these experiments without affecting the results.

The nature of the solubility of PCX-A in various solvents can be summarized as follows:

Water - insoluble in cold, decomposed in hot.

Acetone - soluble in cold, re-precipitated on addition of water.

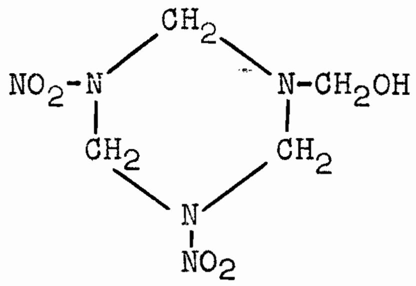
Chloroform - slightly soluble in hot and cold.

Ether - insoluble in cold, slightly soluble in hot.

Nitric Acid (70%) - soluble in cold, but no precipitate on addition of water.

Nitric Acid (2%) - insoluble in cold, recovered unchanged.

The isolation of PCX-A from the reaction of PCX and aqueous alkali was first reported at the Montreal Meeting of the RDX Committee, June 3-4, 1943, and was mentioned in the minutes of the meeting. In the Armament Research Department report of Nov. 4th, 1943 (52), the isolation of a compound, m.p. 136°C. by the trituration of PCX with water was reported. It was suggested that the compound was not formed from PCX by reaction, but was present as an impurity. Its analysis and reactions indicated the following structure:



The melting point, conversion to RDX, and other properties of this N-methylol analogue of PCX make it highly likely that it is identical with PCX-A. In an attempt to condense two molecules of PCX with one of formaldehyde, Wright (53) allowed PCX to react with aqueous sodium hydroxide and formaldehyde, and identified the only water-insoluble product as the 1,3-dinitro-5-methylolcyclotrimethylenetriamine illustrated above. Since formaldehyde (detected by its odour) is formed during the preparation of PCX-A from PCX and aqueous sodium hydroxide, this work of Wright's is almost unequivocal evidence that PCX-A is the same compound.

The following experimental evidence indicates, however, that PCX-A is formed from PCX by reaction and is not present to any appreciable extent as an impurity in PCX prepared by the method already described.

1. When pure water, instead of aqueous sodium hydroxide, was used to dissolve PCX suspended in acetone, the procedure being otherwise as previously outlined, no PCX-A was obtained.

2. When the solution of PCX in aqueous acetone was neutralized immediately with aqueous sodium hydroxide, the yield of PCX-A was approximately five per cent, on a weight basis.

3. One gram of PCX and 0.2 gms. PCX-A were shaken together in 15 ml. of water at room temperature for one hour, filtered, rinsed with a little cold alcohol and ether, and air-dried. Weight of product = 0.2 gms. M.p. 134°C.(corr.).

4. The previous experiment was repeated without adding any PCX-A and only a trace (ca 5 mg.) of a dirty residue remained.

The formation of PCX-A from PCX might occur by the following steps:

(a) Removal of HNO_3 from the PCX molecule to yield the free amine.

(b) Hydrolysis of some of the PCX with the liberation of formaldehyde.

(c) Reaction of formaldehyde with the free amine of PCX to give PCX-A.

Since there is a possibility that PCX-A may be a precursor of PCX, and another intermediate in the direct nitrolysis of hexamine to RDX, a kinetic study of its reaction with nitric acid might be of interest.

Reaction of PCX with Pyridine

In an attempt to prepare the free amine of PCX, nitric acid was removed from the amine nitrate by the action of pyridine. Solid PCX was added with stirring, at about 20°C., to reagent grade pyridine until no more would dissolve. After the addition was complete the solution was cooled with a mixture of solid carbon dioxide and acetone until it had become almost solidified by precipitation of a white solid. The viscous sludge was filtered with suction and the filtrate kept at a temperature below 0°C. The residue on the filter was identified as pyridine nitrate. The filtrate was washed twice by shaking with cold ether to remove unreacted pyridine and a slightly yellow viscous oil, insoluble in ether, remained. When this oil was treated with an excess of 97 per cent nitric acid at room temperature pure RDX was obtained in apparently good yield. The addition of water to the oil precipitated a curdy, white solid which, when dried in the oven at 90°C., melted at 181°-183°C.(corr.). The melting point of a mixture of this material with that melting at 183°C. obtained from PCX and aqueous sodium hydroxide indicated the two to be identical. Here again, it is possible that the product may have been changed by heating in the oven.

Conversion of PCX to RDX in the Presence of BF_3 and P_2O_5

The two following experiments indicate that PCX is converted to RDX by reaction with boron trifluoride. Since they are merely isolated tests they do not represent optimum conditions or yields, but show qualitatively the nature of the reaction.

Boron trifluoride was bubbled into 5 ml. of nitromethane in a test-tube for a few minutes and appeared to be very soluble. The solution, which had become quite warm, was cooled and added to a suspension of 0.80 gms. of PCX in four to five millilitres of nitromethane. The mixture was kept cool by immersion of the test-tube in ice-water, and BF_3 was bubbled through for another three to four minutes, the PCX dissolving completely in two minutes. The solution was diluted to 75 ml., boiled, cooled and filtered. After drying in the oven, the precipitate weighed 0.37 gms., representing 50 per cent of the theoretical yield of RDX. M.p. 201^{o}-202^{o}C.(corr.).

Two grams of hexamine dinitrate was added to 6.3 ml. of 91 per cent nitric acid (molar ratio of nitric acid : hexamine = 20:1) at 0^{o}C., and shaken for two minutes.

Keeping the flask in the ice bath, BF_3 was bubbled in slowly enough to prevent the temperature from rising more than a few degrees. After 20 min. the flow was stopped, the milky white reaction mixture was diluted to 75 ml., boiled, cooled and filtered. After drying in the oven, the precipitate weighed 0.32 gms., representing 19 per cent of the theoretical yield of RDX. M.p. 199°-202°C.(corr.).

The lower yield of the latter experiment may be due to greater destruction of RDX by the greater amount of HF formed from the reaction of BF_3 with water in the nitric acid.

The two following experiments demonstrate the conversion of PCX to RDX by adding P_2O_5 just before and just after its formation.

Seven grams of P_2O_5 and 2.0 gms. of hexamine dinitrate were added to 10.2 ml. of 88 per cent nitric acid, (acid : hexamine molar ratio of 30:1), cooled to about -40°C. The flask containing the mixture was shaken in an ice-water bath for two hours, then diluted to 120 ml., allowed to stand overnight, filtered, and dried in the oven at 100°C. for four hours. The yield of RDX was 0.967 gms. or 58 per cent of the theoretical.

In a second experiment, the above procedure was followed with the exception that the hexamine was allowed to react with the nitric acid at 0°C. for three minutes, before adding the P_2O_5. The yield of RDX was 0.873 gms. or 52.5 per cent of the theoretical.

In both experiments, the P_2O_5 probably reacts with water in the nitric acid to increase the nitracidium ion concentration responsible for the conversion of the PCX to RDX.

The yields from these last experiments in which the PCX formed from hexamine dinitrate is converted to RDX by adding BF_3 and P_2O_5 to the nitrolysis liquors, are not as poor as they might first appear. It will be shown in the next section that the amounts of PCX present under these conditions are well below the theoretical.

The isolation of PCX resulted in many investigations of its reactions by other workers, particularly the Armament Research Department. The elemental analysis of PCX and properties suggesting the cyclic amine nitrate structure were confirmed (52).

American workers have studied the preparation of PCX (54, 55, 56). Early attempts (54, 55) were unsuccessful since the nitric acid contained too much nitrous acid.

From these experiments, a mixture of nitro and nitroso compounds was formed.

A discussion of investigations of PCX which have a bearing on the reaction mechanism are reserved for a later section.

KINETICS OF HEXAMINE DINITRATE DISAPPEARANCE AND PCX FORMATION

The kinetic study of the formation of RDX from hexamine and nitric acid suggested that the active nitrolyzing agent for the rate controlling step was nitracidium ion. The main reason for the large excess of nitric acid required in the direct nitrolysis of hexamine appears to be to maintain the concentration of this ion which may be lowered during a nitrolysis by two factors:

(a) the production of water, which reacts with nitracidium nitrate to give pseudo-nitric acid, $NO_2.OH$,

(b) the production of ionized nitrates, such as hexamine dinitrate, ammonium nitrate, and intermediate products, which repress the ionization of nitracidium nitrate.

The production of water and ionized nitrates seems to interfere mainly with the efficiency of conversion of PCX to RDX, the formation of PCX being affected to a much smaller extent, as evident from the preparation with 30 moles of 88 per cent nitric acid per mole of hexamine. There appeared to be a possibility of increasing the efficiency of the nitrolysis reaction by first preparing PCX with weaker nitric acid, then converting it to RDX with a small amount of very concentrated acid. With such a two-stage process in mind, the kinetics of PCX formation was studied first, then the kinetics of its conversion to RDX. The technical difficulties presented by its instability were to have received attention later.

Experimental

Difficulty was found in analyzing for PCX in the reaction liquor. By cooling and adding ice-water only about 75 per cent recovery was obtained and the instability of the compound made such recovery methods insufficiently accurate to be used as an analytical method. It was found preferable to convert the PCX to RDX without isolation by the addition of a large excess of 97 per cent nitric acid and to determine RDX by the usual methods. Unreacted hexamine dinitrate, which would also be nitrolyzed to RDX under these conditions, had then to be determined separately in a duplicate experiment. The analysis for hexamine dinitrate was made by the iodimetric method in which hexamine dinitrate tetra-iodide is precipitated by the addition of iodine to the diluted nitration liquor, filtered, and the filtrate back-titrated with sodium thiosulphate. The RDX, equivalent to the hexamine dinitrate unreacted prior to the analytical conversion of PCX, then was calculated and subtracted from the total RDX formed. The difference gave the RDX formed from the PCX present at the time the extra nitric acid was added.

Precursors to PCX, other than hexamine dinitrate, would not seem to be present in appreciable amount in the solutions, since about 70 to 75 per cent of the PCX indicated by these results can be isolated by diluting with ice-water, corresponding reasonably well with the amount recoverable by diluting a nitric acid solution of known PCX content under similar conditions.

From a kinetic study of hexamine dinitrate disappearance and RDX producibility, an estimation has thus been possible of the relative amounts of PCX formed with various molar ratios of 85,88 and 91 per cent nitric acid.

The nitric acid generally used was light yellow in colour, but the results agreed within experimental error with those obtained with colourless nitric acid. Acids of the desired concentrations were obtained by diluting 97 - 98 per cent nitric acid with colourless 70 per cent nitric acid, the acid concentrations being checked by titration with standard sodium hydroxide solution.

All experiments have been made at 0°C. and this temperature is to be assumed unless otherwise stated. Nitric acid of the proper concentration and amount was cooled to 0°C. by shaking in 125-ml. Erlenmeyer flasks immersed in a bath containing chopped ice and water. Each flask was stoppered with a paraffin-coated cork fitted with a glass tube leading outside the bath. This permitted escape of evolved gases and prevented moisture from entering and diluting the reaction mixture. Two gram samples of hexamine dinitrate were added to the cold acid and the flasks shaken in the ice bath for various lengths of time.

For analysis of hexamine dinitrate, the flask containing the reaction mixture was removed from the ice bath, and immediately immersed in an acetone - solid carbon dioxide bath at about -70°C. After two or three minutes in this bath, ice-water was added in sufficient quantity to dilute the nitric acid at least ten-fold. Standard one normal iodine solution (containing 180 g. KI per litre) was run into the cold solution from a burette until at least a 100 per cent excess over that required for reaction with the hexamine dinitrate had been added. The iodine was added slowly with stirring, about five to ten millilitres per minute. The mixture was allowed to stand for three to four minutes at 0° - 5°C. after the addition was complete, and then filtered through a sintered-glass crucible. No rinse of the flask or precipitate could be made owing to the solubility of hexamine dinitrate tetra-iodide. Keeping the filtrate cold, it was back-titrated with one normal sodium thiosulphate. The addition of starch indicator was found unnecessary when working with one normal solution since, at the end-point, one drop of thiosulphate resulted in a distinct colour change from yellow to white.

A calculation of the iodine disappeared then showed the amount of hexamine dinitrate in the system.

Total RDX producibility (from unreacted hexamine dinitrate and PCX) was evaluated by adding an amount of 98 per cent nitric acid sufficient to obtain maximum RDX yield within one hour at $0^{o}C$.

In estimating the amount to be added to bring the comcentration to a value such as to attain this rate of conversion, it was assumed that six moles of nitric acid were consumed, and six moles of water produced, per mole of hexamine completely converted.

The value of nitric acid concentration required for reaction at this rate is, in turn, dependent on the molar ratio of nitric acid to hexamine and was found by reference to data obtained from the kinetic study of

RDX formation.

With this additional acid added, the reaction mixture was agitated for another 60 minutes and then diluted with water to ten times the original volume. It was allowed to stand overnight for complete precipitation of RDX, then filtered through sintered-glass crucibles and dried in the oven at 90^0 - 100^0C. for four hours.

Results

The results of the studies on hexamine dinitrate disappearance and PCX formation are given in Tables VII and VIII and in Figures 15 to 23. In many of the tables and figures hexamine dinitrate is abbreviated to HADN.

All values for the molar ratio of HNO_3/hexamine include the two molecules of nitric acid in the hexamine dinitrate used. The yield of RDX obtainable from hexamine under the conditions of the above conversion is approximately 80 per cent and there is no evidence to indicate which step or steps of the nitrolysis is responsible for the 20 per cent loss. When pure PCX is treated with sufficient nitric acid of high concentration, it is converted practically quantitatively to RDX, but under the regular nitrolysis conditions its behaviour

TABLE VII

Disappearance of Hexamine Dinitrate

Hexamine dinitrate at start of reaction = 2.00 gms. (0.0075 mole)

Nitric Acid Concentration (%)	Molar Ratio[*] HNO_3/Hexamine	Time (min.)	Hexamine Dinitrate (%)
91	20.0	2	0.0
88	10.8	10	68.3
"	"	30	47.0
"	"	60	26.5
"	"	110	22.0
"	"	180	15.5
88	14.3	9	36.6
"	"	25	15.7
"	"	41	7.5
"	"	60	4.5
"	"	80	4.1
"	"	130	3.1
88	21.8	2	14.4
"	"	4	5.4
"	"	6	1.9
"	"	10	0.2
"	"	20	0.0

---

[*] Includes the 2 mols. of HNO_3 in hexamine dinitrate.

TABLE VII (cont.)

Disappearance of Hexamine Dinitrate

Hexamine dinitrate at start of reaction=2.00 gms.(0.0075 mole)

Nitric Acid Concentration (%)	Molar Ratio* HNO_3/Hexamine	Time (min.)	Hexamine Dinitrate (%)
88	30.0	2	3.0
85	30.0	2	30.3
"	"	4	12.0
"	"	7	0.63
"	"	18	0.00
85	40.0	2	13.6
"	"	4	0.3

---

* Includes the 2 mols. of HNO_3 in hexamine dinitrate.

TABLE VIII

RDX Producibility

Hexamine dinitrate= 2.00 gms. (0.0075 mole)
Additional 98% HNO_3 (to convert PCX and remaining HADN to RDX)= 16 ml. (pre-cooled), for experiments 1-33.
Additional time at 0°C. = 60 min.

Exp't No.	Nitric Acid Concentration %	Molar Ratio* HNO_3/HADN	Time (min.)	RDX (gms.)	Yield/0.8 (%)
1	91	20	2	.928	69.6
2	"	"	5	.887	66.3
3	"	"	13	.759	56.8
4	"	"	30	.624	46.7
5	"	"	60	.447	33.5
6	"	"	120	.345	25.9
7	91	30	2	1.058	79.3
8	"	"	7	1.014	76.0
9	"	"	15	.912	68.2
10	"	"	30	.864	64.7
11	"	"	80	.794	59.4
	"				
12	88	10.8	15	.795	59.4
13	"	"	25	.670	50.2
14	"	"	40	.493	37.0
15	"	"	60	.347	26.0
16	"	"	94	.280	21.0
17	"	"	120	.246	18.4

(Continued)

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[*] Includes the 2 mols. of HNO_3 in hexamine dinitrate.

TABLE VIII (cont.)

RDX Producibility

Hexamine dinitrate= 2.00 gms. (0.0075 mole)
Additional 98% HNO_3 (to convert PCX and remaining HADN to RDX)=16 ml. (pre-cooled), for experiments 1-33.
Additional time at 0° C.= 60 min.

Exp't No.	Nitric Acid Concentration %	Molar Ratio[*] HNO_3/HADN	Time (min.)	RDX (gms.)	Yield/0.8 (%)
18	88	14.3	6	.818	61.2
19	"	"	10	.687	51.4
20	"	"	19.5	.428	32.1
21	"	"	30	.313	23.4
22	"	"	45	.241	18.0
23	"	"	80	.110	8.2
24	"	"	120	.072	5.4
25	88	21.8	2	.933	69.7
26	"	"	4	.812	60.6
27	"	"	6	.769	57.3
28	"	"	10	.702	52.5
29	"	"	20	.615	46.1
30	"	"	35	.478	35.9
31	"	"	60	.336	25.2
32	"	"	90	.243	18.2
33	"	"	120	.193	14.5

(Continued)

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[*] Includes the 2 mols. of HNO_3 in hexamine dinitrate.

TABLE VIII (cont.)

RDX Producibility

Hexamine dinitrate = 2.00 gms. (0.0075 mole)
Additional 98% HNO_3 (to convert PCX and remaining HADN to RDX) = 18 ml. (pre-cooled), for experiments 34-49.
Additional time at 0° C. = 60 min.

Exp't No.	Nitric Acid Concentration %	Molar Ratio[*] HNO3/HADN	Time (min.)	RDX (gms.)	Yield/0.8 (%)
34	88	27.2	2	.975	73.0
35	"	"	5	.884	66.2
36	"	"	10	.825	61.6
37	"	"	30	.624	46.7
38	"	"	60	.469	35.1
39	88	30.0	2	1.013	76.0
40	"	"	7	.897	67.2
41	"	"	15	.813	60.8
42	"	"	30	.722	54.0
43	"	"	60	.585	43.8
44	85	30.0	2	.997	74.7
45	"	"	7	.697	52.3
46	"	"	15	.555	41.6
47	"	"	30	.415	31.1
48	"	"	60	.346	25.9
49	"	"	120	.196	14.9

(Continued)

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[*] Includes the 2 mols. of HNO_3 in hexamine dinitrate.

TABLE VIII (cont.)

RDX Producibility

Hexamine dinitrate = 2.00 gms. (0.0075 mole)
Additional 98% HNO_3 (to convert PCX and remaining HADN to RDX)=17 ml. (pre-cooled), for experiments 50-54,
Additional time at $0^{o}C$. = 60 min.

Exp't No.	Nitric Acid Concentration %	Molar Ratio* HNO_3/HADN	Time (min.)	RDX (gms.)	Yield/0.8 (%)
50	85	40.0	2	.950	71.1
51	"	"	7	.746	55.8
52	"	"	15	.679	50.8
53	"	"	35	.535	40.1
54	"	"	80	.338	25.3

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* Includes the 2 mols. of HNO_3 in hexamine dinitrate.

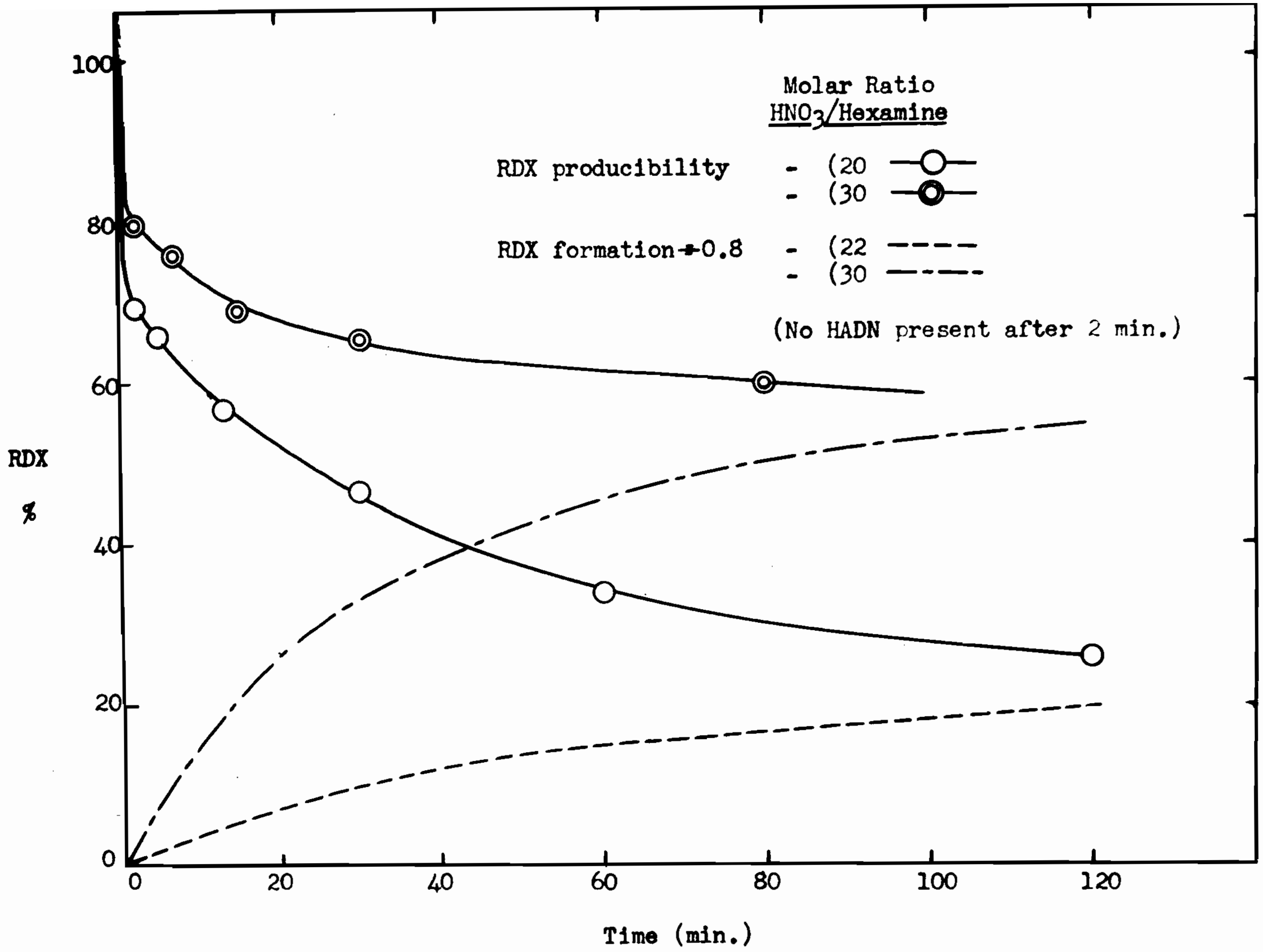


Fig. 15. RDX Producibility and RDX Formation with 91% Nitric Acid.

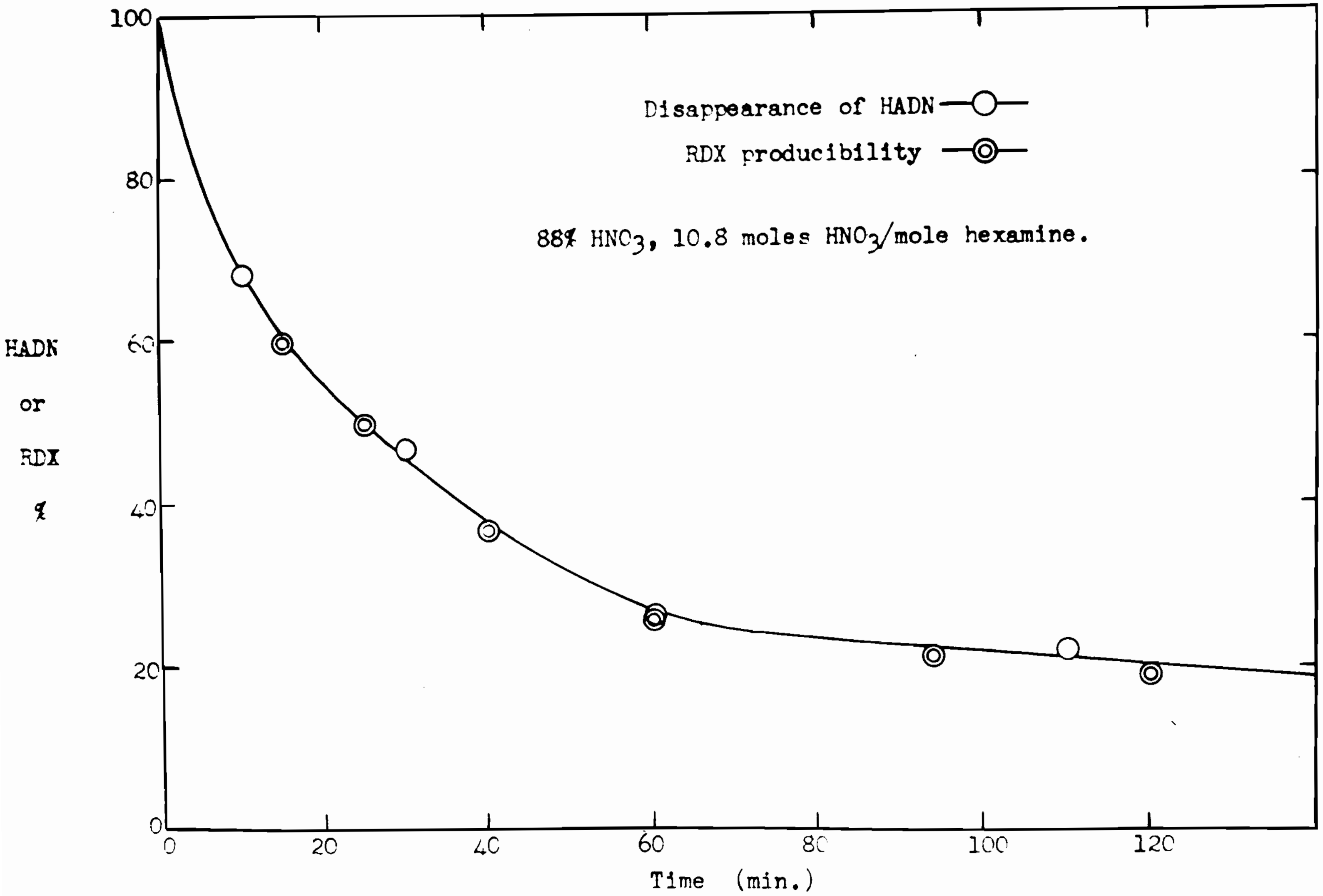


Fig. 16. Disappearance of Hexamine Dinitrate and RDX Producibility with 88% Nitric Acid.

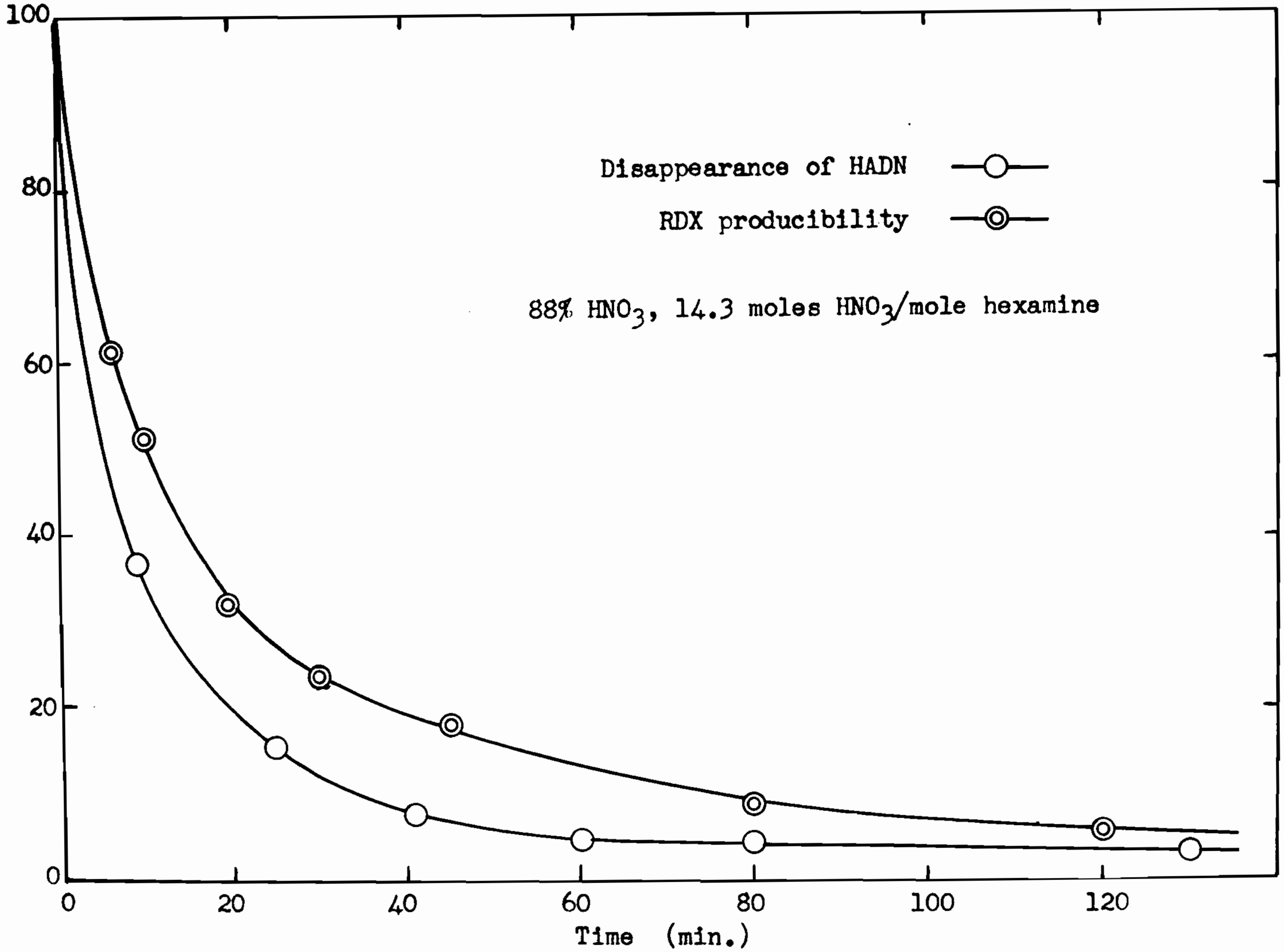


Fig. 17. Disappearance of Hexamine Dinitrate and RDX Producibility with 88% Nitric Acid.

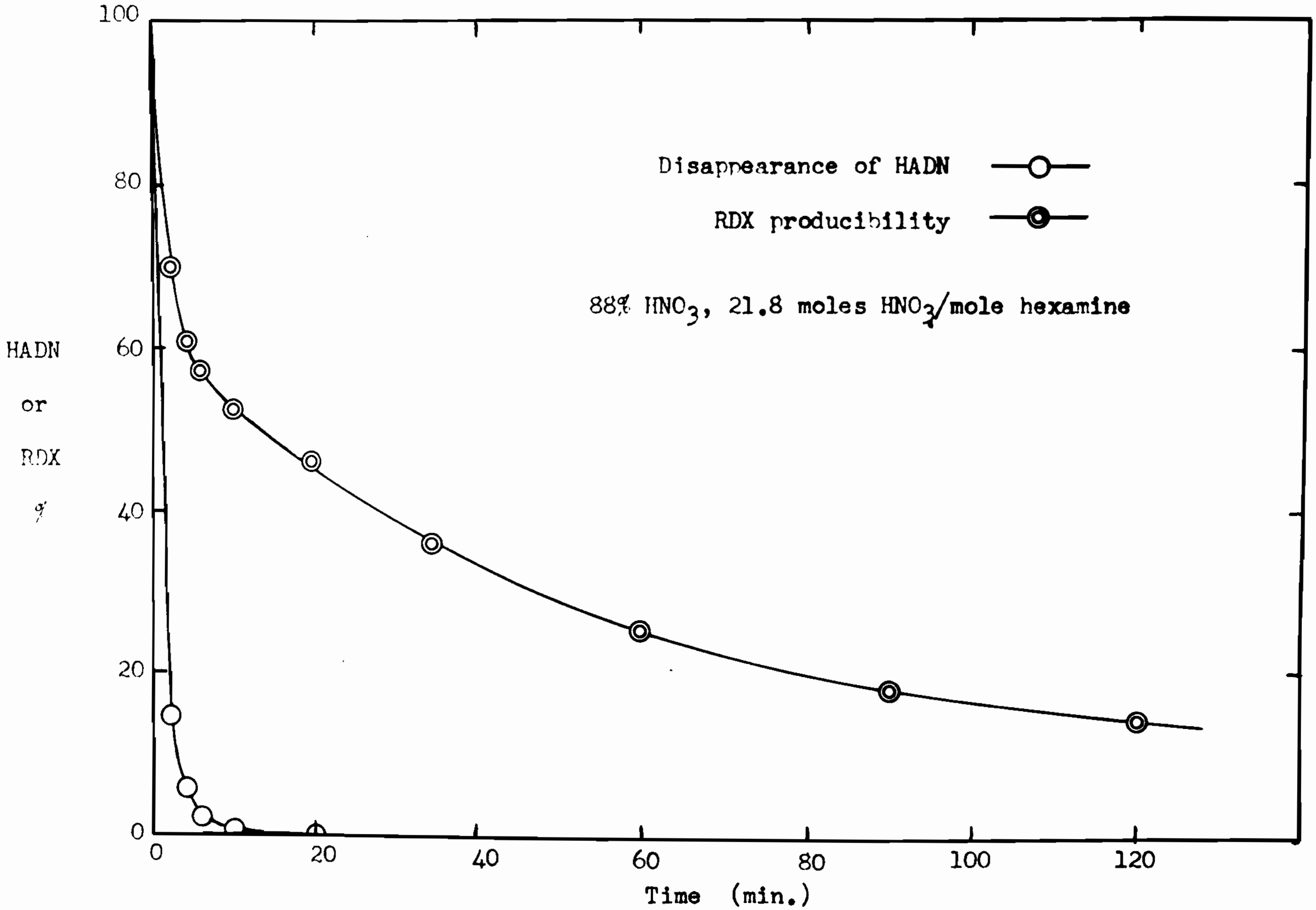


Fig. 18. Disappearance of Hexamine Dinitrate and RDX Producibility with 88% Nitric Acid.

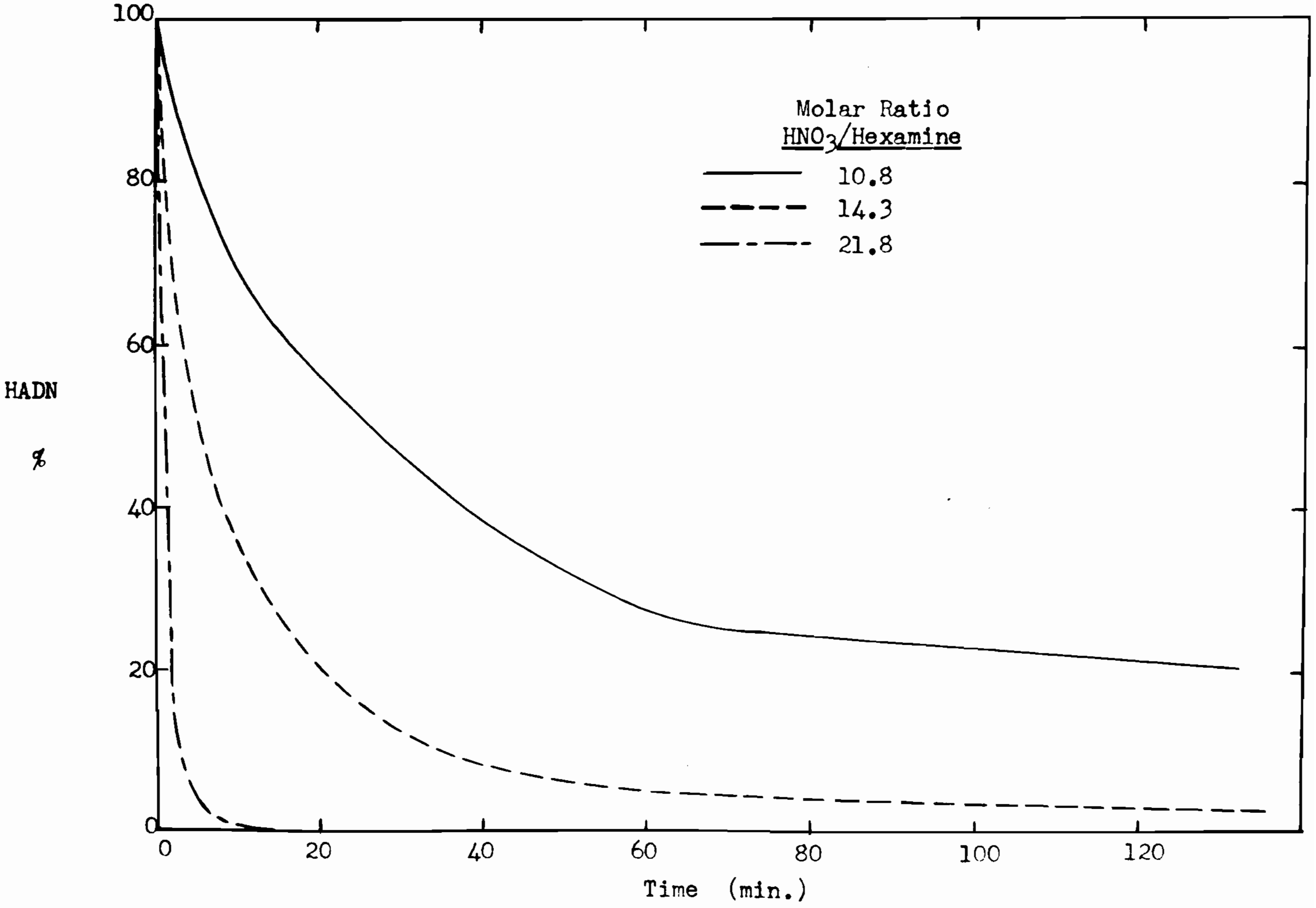


Fig. 19. Disappearance of Hexamine Dinitrate in 88% Nitric Acid.

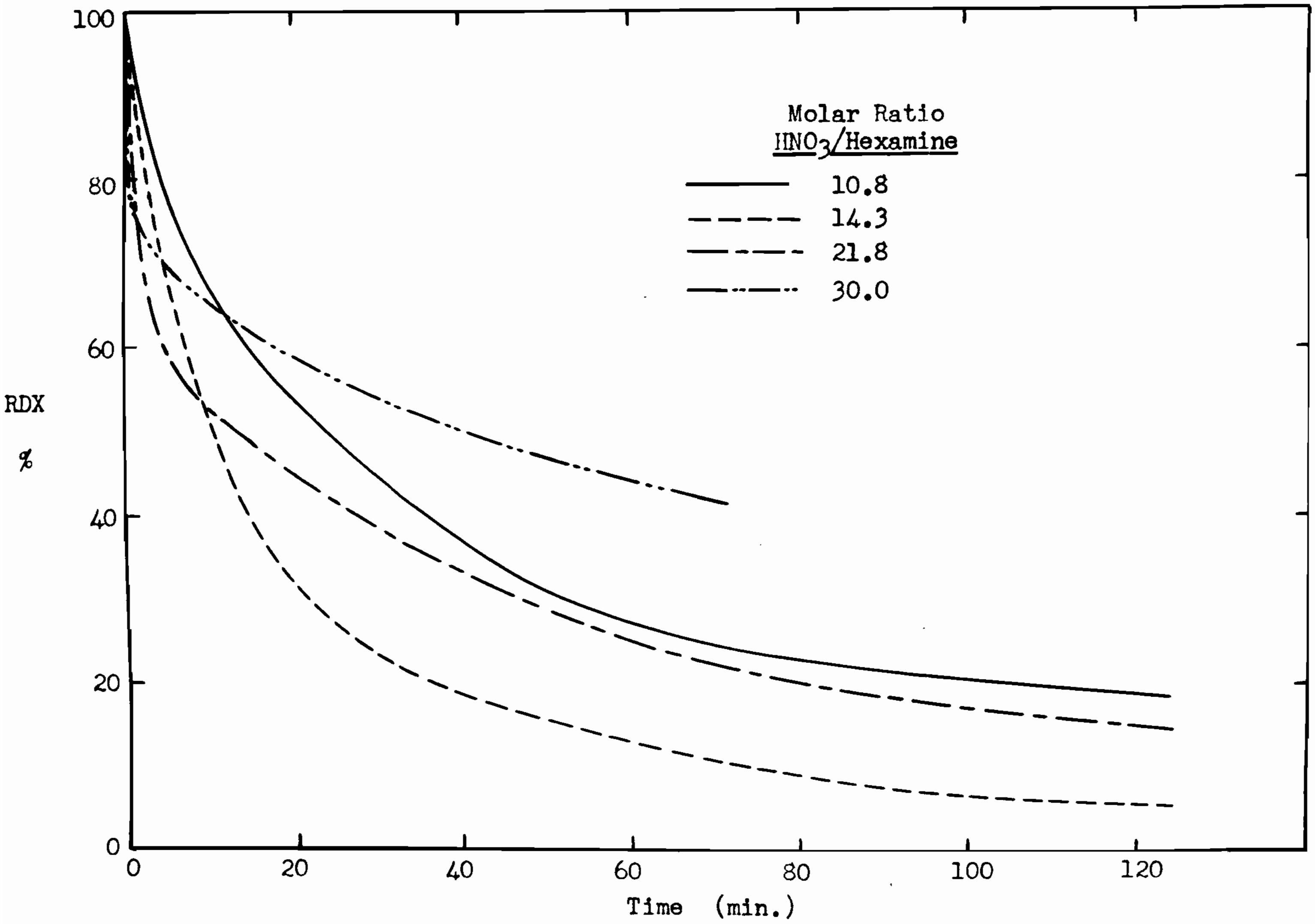


Fig. 20. RDX Producibility with 88% Nitric Acid.

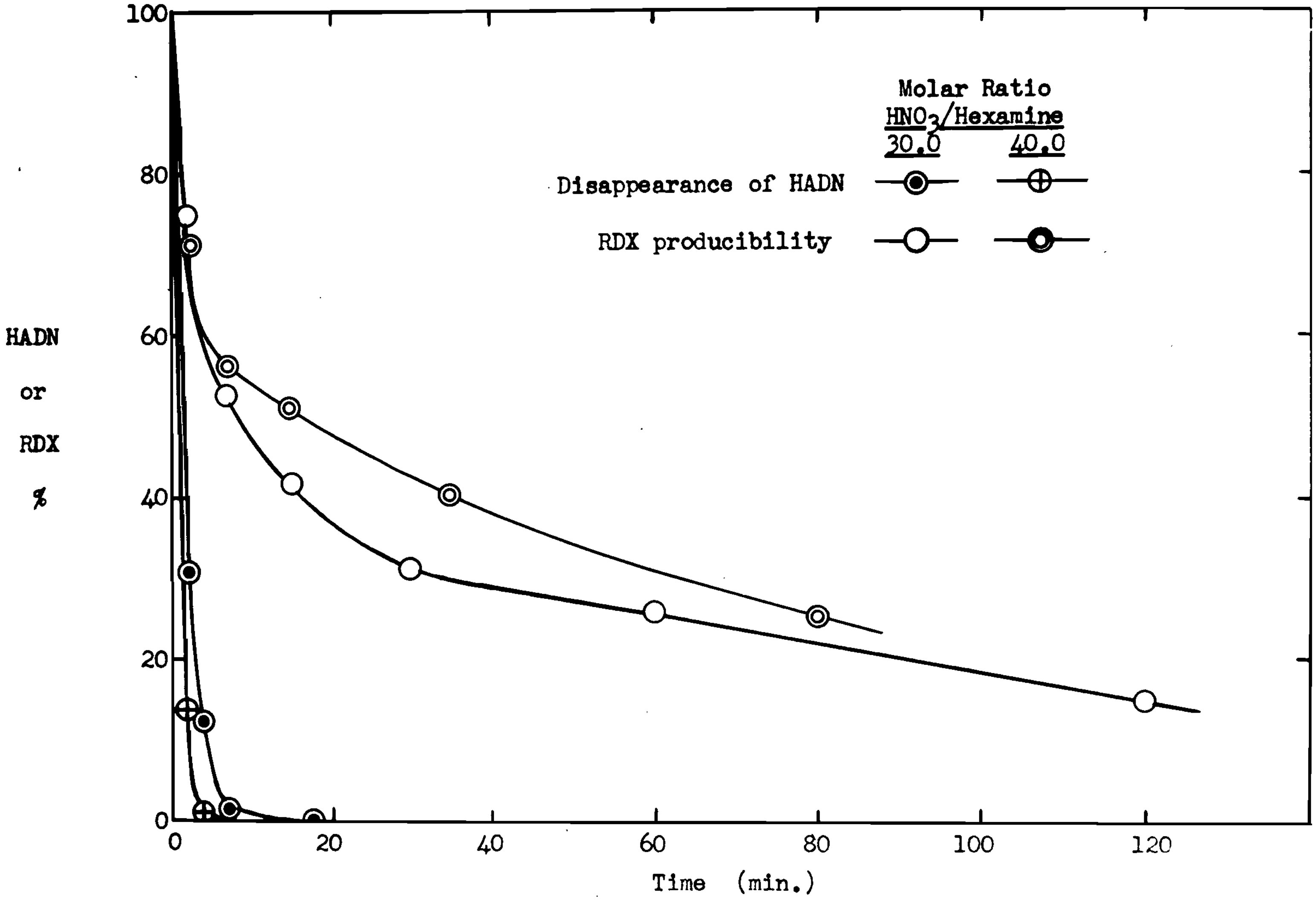


Fig. 21. Disappearance of Hexamine Dinitrate and RDX Producibility with 85% Nitric Acid.

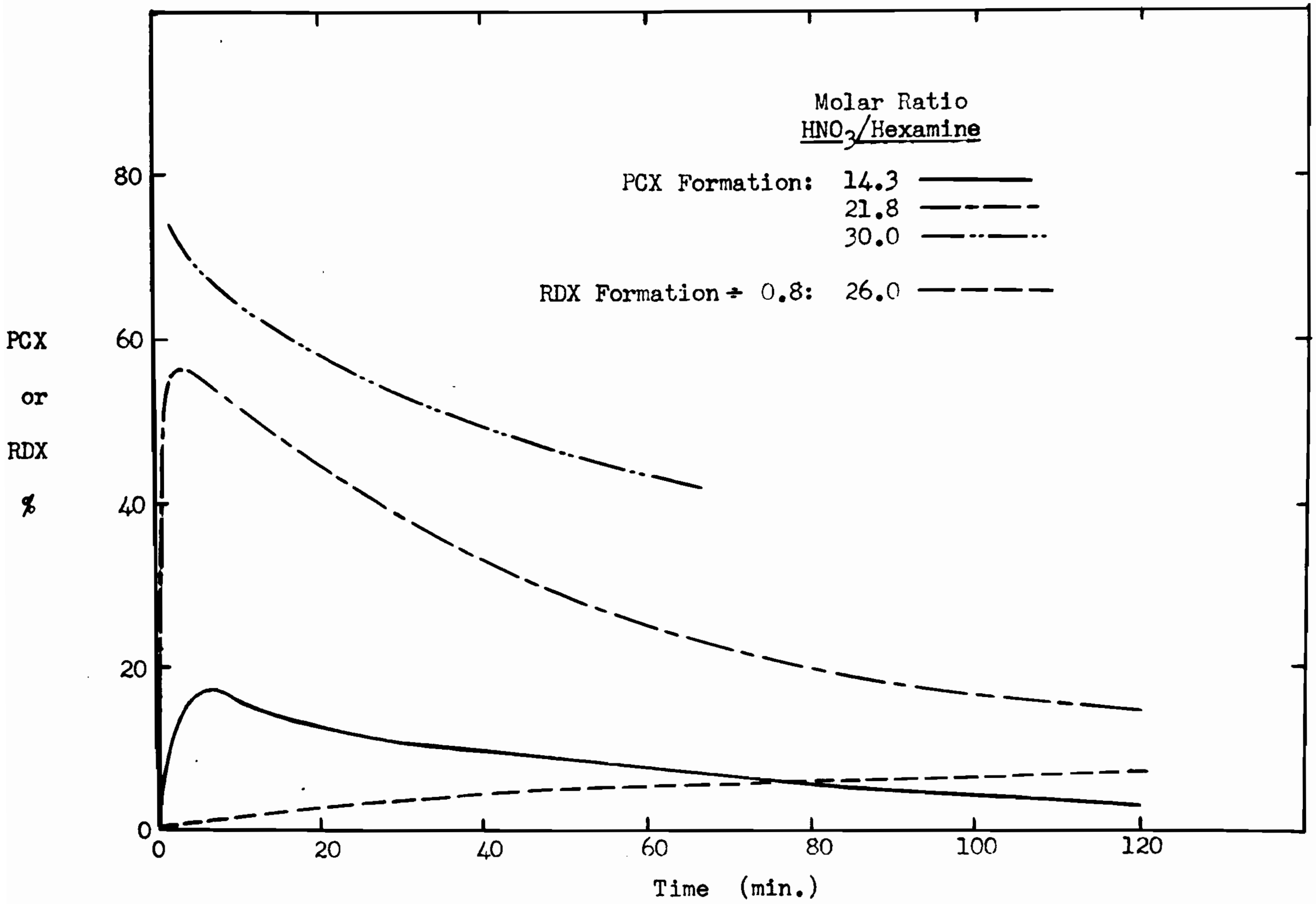


Fig. 22. Formation of PCX and RDX with 88% Nitric Acid.

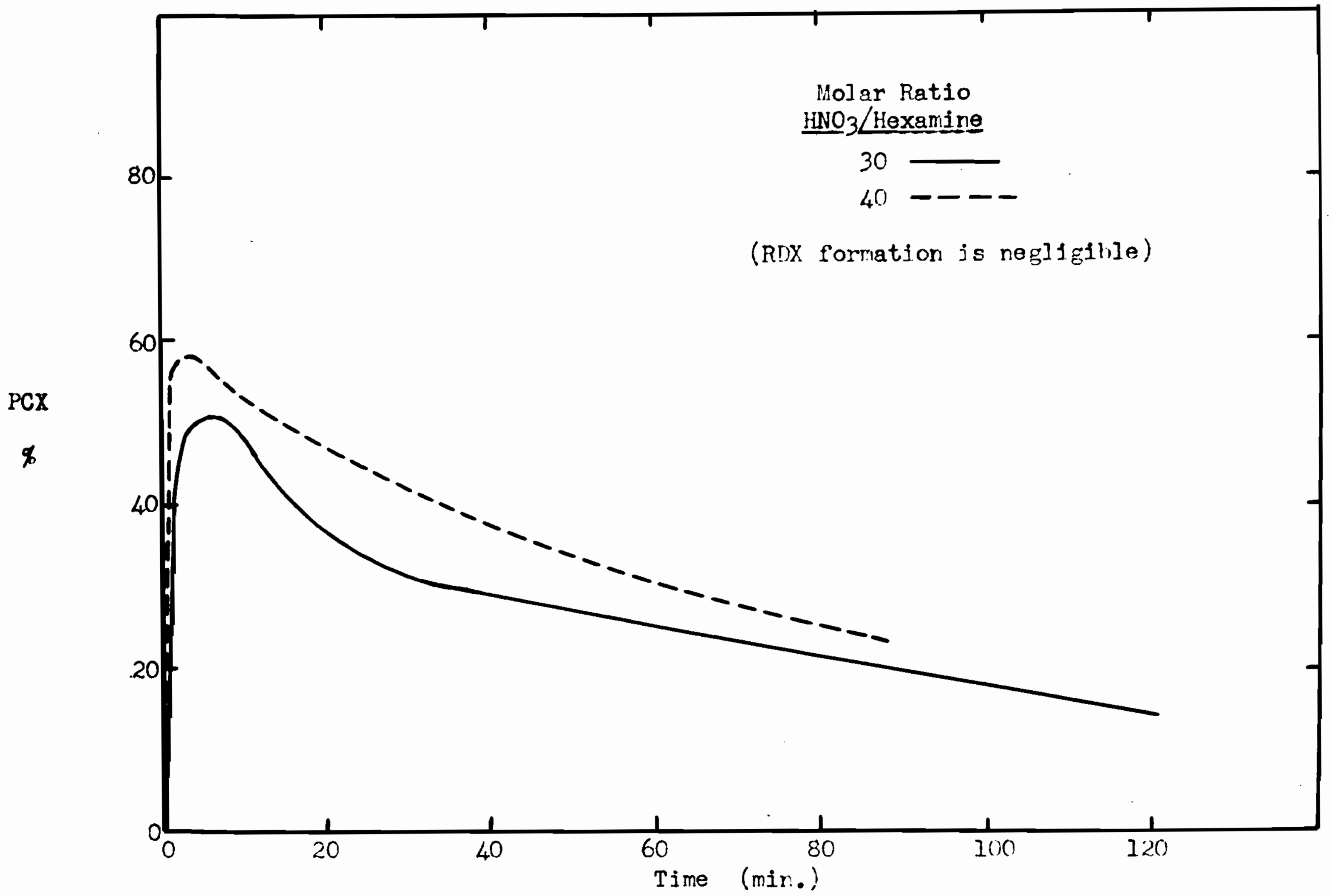


Fig. 23. Formation of PCX with 85% Nitric Acid.

is quite different, presumably owing to the presence of by-products. Its conversion to RDX is slowed greatly and its rate of decomposition is markedly increased (see below), so there is a possibility of at least part of the 20 per cent loss being due to decomposition of PCX. If 20 per cent of the PCX were decomposed during a hexamine nitrolysis it would follow that 100 per cent of the theoretical yield of PCX must have been formed. For purposes of comparison of the RDX producibility with the disappearance of hexamine dinitrate, it has been assumed that under optimum nitrolysis conditions PCX is formed in theoretical yield but decomposes to the extent of about 20 per cent during its conversion to RDX. On this basis the yields of RDX obtained from the addition of excess 98 per cent nitric acid have been divided by 0.8, giving curves for RDX producibility from which the respective curves for disappearance of hexamine dinitrate can be subtracted to give curves for the formation of PCX and its subsequent decomposition in the reaction system.

The validity of the above assumption may be questioned. However, if no decomposition of PCX occurs during its conversion to RDX under the usual nitrolysis conditions, then the curves for both PCX formation and decomposition should be 20 per cent lower, but the essential relations will remain unchanged.

Subtracting the hexamine dinitrate present from the RDX producibility at any instant obviously should give the PCX plus the RDX present at that instant (neglecting precursors of PCX). The curves for PCX formation and decomposition thus do not take into account any conversion of PCX to RDX prior to addition of the excess nitric acid. However, in all runs except those with 91 per cent nitric acid and with 30 mols. of 88 per cent nitric acid the RDX produced by the initial acid is negligible. Two curves from Figure 3, for the rate of RDX formation with 30 and 22 mols. of 91 per cent nitric acid are reproduced in Figure 15. Another from Figure 4, for the rate with 26 mols. of 88 per cent acid, is reproduced in Figure 22. For comparison these yields, also, have been divided by 0.8. It is seen that, even under these conditions, the maxima in the PCX curves are affected only slightly by the RDX production, the main effect of this conversion of PCX to RDX being to make the PCX appear more stable in the system than it is actually.

Discussion

The disappearance of hexamine dinitrate in the nitrolyses with 85 to 91 per cent nitric acid represents reaction to PCX plus reaction to other products not capable of giving RDX under the nitrolysis conditions. The latter reaction apparently does not involve hydrolysis of hexamine dinitrate, since this is relatively stable in 70 per cent nitric acid at 0°C., but is more likely a hydrolysis of one or more of the precursors of PCX.

With all the concentrations of nitric acid studied, an increase in the molar ratio of HNO_3/HADN led to an increase in the rate of disappearance of hexamine dinitrate and also to an increase in the yields of PCX. Keeping this in mind, the overlapping of RDX producibility curves in Figure 20 is readily understandable. When the molar ratio is increased from 10.8 to 14.3, the rate of disappearance of hexamine dinitrate increases considerably (Fig. 19), but the yield of PCX rises from zero to seventeen per cent (Fig. 22). Thus the total RDX producibility (hexamine dinitrate + PCX) is decreased. With a further increase of the molar ratio to 21.8, an increase of the PCX yield to 56.5 per cent outweighs the increase in rate of hexamine dinitrate disappearance and the RDX producibility is increased. Still further increases in the rate of hexamine dinitrate disappearance are limited by its rate of solution, but the yields of PCX continue to increase as higher molar ratios of HNO_3/HADN are used.

With 88 per cent nitric acid, molar ratios higher than 30 were not studied since it was felt that they would be of little interest in a consideration of practical aspects of the reactions concerned.

Figures 22 and 23 indicate that PCX is formed very rapidly but is unstable in the reaction system and begins to decompose immediately. As with RDX production, here also higher rates of formation give higher yields of PCX. With 20 and 30 mols. of 91 per cent nitric acid (Fig. 15) and 30 mols. of 88 per cent nitric acid (Fig. 22), the rate of PCX formation is so great that the maxima in the curves are reached before all the hexamine dinitrate has dissolved. If solution of the hexamine dinitrate occurred instantaneously, the maxima would be higher and sharper. The average time required for the hexamine dinitrate to dissolve completely was two minutes. Thus experiments with reaction times shorter than this were not possible.

The relation of RDX producibility to hexamine dinitrate disappearance, changing with the molar ratio of HNO_3/HADN, is shown for 88 per cent nitric acid in Figures 16, 17, 18, and for 85 per cent nitric acid in Figure 21. With 10.8 mols. of 88 per cent nitric acid (Fig. 16) the disappearance of hexamine dinitrate coincides exactly with the RDX producibility, indicating that at any instant there is insufficient PCX accumulated in the system to be detected by the methods employed. From a measurement of the rate of decomposition of some PCX added to this system (see Table X,F, in next section), it was concluded that PCX was absent, not because of extremely rapid decomposition but because it was not formed in the system.

KINETICS OF PCX DECOMPOSITION AND CONVERSION TO RDX

A kinetic study of the conversion of PCX to RDX necessarily involves a kinetic study of the decomposition of PCX since these reactions occur simultaneously. The results from the kinetic study of PCX formation suggested that more information on the decomposition of PCX in nitric acid also would be desirable. It was of interest to determine whether the reaction was a hydrolysis whose rate was dependent on the water and hydrogen ion concentrations in the nitric acid and, if this were so, whether a calibration curve of the initial rate of decomposition as a function of acid concentration could be used to find the amount of water formed during the normal nitrolysis of hexamine. Alternatively, if the decomposition of PCX was influenced by the action of some by-product of the nitrolysis of hexamine, elimination of such influence should increase the stability of PCX and thereby increase the yields of RDX obtained.

A kinetic study was made of the decomposition of PCX in nitric acids of 75 to 90 per cent, and the effect of adding other compounds, occurring as by-products in the nitrolysis of hexamine, was observed. The conversion of PCX to RDX was studied kinetically with 98,94 and 90 per cent nitric acid, and various molar ratios of reagents.

Experimental

The apparatus and nitric acid was the same as that used for the kinetic study of hexamine dinitrate disappearance and RDX producibility. Most of the reactions were studied at 0°C., and this temperature is to be assumed unless otherwise stated. The PCX was prepared from 88 per cent nitric acid by the procedure given earlier, and was shown to be free from hexamine dinitrate and RDX by the tests already described.

The samples of PCX were added to the nitric acid at 0°C., and the flasks were shaken in the ice-water bath for the desired lengths of time. To follow the decomposition of PCX, 98 per cent nitric acid was then added in sufficient amount to convert all unreacted PCX rapidly to RDX. After the flasks had been shaking for another hour, water was added to dilute the reaction mixture to ten times its volume. To follow the conversion of PCX to RDX no additional nitric acid was added, but instead, the reaction was stopped by adding 25-30 ml. of water. The mixture was then boiled for one to two minutes to decompose the unreacted PCX, and further diluted to about 100 ml. After standing overnight, the diluted mixtures were filtered through sintered-glass crucibles and the RDX dried in the oven at 90 - 100°C. for 4 hours. Yields were calculated as per cent of the theoretical.

The activation energy of the conversion of PCX to RDX, was measured by determining the rate of reaction at -15°, 0° and 10°C. with 91 per cent nitric acid. The initial rate at each temperature was estimated by drawing tangents to the rate curves at zero time.

For comparison, the activation energy of the conversion of hexamine to RDX was also measured by determining the initial rates of RDX formation with 91 per cent nitric acid at -15°, 0° and 10°C. The procedure followed in these experiments was the same as that used for the kinetic study of RDX formation described previously.

Results

Data for the decomposition of PCX are given in Tables IX and X, and Figures 24 and 25, for the conversion of PCX to RDX in Table XI and Figures 25 and 26, and for the determination of the activation energies in Tables XII and XIII, Figure 27.

For the decomposition experiments corresponding to no reaction time, the additional 98 per cent nitric acid was added before the PCX. The percentage of the theoretical yield of RDX thus obtained was taken as representing the

TABLE IX

Decomposition of PCX in Pure Nitric Acids

HNO_3 Conc'n. (%)	Molar Ratio HNO_3/PCX	Initial PCX		Time for Decomp. (min.)	Add'nl. 98% HNO_3 (ml.)	RDX (gms.)	Yield (% of theor.)
		gms.	moles				
75	17	.888*	.0036	0	18	.820	100
"	"	"	"	3	"	.822	100
"	"	"	"	10	"	.811	98.8
75	28	.883*	.00368	0	18	.817	100
"	"	"	"	3	"	.796	97.5
"	"	"	"	10	"	.786	96.3
80	33	1.210	.00505	0	17	1.118	100
"	"	"	"	2	"	1.105	98.5
"	"	"	"	10	"	1.026	91.8
"	"	"	"	10	0	.000	-
83	20	.915	.00381	0	12	.847	100
"	"	"	"	22.5	"	.726	85.8
"	"	"	"	49	"	.591	69.8
"	"	"	"	77	"	.487	57.4
"	"	"	"	120	"	.354	41.8
"	"	.570	.00238	60	0	.060	(11.4)
85	18	.837	.00349	0	10	.774	100
"	"	"	"	3	"	.759	98.0

* Incomplete solubility.

TABLE IX (cont.)

Decomposition of PCX in Pure Nitric Acids

HNO_3 Conc'n. (%)	Molar Ratio HNO_3/PCX	Initial PCX		Time for Decomp. (min.)	Add'nl. 98% HNO_3 (ml.)	RDX (gms.)	Yield (% of theor.)
		gms.	moles				
85	18	.837	.00349	10	10	.713	92.1
"	"	"	"	10	0	.000	-
85	22	.893	.00372	0	10	.826	100
"	"	"	"	5	"	.795	96.3
"	"	"	"	10	"	.765	92.6
"	"	"	"	20	"	.705	85.4
"	"	"	"	10	0	.047	(5.7)
"	"	"	"		0	.369	(44.7)
85	30	.825	.00344	0	12	.763	100
"	"	"	"	3	"	.740	97.0
"	"	"	"	10	"	.705	92.5
90	17	.873	.00364	0	7	.798	100
"	"	"	"	5	"	.774	97.0
"	"	"	"	13	"	.737	92.3
"	"	"	"	25	"	.691	86.5
"	"	"	"	50	"	.668	83.6
"	"	"	"	80	"	.663	82.9
"	"	"	"	120	"	.682	85.4

TABLE X

Catalyzed Decomposition of PCX

Reaction Media:

A: Normal undiluted nitrolysis liquor. 1.11 gms. HADN was added to 3.58 ml. 98% HNO_3 (22 moles HNO_3 per mole hexamine) at **ca**. -40°C. and shaken at 0°C. for 120 min., then the **PCX** was added.

B: The PCX was added to the reaction mixture of 2.00 gms. HADN in 7.22 ml. 88% HNO_3 (21.8 moles HNO_3 per mole hexamine) after shaking at 0°C. for 20 min. (See Figures 18, 22)

C: The PCX was added to the undiluted reaction liquor obtained after 0.893 gm. PCX had been allowed to decompose in 4.1 ml. 85% HNO_3 (22 moles HNO_3 per mole PCX) at 0°C. for infinite time (24 hours). (See Table IX).

D: 0.23 gm. (.0075 mole) of paraform was dissolved in 5.25 ml. (0.105 moles) 85% HNO_3 by shaking at 0°C. The nitric acid turned brown and a little NO_2 was evolved. The PCX was added after 15 min.

E: 0.60 gm. (.0075 mole) NH_4NO_3 was dissolved in 5.25 ml. (0.105 moles) 85% HNO_3 at 0°C., and the PCX was added.

F: The PCX was added to the liquor from a reaction with 10.8 moles of 88 % HNO_3 per mole of hexamine in which the rate of HADN disappearance coincided with the RDX producibility (Tables VII **and** VIII, Fig. 16). The addition of PCX was made after the nitrolysis had proceeded for 40 min. at 0°C.

Reaction Medium	PCX added		Time for Decomp.	Add'nl. 98% HNO_3	Total RDX	RDX from PCX added	Yield from PCX added
	gms.	moles	(min.)	(ml.)	(gms.)	(gms.)	(% of theor.)
A	0.904	.00377	0	8	1.548	0.836	100
"	"	"	3	"	1.494	0.782	93.6
"	"	"	10	"	1.457	0.745	88.2
"	"	"	10	0	0.864	0.153	18.3
"	0.000	.000	-	8	0.712	-	-

TABLE X (cont.)

Catalyzed Decomposition of PCX

Reaction Medium	PCX added gms.	PCX added moles	Time for Decomp. (min.)	Add'nl. 98% HNO_3 (ml.)	Total RDX (gms.)	RDX from PCX added (gms.)	Yield from PCX added (% of theor.)
B	1.24	.00517	0	17	1.763	1.150	100
"	"	"	3	"	1.622	1.040	90.5
"	"	"	10	"	1.385	0.862	75.0
C	0.893	.00372	0	12	1.195	0.826	100
"	"	"	5	"	1.154	0.785	95.1
"	"	"	10	"	1.111	0.743	90.0
"	"	"	21	"	1.028	0.659	79.8
"	0.000	.0000	-	0	0.369	-	-
D	0.925	.00385	0	12	0.854	0.854	100
"	"	"	10	"	0.777	0.777	91.0
E	0.840	.0035	0	12	0.776	0.776	100
"	"	"	3	"	0.735	0.735	94.7
"	"	"	11	"	0.686	0.686	88.4
F	0.883	.00367	0	16	1.329	0.815	100
"	"	"	9	"	1.227	0.713	87.5
"	"	"	18	"	1.111	0.597	73.2
"	0.000	.0000	-	0	0.514	-	-

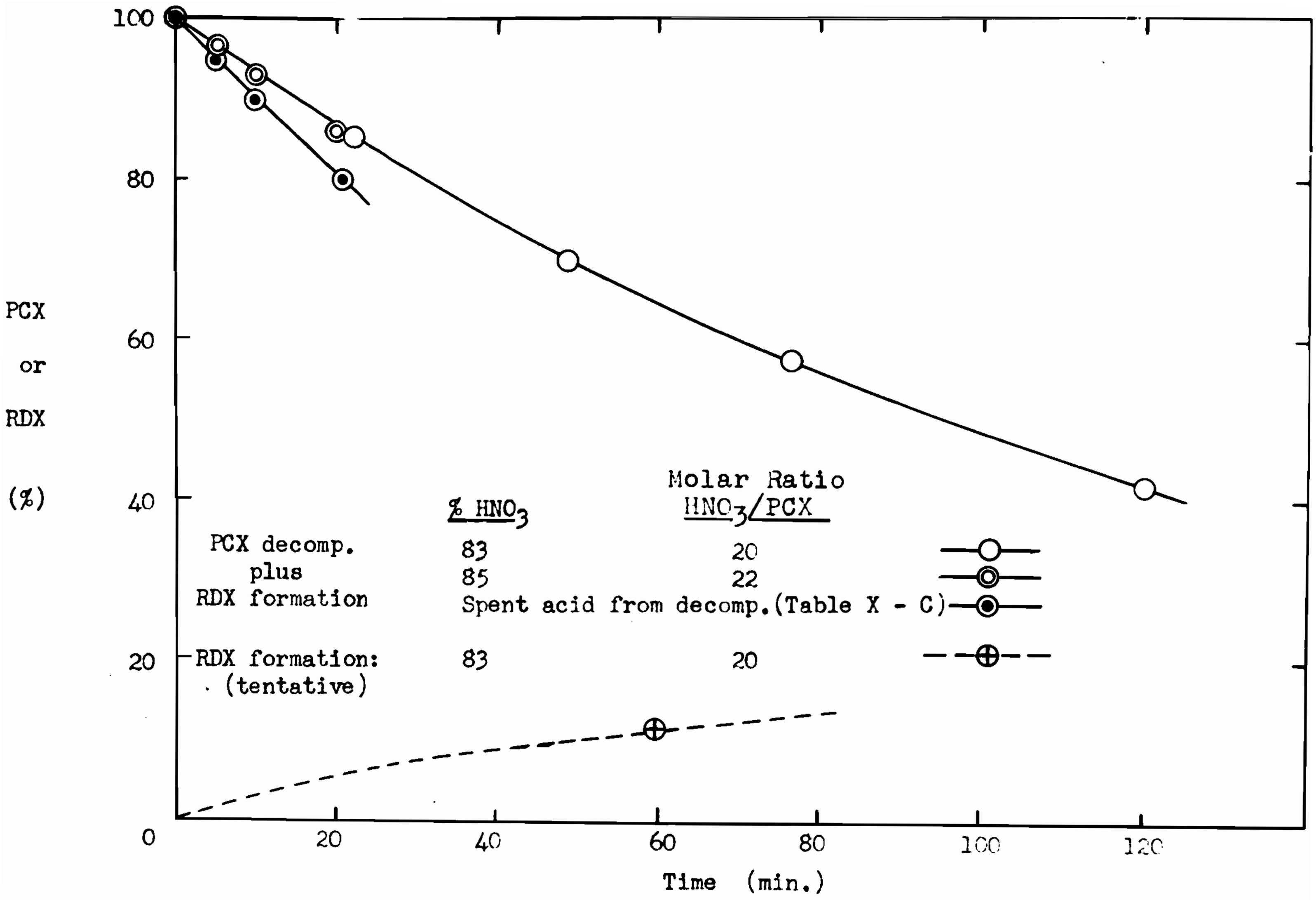


Fig. 24. PCX Decomposition and RDX Formation.

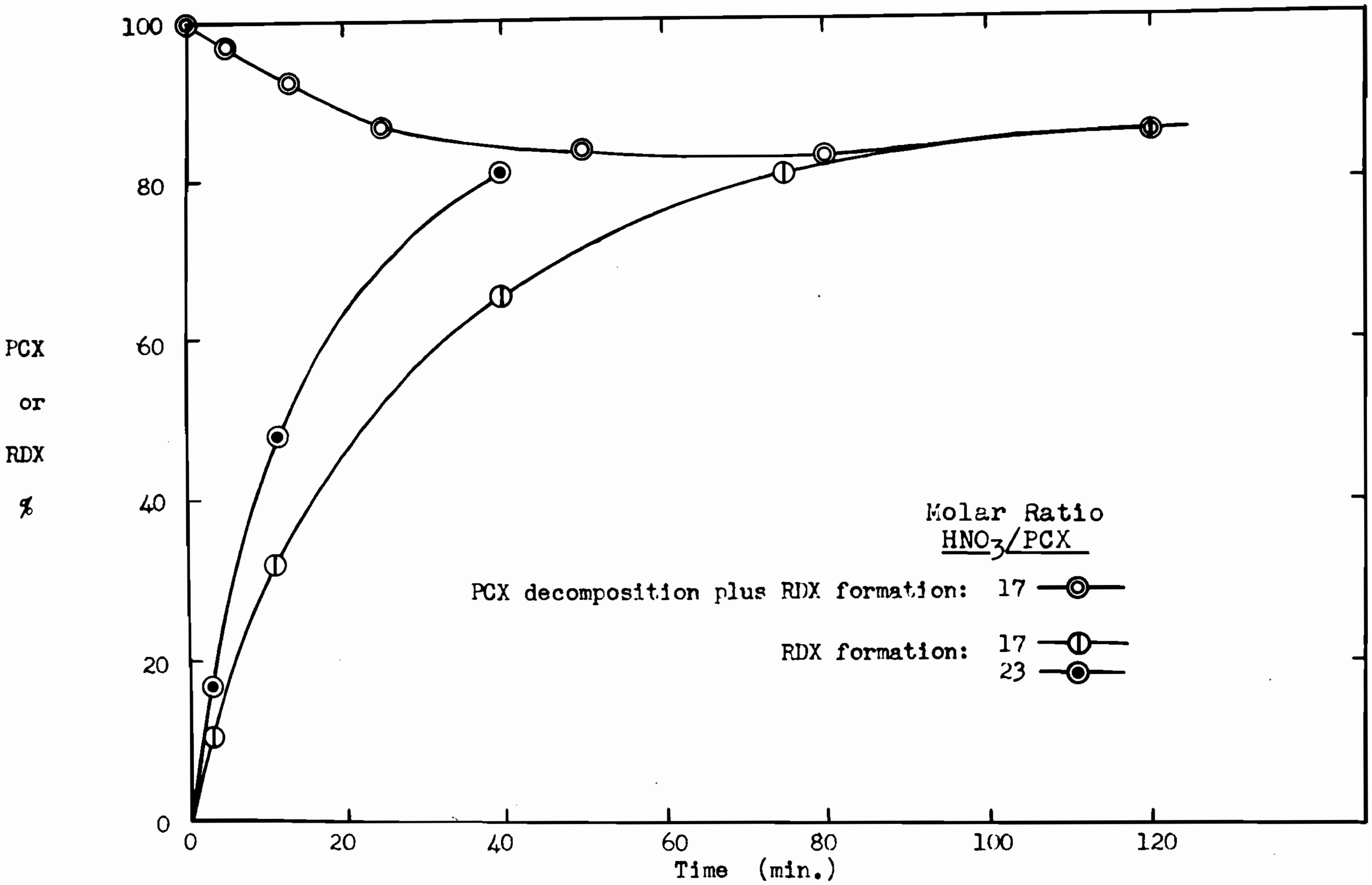


Fig. 25. PCX Decomposition and RDX Formation with 90% Nitric Acid.

TABLE XI

Conversion of PCX to RDX

HNO_3 Conc'n. (%)	Molar Ratio HNO_3/PCX	Initial PCX		Reaction Time (min.)	RDX (gms.)	Yield (% of theor.)
		gms.	moles			
98	5	1.50*	.00625	10	0.923	66.5
"	"	"	"	50	1.183	85.5
"	"	"	"	120	1.290	93.2
94	7	1.50*	.00625	11	.282	20.3
"	"	"	"	30	.588	42.3
"	"	"	"	54	.870	62.6
"	"	"	"	114	1.019	73.5
94	5	1.50*	.00625	12	.084	6.1
"	"	"	"	28	.157	11.3
"	"	"	"	50	.250	18.0
"	"	"	"	95	.299	21.5
90	23	0.88	.00367	3	.132	16.3
"	"	"	"	12	.389	47.8
"	"	"	"	40	.657	80.7
90	17	0.92	.00383	3	.088	10.3
"	"	"	"	11	.270	31.8
"	"	"	"	40	.564	65.2
"	"	0.88	.00367	75	.654	80.4
"	"	"	"	120	.694	85.5

* Not corrected for purity of PCX.

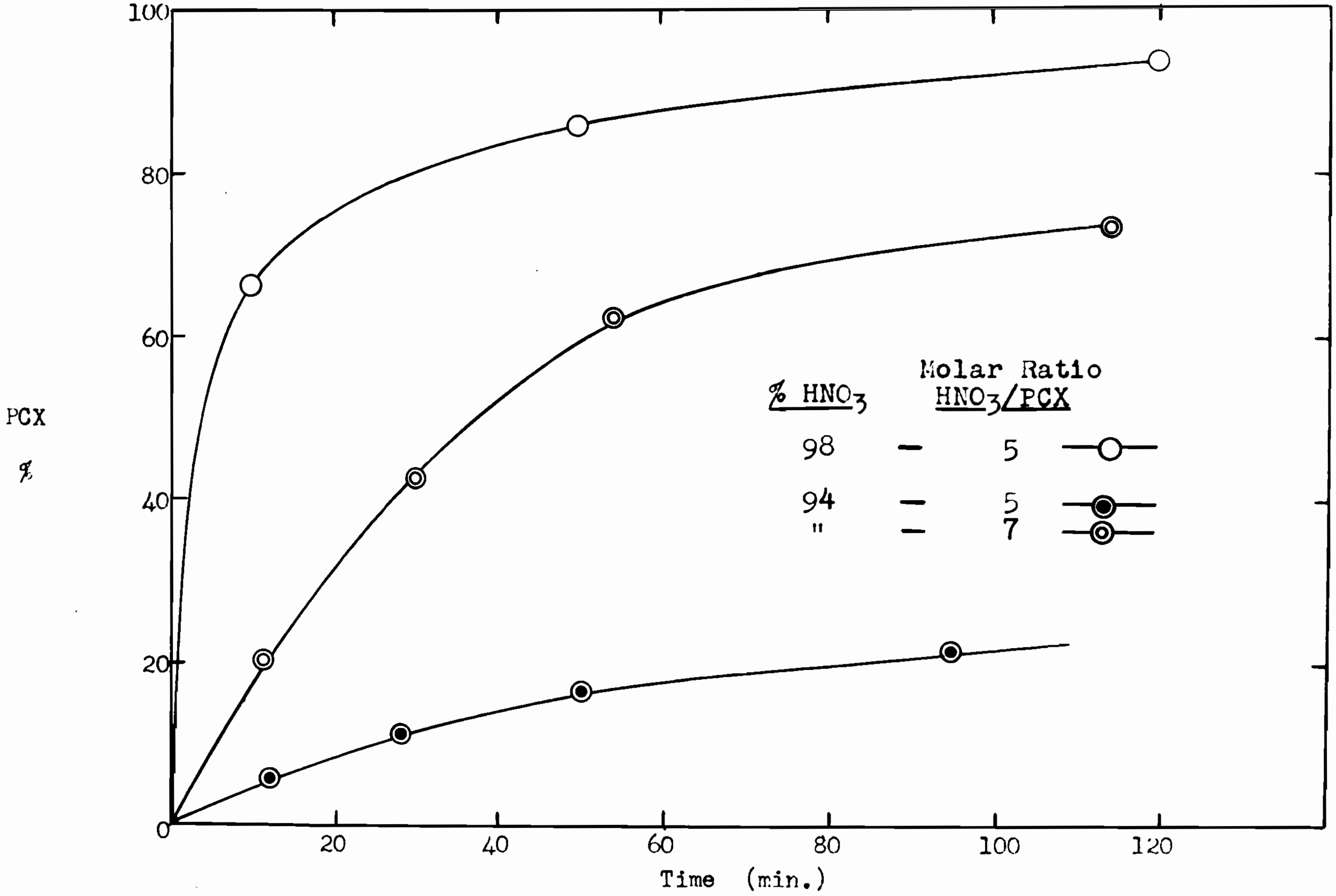


Fig. 26. Rates of Conversion of PCX to RDX

TABLE XII

Effect of Temperature on Initial Rate of Conversion of PCX to RDX

Samples of PCX = 1.50 gm. (87% pure for exp'ts. at -15°C., 86% pure for other exp'ts.)
Nitric Acid = 91 per cent, 5.2 ml.

Temp. of Reaction	Reaction Time (min.)	RDX (gms.)	Yield (%)	Initial Rate moles/min.
-15°C.	4	0.072	6.0	0.016
"	8	0.138	11.5	
"	15	0.238	19.7	
0°C.	2	0.225	18.9	0.100
"	4	0.392	32.9	
"	8	0.629	52.8	
"	15	0.853	71.7	
10°C.	2	0.538	45.2	0.340
"	4	0.776	65.2	
"	10	0.998	83.8	

TABLE XIII

Effect of Temperature on Initial Rate of Conversion of Hexamine to RDX

Hexamine dinitrate = 2.00 gms.
Nitric acid = 91 per cent, 14.0 ml.

Temp. of Reaction	Reaction Time (min.)	RDX (gms.)	Yield (%)	Initial Rate (moles/min.)
-15°C.	8	0.045	2.7	0.004
"	15	0.089	5.3	
0°C.	4	0.200	12.0	0.031
"	8	0.366	21.9	
"	15	0.559	33.5	
10°C.	3	0.445	26.7	0.112
"	6	0.659	39.5	
"	12	0.852	51.0	

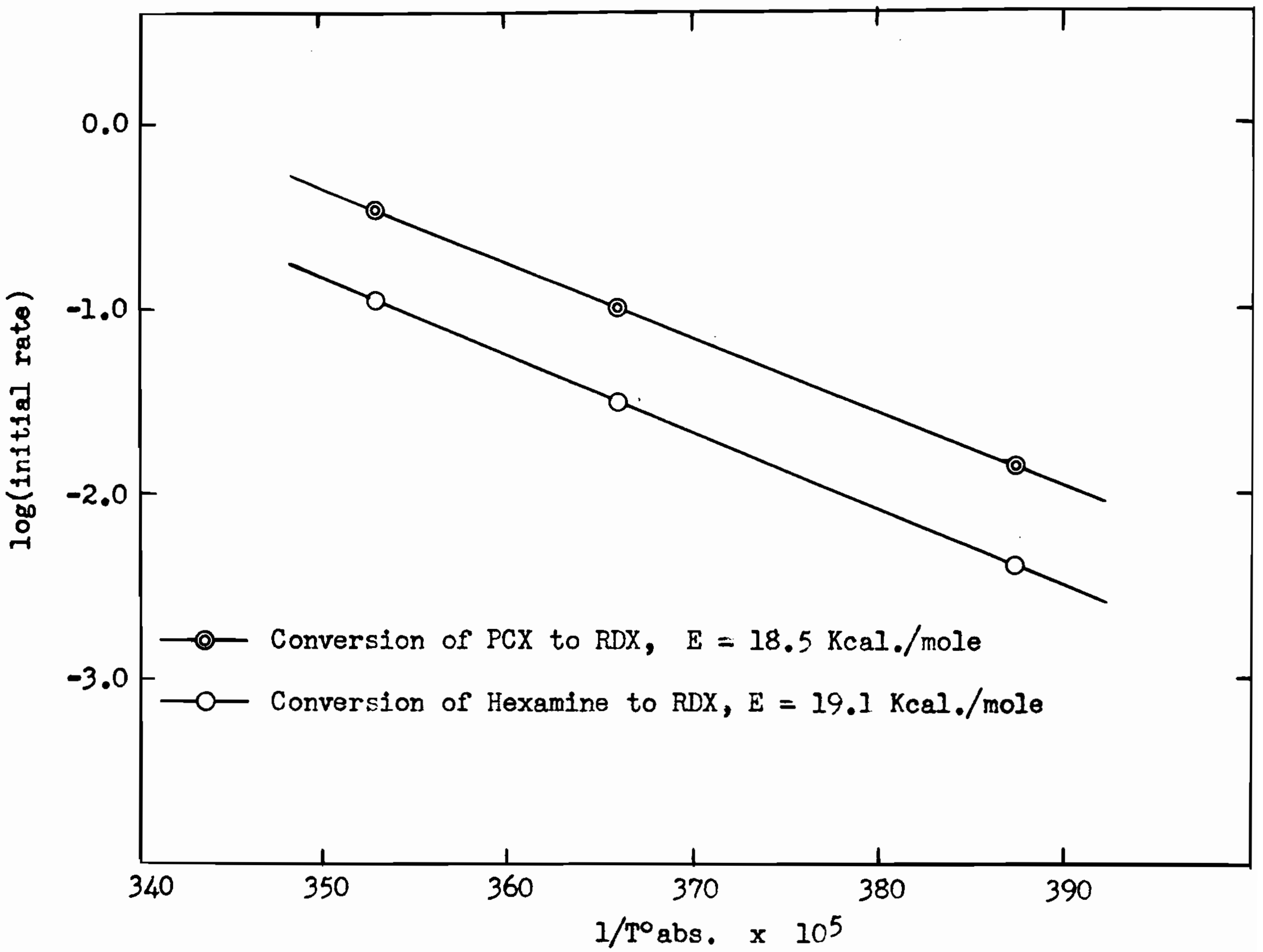


Fig. 27. Arrhenius Lines for Conversion of PCX to RDX and for Nitrolysis of Hexamine.

purity of the PCX, assuming that 100 per cent pure PCX gives the theoretical yield under these conditions. The values for "Initial PCX" given in Tables IX and X have been calculated on this basis from the sample weight and thus represent pure PCX. The values for "Yield (% of theor.)", except where no additional acid was added, represent the PCX plus the RDX present prior to the addition of the extra nitric acid.

The conversions of PCX to RDX with 90 per cent nitric acid (Fig. 25) have been corrected for impurities in the PCX, as above, but the data were not available to correct those with 98 and 94 per cent nitric acid (Fig. 26). The yields from the latter experiments thus are probably five to ten per cent low.

The effect of temperature on the initial rate of conversion of PCX to RDX is indicated in Table XII. The logarithm of the initial rate has been plotted against the reciprocal of the absolute temperature to give the Arrhenius line shown in Figure 27. By reading the slope of this line and multiplying by 2.303R, in accordance with the relation

$$E = \frac{2.303R \log k_2/k_1}{\frac{T_2 \quad T_1}{T_1T_2}}$$

the activation energy, E, of the reaction was found to be 18.5 Kcal. per mole.

Treating the initial rates for the conversion of hexamine to RDX at different temperatures (Table XIII) in a similar manner, the Arrhenius line for this reaction was drawn (Fig. 27), and the activation energy was calculated to be 19.1 Kcal. per mole. Since the difference between this value and that for the conversion of PCX to RDX is within the limits of possible experimental error, the two activation energies may be considered to be identical.

Discussion

As shown in Table IX, the initial rate of decomposition of PCX in 80 to 90 per cent nitric acid appears to be independent of both the acid concentration and the molar ratio of nitric acid to PCX in the range of molar ratios studied. In the experiments with 75 per cent nitric acid the PCX did not dissolve completely and this is assumed to account for the decreased rate of decomposition and the variation of rate with molar ratio.

This suggests that the reaction is first order (see also Fig. 24), the initial rate being proportional to the amount of PCX present in solution.

Conversion of PCX to RDX, occurring simultaneously with the decomposition of PCX, tends to increase the apparent stability of the PCX since the figures representing the decomposition include any RDX formed simultaneously. An increase in the acid concentration or molar ratio of nitric acid to PCX, or both, does not influence the true rate of PCX decomposition but it increases the rate of conversion of PCX to RDX. The result is a marked retardation in the apparent rate of PCX decomposition. The RDX production in the amounts of 80 to 90 per cent nitric acid used to study PCX decomposition is sufficiently slow to affect inappreciably the amount of decomposition in the first ten minutes. However, when the reaction of PCX with 90 per cent nitric acid is allowed to proceed for longer times, the retardation effect becomes very noticeable (Fig. 15). The slight increase of three per cent in the RDX producibility between one and two hours may be an indication that some of the decomposition products of PCX can re-combine under these conditions to give a compound which yields RDX.

The rates of decomposition of PCX in hexamine nitrolysis liquors (Figures 22 and 23), following its formation, were two to three times as great as the rate of decomposition in pure nitric acids of similar concentrations. The only apparent difference in the two types of reaction media was that the hexamine nitrolysis liquors contained decomposition products of precursors to PCX and other by-products. Table X gives the preliminary results of an attempt to find the agent responsible for this rapid decomposition of PCX.

The addition of PCX to a spent liquor from a normal hexamine nitrolysis with 98 per cent nitric acid showed that the decomposition in ten minutes was about 1.5 times the normal amount in that time in pure acid. The effect of lowering the initial acid concentration to 88 per cent and adding the PCX after twenty minutes was to increase the decomposition in ten minutes to about three times the normal amount.

The addition of PCX to the liquor resulting from the decomposition of PCX in 85 per cent nitric acid showed the decomposition in ten minutes to be increased over the normal amount by a factor of approximately 1.3 (Fig. 24). This was taken as evidence for the fact that the decomposition products of PCX were not largely responsible for the abnormally high rates of decomposition in hexamine nitrolysis liquors.

The decomposition of PCX in the reddish-brown acid obtained by adding some paraform to 85 per cent nitric acid showed that neither formaldehyde nor nitrogen dioxide appreciably affected the rate. However, the addition of PCX to a solution of ammonium nitrate (ca 2 moles NH_4NO_3

per mole PCX) in 85 per cent nitric acid gave approximately the same decomposition in ten minutes as that obtained with the spent liquor from the normal hexamine nitrolysis. This indicates that ammonium nitrate, or similar compounds, may possibly be the cause of the great instability of PCX under certain conditions.

One of the most interesting points illustrated by the experiments on the conversion of PCX to RDX is the relatively small quantity of strong nitric acid required for high yields of RDX. As seen from Figure 26, approximately five moles of 98 per cent nitric acid, or probably eight or nine moles of 94 per cent, per mole of PCX is sufficient for essentially complete reaction. In the nitrolysis of hexamine, however, this conversion is assumed to be the rate-controlling step and is the one requiring the large amount of acid. Here again, the behaviour of PCX under hexamine nitrolysis conditions is strikingly different from that in pure nitric acids. The greater ease of conversion to RDX in pure nitric acids can be explained by the absence of the ionized nitrates, mainly by-products, which repress the ionization of nitracidium nitrate in the hexamine nitrolysis liquors. It may be these same compounds which also accelerate the decomposition of PCX.

The fact that the activation energy for the conversion of PCX to RDX is the same as that for the conversion of hexamine to RDX is additional evidence (a) that PCX is a true intermediate and is not formed by hydrolysis during the drowning-out process, and (b) that the conversion of PCX to RDX is the rate controlling step of the nitrolysis of hexamine. A thermochemical study of the preparation of PCX and its conversion to RDX should be of interest, since if the heat of reaction of hexamine to PCX plus the heat of conversion of PCX to RDX were found to add up to the heat of reaction of hexamine to RDX, it would indicate unequivocally that PCX is a true intermediate. Unfortunately, time was not available to make a thermochemical investigation of these reactions.

GENERAL DISCUSSION OF THE MECHANISM OF HEXAMINE NITROLYSIS

The results of the kinetic study of the formation of RDX from hexamine indicate strongly that nitracidium ion is the agent responsible for the rate controlling step. All the results are explicable on this basis and no contrary evidence was obtained. The initial rate of RDX formation is seen to be directly proportional to values interpreted from absorption data as representing concentrations of nitracidium ion. The extremely high molar ratios of nitric acid to hexamine necessary for the maximum initial rate suggest that the active nitrolyzing agent is present in the nitrolysis liquor in only very small concentrations, even with optimal conditions, and thus could not be pseudo-nitric acid or the undissociated bimolecular complex believed to be the main component of anhydrous nitric acid. The behaviour on reducing the molar ratio below that which gives the maximum initial rate is explicable on the basis of a repression of ionization of the nitrolyzing agent and would thus suggest an ionic nitrolyzing agent. Other evidence supports this view. The effects of water formation during the nitrolysis are not sufficient, without an ionization repression by hexamine dinitrate and its reaction products, to cause the observed behaviour.

A recent report by Carruthers et al (54) advances the idea that nitracidium ion is not essential to RDX production and that its presence actually results in the decomposition of RDX. It is obvious that RDX is not decomposed even slowly by nitracidium ion in the nitrolysis liquor since the yield is not decreased by allowing reaction mixtures to stand undiluted for long periods. Moreover, the results of the experiments on which the idea was founded appear to be invalid for several reasons. The yield of RDX from a 100:1 weight ratio of 99 per cent nitric acid : hexamine was observed to be increased from 70 to 77 per cent when the reaction was carried out in the presence of a large excess of ammonium nitrate. The solubility correction had previously been found to be 7 per cent in the absence of ammonium nitrate. The solubility loss of RDX in the drown-out liquor containing ammonium nitrate was not determined, but was assumed to be the same as that where no ammonium nitrate was present. This assumption appears to be erroneous since Gauvin and Winkler (55) found ammonium nitrate to be very effective in salting out RDX from nitric acid. The increased yield with ammonium nitrate would thus appear to be due largely to the reduced solubility loss. It is then clear why no increase in yield by ammonium nitrate was found when the weight ratio of 99 per cent nitric acid : hexamine was reduced to 12.5:1 where the solubility loss was negligible even without ammonium nitrate.

Experiments in which potassium nitrate was added before and after nitrolysis with a 100:1 weight ratio of 99.9 per cent nitric acid : hexamine gave yields of 70.3 and 65.2 per cent, respectively. It was suggested that potassium nitrate added before nitrolysis behaved like ammonium nitrate and gave higher yields because the repressed ionization of nitracidium nitrate resulted in less decomposition of RDX. However, the yield of 65.2 per cent, obtained by nitrolyzing in the absence of potassium nitrate appears to be low since the yield for similar reaction conditions reported in Table I of the same report is 70.8 per cent.

When using extremely high ratios of nitric acid : hexamine, such as 100:1 by weight, the ionization repression of nitracidium nitrate caused by adding ammonium or potassium nitrate should result in a lowered rate of nitrolysis, but the normal rate with these high ratios is so great that it would have to be lowered tremendously before any reduction in final yield would be observed.

It should also be pointed out that PCX is not decomposed by nitracidium ion since the rate of decomposition was found to be independent of nitric acid concentration or amount.

The extremely rapid disappearance of hexamine dinitrate, in reaction liquors capable of producing maximum yields of RDX, is evidence that the rate controlling step must be one of the latter steps in the chain of consecutive reactions. The isolation and the behaviour of PCX both indicate the rate controlling step to be the final conversion of PCX to RDX, retarded somewhat by by-products. Any kinetic study of RDX formation by the direct nitrolysis of hexamine would thus appear to be a kinetic study of this conversion under relatively adverse conditions.

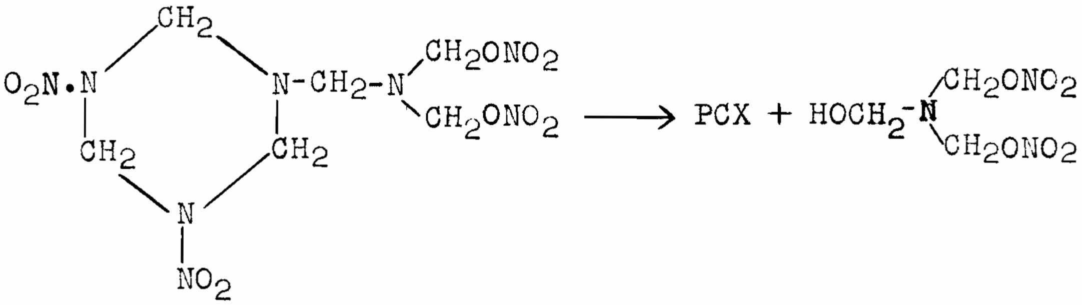
Investigations of the heats of nitrolysis by the Armament Research Department (32) showed that the rate of heat evolution was more rapid than the rate of RDX formation. This is in agreement with the rapid disappearance of hexamine dinitrate and formation of PCX. Heat measurements of the nitrolysis with mixtures of nitric acid and sulphuric acids (54) suggest that the amount of intermediate formed is not affected by the presence of sulphuric acid, but that RDX, and possibly the intermediate are decomposed quite rapidly by sulphuric acid.

The relations of initial rate of RDX formation to yield of RDX suggest that during the rate controlling step another competing reaction occurs, viz., the decomposition of the intermediate to water-soluble products. The rate of decomposition does not appear to vary appreciably with nitric acid concentration or amount, since the main reaction to RDX appears to be almost complete within two hours at 0°C., irrespective of the conditions of nitric acid. Any further increase in yield after this time is attributed chiefly to a secondary reaction of a different nature since its behaviour with respect to acid concentration and amount is entirely different. The implication is that the rate of decomposition of the intermediate is such that if the intermediate is not converted to RDX within two hours it is largely decomposed. On this basis, yields of RDX below the maximum are attributed to reaction rates too slow to convert all the intermediate to RDX within two hours at 0°C.

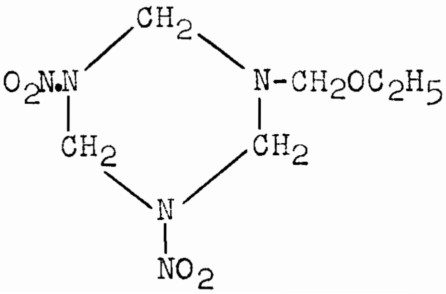
The above conclusions are confirmed by the kinetic study of PCX decomposition which shows that the rate of decomposition is independent of nitric acid concentration and amount, and is of sufficient magnitude to cause the observed decomposition within two hours.

Further strengthening the above argument is the observation that the activation energy of the conversion of PCX to RDX is the same as that of the rate controlling step of the nitrolysis of hexamine. This combined evidence leaves little doubt that PCX is a true intermediate and that the conversion of PCX to RDX is the actual rate controlling step.

Contrary to this viewpoint is the suggestion by the Armament Research Department (52) that PCX might be formed during the drowning-out process by a hydrolysis reaction such as the following:

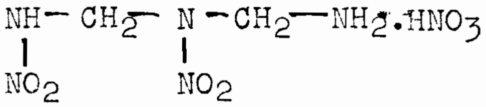


They were unable to isolate PCX from a gummy precipitate, smelling strongly of formaldehyde, obtained when ether was added in place of ice to an otherwise normal low temperature reaction mixture for preparing PCX. The gummy precipitate was worked up with cold ethanol, an ethanol-water mixture, and finally recrystallized from ether. From 40 gms. of hexamine dinitrate, there was obtained 1-2 gms. of a compound, melting at 114-115°C., whose elemental analysis suggested the structure:



The formation of this compound was attributed to a reaction of ethanol with the N-methylol compound (PCX-A), or its nitroxy derivative, whose presence was taken as an indication of a degradation of the side chain of the postulated intermediate. It has been shown, however, that PCX is converted to PCX-A in the presence of formaldehyde, so the isolation of the ethyl ether of PCX-A does not appear to indicate the absence of PCX in the original gummy precipitate. Furthermore the yield is too low to be really significant.

Evaporating the ethanol filtrate from the above isolation experiments, and washing the product with ice-water, more ethanol, acetone, and ether yielded another compound, also in minute yield, identified as



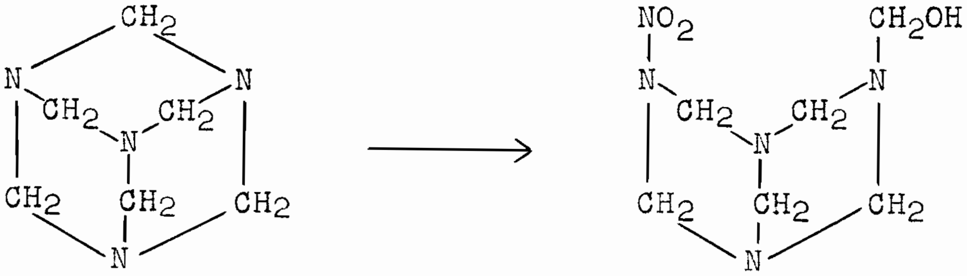
$$\underset{\substack{|\\ NO_2}}{NH}-CH_2-\underset{\substack{|\\ NO_2}}{N}-CH_2-NH_2\cdot HNO_3$$

This would be the compound expected from partial hydrolysis of PCX with loss of one molecule of formaldehyde.

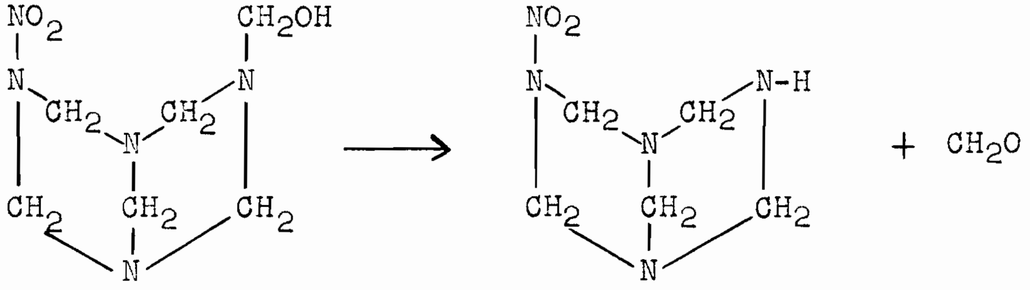
The inability of ether to precipitate pure PCX from a nitrolysis mixture prompted the author to try some experiments with added PCX. When PCX was dissolved in 97 per cent nitric acid at -40°C. and ether added, a clean precipitate of PCX was obtained, but when PCX was dissolved in a nitrolysis mixture at the same temperature just before adding the ether, the usual gummy precipitate resulted. Washing with cold ethanol and ether was ineffective in separating the PCX from the oily products, possibly P_1 and P_2 or other nitrated hexamine fragments. The instability of PCX, especially in the presence of such compounds, greatly limits the methods of purification that are applicable.

Hence, there appears to be no evidence to indicate that PCX is not present in the gummy material from the ether precipitation or in similar gummy materials from precipitation with dioxane (32).

There have been many recent speculations as to the reaction mechanism involved in the production of RDX by the direct nitrolysis of hexamine. The isolation of PCX made any mechanism, such as the original one of the Research Department, involving a break-down to a one-carbon intermediate, appear quite unlikely. The first step was generally accepted to be the following:

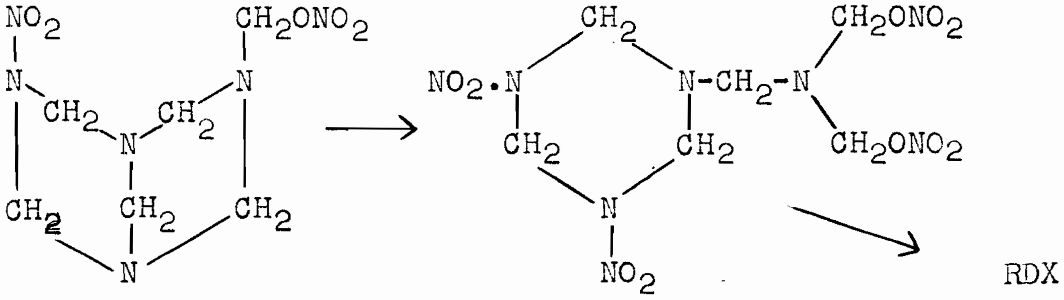


Connor suggested (56) that the succeeding step may result from the instability of methylol compounds:



He believed the compound so formed would then undergo rupture of the ring containing the secondary amine group, with the eventual formation of RDX.

Linstead, in his second monograph (57), suggested that esterification of the above methylol compound might cause stabilization so that succeeding reactions would be :

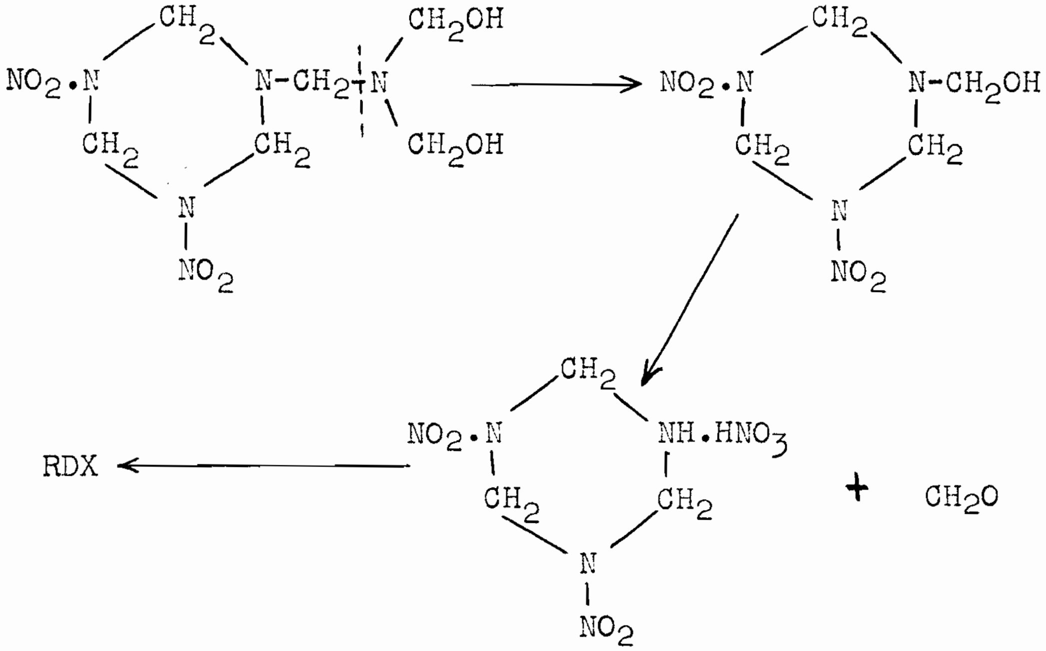


Essentially the same mechanism was put forward by Wright a few months later (58). Both Linstead and Wright believed PCX to be formed only on dilution, but as indicated above, this view appears to be untenable.

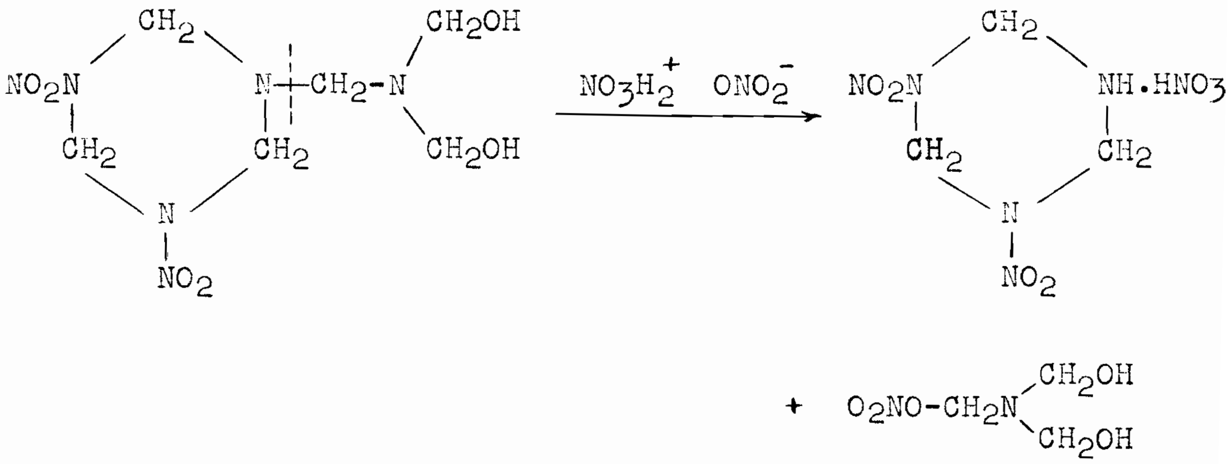
Wright obtained indirect evidence that dimethylol nitramide was present in the normal nitrolysis liquor after dilution. However, the amount was estimated to be only one-fifth of a mole per mole of hexamine so this observation does not necessarily have a bearing on the mechanism of RDX formation since it may arise from the fifth of a mole of hexamine which does not go to RDX. Likewise a discussion of other by-products, such as 106, ATX, and HMX (57), has been omitted since they occur in too small yields to have any possible bearing on the mechanism of RDX formation.

Carruthers (59) has discussed the various possible steps after the formation of the primary nitrolysis product, the N-methylol compound. His views are also essentially in agreement with those of Linstead and Wright with respect to the second nitrolysis step, but he does not necessarily preclude the formation of PCX. He points out that the N-methylol link is resistant to nitration as such, and that a decomposition and rearrangement usually occurs, giving the amine nitrate. When methylene dimorpholine is added to concentrated nitric acid at 0°C., and then diluted with water, morpholine nitrate is obtained. When PCX-A (N-methylol PCX) is dissolved in concentrated nitric acid at -40°C., and the solution is diluted with water, the product is PCX. Attempts by Springall and Woodbury (60) to obtain derivatives of similar N-methylol compounds were unsuccessful owing to the great tendency of these compounds to lose formaldehyde and revert to the amine.

Thus it is seen that if PCX-A is formed during the nitrolysis of hexamine it would be expected to be converted rapidly to PCX with loss of formaldehyde:



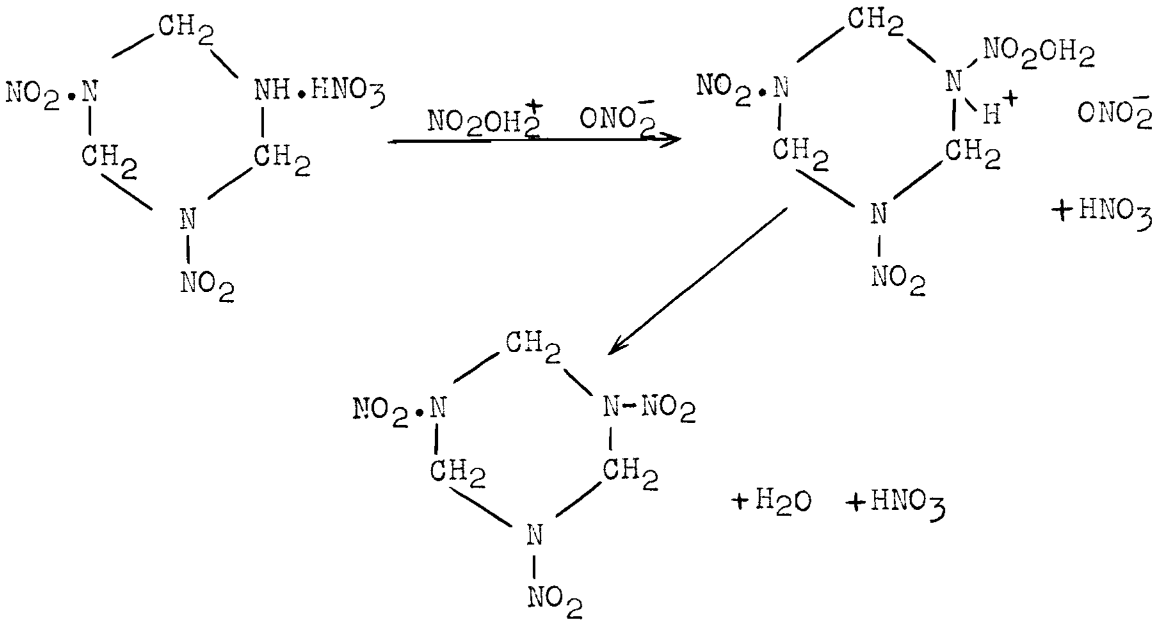
Alternatively, however, there appears to be no necessity for the formation of PCX-A before the formation of PCX. Assuming that nitracidium ion (nitric acid plus a proton) is the nitrolyzing agent, the following reaction may well represent the formation of PCX:



In this reaction, a molecule of nitric acid may be thought of as a carrier for the hydrogen ion which forms the amine, the involved nitric acid molecule then forming the acid salt of the amine.

Although methylol groups are written as such in the above equations, it should be understood that they may be esterified at the time of nitrolysis or subsequently. Since each esterification involves the elimination of one molecule of water and there are indications that water is formed early in the overall nitrolysis reaction, esterfication of the methylol groups is probably quite rapid.

It has been shown that the conversion of PCX to RDX, also is brought about by nitracidium ion. This dehydration reaction may proceed according to the following scheme:


CH2
NO2.N
NH.HNO3
CH2
CH2
N
NO2
NO2OH2+
ONO2-
CH2
NO2OH2
NO2.N
N
H+
ONO2-
CH2
CH2
+HNO3
N
NO2
CH2
NO2.N
N-NO2
CH2
CH2
+H2O
+HNO3
N
NO2

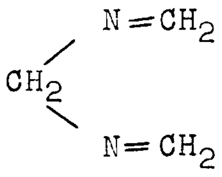
REACTION OF AMMONIA AND FORMALDEHYDE IN THE GAS PHASE

Introduction

It was suggested previously that the two main weaknesses of the direct nitrolysis of hexamine as an industrial process for RDX manufacture were: (a) the large excess of very concentrated nitric acid required, and (b) the loss of half the potential formaldehyde in the hexamine. The previous investigations indicate the necessity and function of the excess acid. However, the loss of half the formaldehyde (the most valuable raw material) prompted a study of the reaction of ammonia and formaldehyde with a view to obtaining a starting material better than hexamine for the manufacture of RDX.

It is well known that the reaction of ammonia and formaldehyde leads to hexamine, but the nature of the intermediate compounds is still in doubt. Duden and Scharf (61) obtained indications that an equimolar mixture of ammonium chloride and formaldehyde, neutralized with alkali, contained the hypothetical cyclotrimethylenetriamine. Henry (62), on the other hand, considered that the liquid he obtained by drying an equimolar solution of aqueous ammonia and formaldehyde with potassium carbonate was trimethylolamine. It has recently been shown by Wright (58), that Henry's solution was not trimethylolamine, but more probably a 40-50 per cent aqueous solution of cyclotrimethylenetriamine, possibly in equilibrium with methyleneimine, $CH_2{=}NH$, or methylolamine, $HOCH_2NH_2$. With rigorous drying, or long standing, Henry's solution precipitated hexamine.

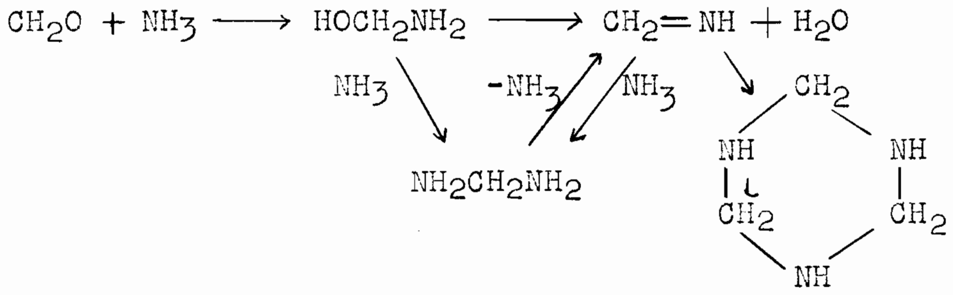
Investigations by the Research Department, Woolwich (10,63), confirm the observation that the primary product of the reaction between ammonia and formaldehyde in aqueous solution is not hexamine. However, from these investigations it was considered that the reaction to form hexamine proceeded through a "hemi-hexamine" molecule:



Dimerization fo this would yield hexamine. It will be recalled that the original mechanism postulated by the Research Department for the direct nitrolysis of hexamine to RDX involved a preliminary depolymerization of hexamine to the same compound.

Cyclotrimethylenetriamine would appear to be an ideal starting material for the manufacture of RDX since, if the reaction proceeded by a direct nitration of the three amine groups, no formaldehyde would be lost and no by-products other than water would be formed. The isolation of cyclotrimethylenetriamine by the dehydration of its aqueous solution appeared to be impossible owing to the accompanying hexamine formation. It was hoped to overcome this difficulty by reacting ammonia and formaldehyde in solvents other than water. However, this study was soon discontinued because the water formed in the reaction presented a similar difficulty.

A likely mechanism for the formation of cyclotrimethylenetriamine appeared to be the following:



It was thought that, in a gas phase reaction of ammonia and formaldehyde at about 50° to 100°C., water possibly could be removed by some dehydrating agent and gaseous methyleneimine might then be condensed and trimerized on cooling.

For reasons given below, this technique was unsuccessful, and it was found preferable to conduct the reaction at temperatures above 100°C. to prevent condensation of water.

Experimental Procedure and Results

The final form of the apparatus is illustrated in Figure 28. Gaseous ammonia was obtained directly from a cylinder of liquid ammonia. Gaseous formaldehyde was produced by heating paraformaldehyde with an oil bath (A) at 150°-170°C. The rates of flow of both gases were measured with differential manometer type flowmeters (B,C), filled with dibutyl phthalate. The flowmeter for formaldehyde (C) was wound with nichrome wire and thus heated electrically to 80°-100°C. to prevent condensation of the formaldehyde.

The first type of reactor used was a U-tube (not illustrated) of one centimetre diameter Pyrex tubing, filled with soda-lime (#8 mesh). It was heated with an oil bath over a flame and the temperature was maintained within 5° of the desired temperature. The gases were mixed at a point just below the surface of the bath. Any unreacted gases or gaseous products passed through and were condensed in a dry ice trap.

Mixing formaldehyde and ammonia in this manner at the rates of 75 and 100 cc. per min., respectively, with a reactor temperature of 90°-100°C. resulted in the

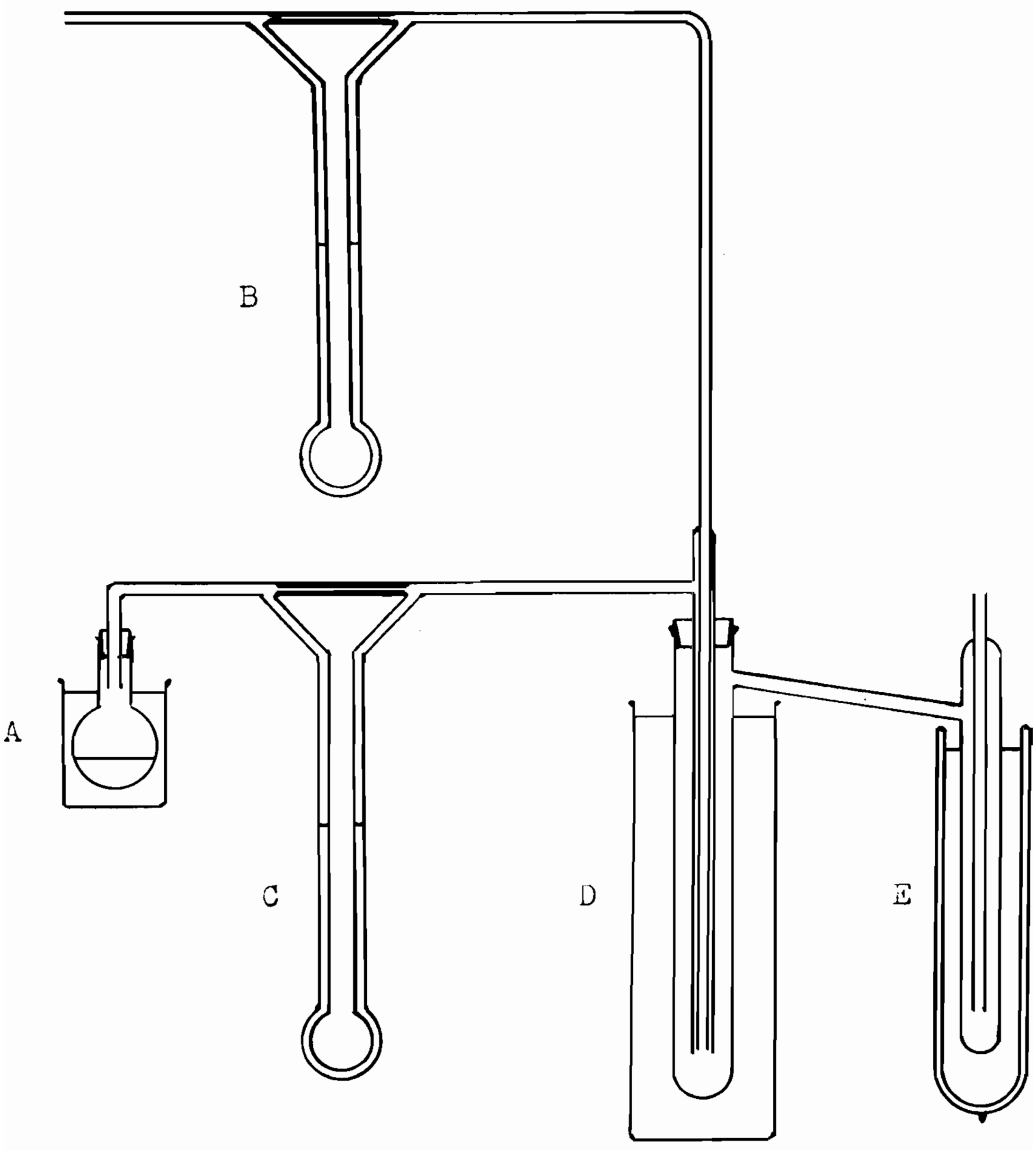


Fig. 28. Apparatus for Gas Phase Reaction of Ammonia and Formaldehyde.

condensation of white solid material at the point where the gases met. This product contained a small amount of chloroform-soluble material. The remainder gave only a trace of RDX when treated with 97 per cent nitric acid, and consisted largely of paraformaldehyde.

It was observed that formaldehyde condensed much more readily on a moist glass surface than on a dry one. Therefore, to keep the walls of the reactor free from moisture, the oil bath was maintained for future experiments at temperatures higher than 100°C.

The soda-lime was omitted and a reaction was carried out at 115°C. with the above flow rates. After running for 20-30 minutes, the flow of gases was stopped and the reactor bath heated to 165°C. to sublime out any paraform. However, the condensate on the wall of the U-tube remained unchanged and after breaking open the tube, was found to be a glassy film with imbedded crystalline masses.

The product was powdered with a mortar and pestle, and shaken for two or three minutes with about fifteen times its weight of hot chloroform. Very little dissolved, and the residue was found to be also insoluble in water, acetone, alcohol, dioxane, pyridine and acetic anhydride. Two millilitres of 97 per cent nitric acid was cooled to -40°C. and 0.100 gm. of the chloroform-insoluble material was added. The mixture was permitted to warm to room temperature for 30 minutes, and diluted. After standing overnight, the precipitate was filtered off and dried in the oven at 100°C. Yield of RDX 0.075 gm. M.P. 202-3°C. (corr.).

To avoid breaking the reactor to remove the product, the design was changed to that illustrated (Figure 28,D). This comprised a Pyrex test-tube, 8" x 1", fitted with a rubber stopper and a glass tube assembly reaching almost to the bottom of the test-tube. The gases passed down the concentric inner tubes, mixed at the bottom, and the solid reaction product condensed on the wall of the outer tube. The outlet tube sloped downward so that liquid condensing in it would not run back into the reactor. The exit gases, mainly steam and unreacted ammonia, were condensed in the solid carbon dioxide trap (E).

Using this apparatus, a number of experiments were made, varying the reactor bath temperature in successive experiments from 110°C. to 150°C. and the molar ratio of ammonia : formaldehyde from 1:2 to 5:1. In the early experiments the gases were allowed to flow at rates of 25 to 150 ml. per min. for 30 to 45 minutes, then the outer tube of the reactor was removed and the solid condensate scraped from the wall. Some white solid was usually found on the wall of the tube above the surface of the oil bath, but the material condensing on this cooler surface was removed first and kept separate from the more glassy condensate in the hot zone of the reactor.

Both products were ground to a fine powder and treated with chloroform, as previously, to remove any hexamine. When the chloroform-insoluble materials were heated, they sublimed to hexamine (identified crystallographically), and in dilute nitric acid they gave hexamine dinitrate (identified by the iodine test and melting point). They dissolved in boiling water, giving off an odour of formaldehyde and ammonia (hexamine is relatively stable in boiling water).

The yields of RDX obtained by treatment with 97 per cent nitric acid as previously described were taken as indications of the relative purity of different samples. Products obtained under different reaction conditions gave yields of RDX varying from 60 to 85 per cent by weight. A second grinding of a product giving 67 per cent by weight of RDX, followed by another wash with hot chloroform, did not lead to any change in the RDX producibility of the sample.

A chloroform-insoluble product, giving 60 per cent by weight of RDX when treated with 97 per cent nitric acid, yielded 175 per cent by weight of RDX (B), m.p. 194-197°C. (corr.), when treated with acetic anhydride, nitric acid ammonium nitrate, and acetic acid under the normal conditions of the Bachmann Reaction. Shaking with an equimolar mixture of acetic anhydride and nitric acid at 50°C. for one hour gave a 70 per cent yield by weight of a substance (probably impure BSX (57)), melting at 136°-140°C., which decomposed when heated with 70 per cent nitric acid.

The following generalizations of the reaction behaviour can be made:

(a) When the reator temperature was higher than 135-140°C., most of the solid product occurred in the cooler portions of the reactor, above the surface of the oil bath. only a small proportion of glassy film condensed in the hot zone.

(b) The condensate in the cooler zone usually consisted largely of hexamine, while that from the hot zone seldom contained more than small amounts of hexamine.

(c) Thus, from (a) and (b), reaction temperatures over 135-140°C. apparently lead to relatively high yields of hexamine and only small amounts of chloroform-insoluble material.

(d) After the chloroform wash, the yields of RDX were usually higher from the condensate in the hot zone than from that in the cooler zone.

(e) All other conditions remaining constant, an increase in the duration of reaction tends to increase the yield of hexamine at the expense of the chloroform-insoluble product, and this is accompanied by a decrease in the RDX producibility of the chloroform-insoluble product.

(f) The yield of chloroform-insoluble material is estimated roughly to be between 20 and 50 per cent of the weight of formaldehyde used, depending upon the reaction conditions.

The general insolubility of the product made purification very difficult and thus interfered with accurate analyses. Following the method of Carmack, Kuehl and Leavitt (64) the chloroform-insoluble product was analyzed for ammonia and formaldehyde. The results suggested the crude product to be a mixture of paraformaldehyde and another compound giving the same analysis as hexamine, in about 1:3 ratio by weight.

Other indications of the presence of free paraformaldehyde were also obtained. When a sample was heated in the bottom of a small test-tube by partial immersion in an oil bath at 160-170°C. for three or four minutes, a strong odour of formaldehyde was detected and paraformaldehyde condensed as a white solid on the upper cooler wall of the test tube. Heating a sample overnight in the oven at 110°C. caused a 27 per cent loss in weight, presumably due to vaporization of paraformaldehyde and a small amount of water and converted the material almost completely to hexamine.

By swirling some of the crude product with ammonium hydroxide solution it was hoped to dissolve out paraformaldehyde which is known to react with ammonium hydroxide to give hexamine. After keeping the crude product in contact with ammonium hydroxide for about five minutes it was removed by filtration, washed well on the filter with acetone, then shaken with an excess of chloroform for about three minutes to remove all traces of hexamine.

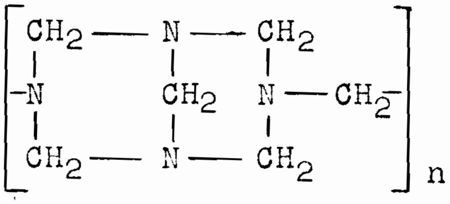
Analyses of samples purified in this manner and dried in a vacuum desiccator for three days gave values for ammonia and formaldehyde close to the values calculated for hexamine. Typical figures are the following:

NH_3 - 47.5% CH_2O - 126.7%

Calc'd. for $C_6H_{12}N_4$: NH_3-48.6%; CH_2O-128.5%

Discussion

The structure of the chloroform insoluble compound giving the same ammonia - formaldehyde analysis as hexamine may be that of the following polymer:



Ring closure between the ends of this unit would lead to hexamine.

It is conceivable that under certain conditions polymerization, rather than ring closure, might occur as formaldehyde reacts with ammonia. However, again under the proper conditions, the polymer might break down to its units which could then cyclize to hexamine.

Supporting this view is the observation that the length of reaction time affects the quality of the solid condensate in the reactor. An increase in the reaction time or temperature has been seen to cause an increase in yield of hexamine at the expense of the chloroform-insoluble product. The accompanying decrease in the RDX producibility of the remaining chloroform-insoluble product would be expected from the presence of paraformaldehyde.

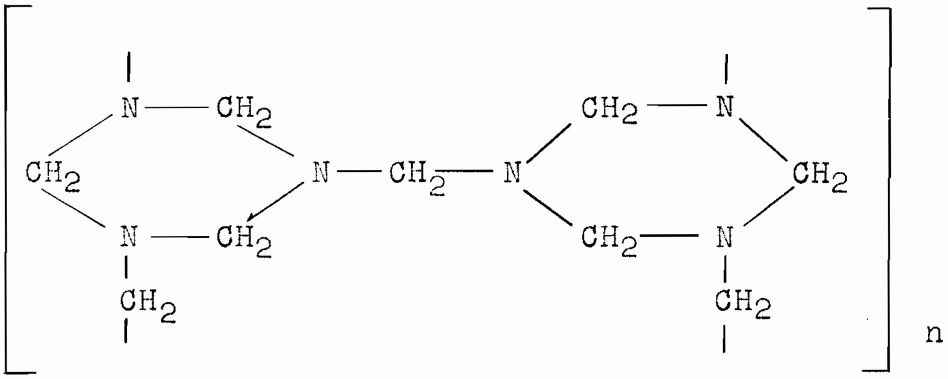
At least part of the hexamine produced is thus probably formed by degradation of the polymer during the reaction, since it was shown that the chloroform-insoluble material is relatively unstable at temperatures as low as 110°C.

The thermal instability of the product explains why reaction temperatures over 135-140°C. gave relatively high yields of hexamine and only small amounts of chloroform-insoluble product.

The observation that the chloroform insoluble product from the hot zone of the reactor gave higher yields of RDX than that from the cooler zone is explicable on the basis that more paraformaldehyde would condense in the cooler zone.

The ease with which dilute mineral acids convert the chloroform-insoluble compound to the acid salt of hexamine is in accord with the formula postulated above, and the general insolubility of the compound in all inert solvents suggests a high molecular weight.

Another possible structure which should not be overlooked is the lattice type molecule:



This structure does not appear to fit the facts as well, however, e.g. it is more difficult to picture the readily occurring transformation to hexamine.

These investigations of the gas phase reaction between ammonia and formaldehyde are not to be considered complete in themselves. More properly, they are introductory to a search for a starting material better than hexamine for the manufacture of RDX.

SUMMARY

Maximum yields, of about 80 per cent, of RDX are obtainable with nitric acid of all concentrations down to 88 per cent, if the molar ratio of nitric acid to hexamine is sufficiently high.

The rate of nitrolysis increases rapidly as the molar ratio of nitric acid to hexamine is increased and continues to do so after the molar ratio is raised above that required for maximum yields. The initial rate is shown to have an upper limit, however, at very high molar ratios.

The yields of RDX on the nitric acid basis plotted against the molar ratio show that an optimum molar ratio exists, and that the addition of further hexamine inhibits the nitrolysis.

The initial rate of RDX formation is seen to be directly proportional to values interpreted from absorption data as representing concentrations of nitracidium ion. This and other observations indicate strongly that nitracidium ion is the nitrolyzing agent in rate controlling step of the direct nitrolysis of hexamine. All the results appear to be explicable on this basis.

A marked decrease in the rate constant for RDX formation during the first few minutes of reaction at 0°C. indicates a corresponding decrease in the concentration of nitracidium ion caused probably by formation of water and nitrate ion. For the major part of the reaction, the rate constant does not vary appreciably. This is characteristic of first order reactions and suggests that, after the initial dilution of the acid, the large excess of acid used functions mainly to maintain the concentration of nitracidium ion at a reasonably constant level.

It is observed that when the initial rate of RDX formation falls below a certain value, which varies only slightly with the initial acid concentration, the yield of RDX begins to decrease.

The relation of initial rate of RDX formation to yield of RDX suggests that during the rate controlling step another competing reaction occurs, viz., the decomposition of an intermediate to water-soluble products. The rate of decomposition does not appear to vary appreciably with nitric acid concentration or amount, and seems to be such that if the intermediate is not converted to RDX within two hours it is largely decomposed. Yields of RDX below the maximum are thus attributed to reaction rates too slow to convert all the intermediate to RDX before decomposition becomes appreciable.

An intermediate, PCX, has been isolated from the nitrolysis reaction and identified as 1,3-dinitrocyclotrimethylenetriamine-5-nitrate. It is dehydrated to RDX quantitatively by relatively small amounts of very concentrated nitric acid, by acetyl nitrate solutions, and less efficiently by acetic anhydride. Its behaviour in nitric acid and the activation energy of its conversion to RDX both indicate this conversion to be the rate controlling step of the nitrolysis of hexamine to RDX. The rate of conversion of PCX to RDX is decreased greatly by the presence of nitrate by-products from the nitrolysis reaction. This effect is explained by a repression of the ionization of nitracidium nitrate by the nitrate by-products. Nitracidium ion appears to be the agent responsible for the conversion of PCX to RDX in nitric acid.

Kinetic studies of the disappearance of hexamine dinitrate and of the RDX producibility during the nitrolysis of hexamine show that PCX is formed rapidly in 85 to 91 per cent nitric acid at 0^{o}C., but has a high rate of decomposition.

Kinetic studies of the decomposition of PCX and of its conversion to RDX show that the initial rate of decomposition is independent of both acid concentration and molar ratio of nitric acid to PCX, with 80 to 90 per cent nitric acid. The rate of decomposition of PCX added to a spent nitrolysis liquor is such that practically none remains after two hours at 0°C.

The N-methylol analogue of PCX, referred to as PCX-A, has been obtained from the decomposition of PCX with aqueous alkali. This compound is possibly a precursor of PCX in the nitrolysis of hexamine. The mechanism of formation of RDX by direct nitrolysis of hexamine is discussed on the basis of the experimental results.

The reaction of ammonia and formaldehyde in the gas phase at 110°-150°C. yields, in addition to hexamine, a compound which is nitrolyzable to RDX and which appears to be a polymerized form of hexamine.

CLAIMS TO ORIGINAL RESEARCH

1. The kinetics of the formation of RDX by the direct nitrolysis of hexamine has been studied with 88 to 97 per cent nitric acids and various molar ratios of nitric acid to hexamine.

2. An intermediate has been isolated from the direct nitrolysis of hexamine and its conversion to RDX probably represents the rate controlling step of the conversion of hexamine to RDX. The properties and reactions of the intermediate were investigated.

3. The kinetics of hexamine dinitrate disappearance and RDX producibility during the nitrolysis of hexamine has been studied with 85 to 91 per cent nitric acids and various molar ratios of nitric acid to hexamine. This has enabled an estimation of the rates of formation and decomposition of the intermediate under these conditions.

4. A kinetic study of the decomposition of the isolated intermediate has been made with 80 to 90 per cent nitric acids and various molar ratios of reactants.

5. A kinetic study of the conversion of PCX to RDX has been made with 90 to 98 per cent nitric acids and various molar ratios of reactants.

6. The experimental results are explained by introducing the concept of nitracidium ion being the active nitrolyzing agent in very concentrated nitric acid.

7. A mechanism for the formation of RDX by the direct nitrolysis of hexamine has been postulated.

8. The reaction of ammonia and formaldehyde in the gas phase has been studied and a compound which appears to be a polymerized form of hexamine has been isolated.

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