WAR RESEARCH

Part A

NICKEL IMPREGNATED RESPIRATOR CHARCOALS

Part B

AN X-RAY INVESTIGATION OF H.M.X. CRYSTALS

Part C

THE KINETICS OF THE REACTIONS TO PRODUCE R.D.X.

a thesis by

H. Leverne Williams, M.Sc.

under the supervision of

Dr. J. H. Barnes and Dr. C. A. Winkler

submitted to the Faculty of Graduate Studies and Research of McGill University in partial fulfilment of the requirements for the degree of Doctor of Philosophy

McGill University

Montreal, Canada

April 1943

ACKNOWLEDGMENTS

During the session 1942-1943 the National Research Council honoured the author with a Studentship, for which he is most grateful.

The material assistance of the Advisory Committee for Industrial Chemists was invaluable in carrying out many of the investigations.

Many of the investigations were aided by assistance and advice from Dr. R. McIntosh and his students, in particular R. Mungen, F. Lossing, J. Davis, R. Livingstone and J. C. Arnell.

Dr. F. W. Matthews kindly made many of the x-ray diffraction powder photographs using the facilities at his disposal.

Particular mention must be made of the extensive co-operation and assistance of the group headed by Dr. R. Boyer and Dr. J. H. Ross, and mention should be made in particular to J. Edward, G. C. Pickard, D.L. Garmaise and O.M. Friedmann.

TABLE OF CONTENTS

Experimental (Continued)

Experimental - Bachmann or Combination Process

LIST OF TABLES

Part A

NICKEL IMPREGNATED RESPIRATOR CHARCOALS

COPPER IMPREGNATED RESPIRATOR CHARCOALS

Part B

AN X-RAY INVESTIGATION OF H.M.X. CRYSTALS

Part C

KINETICS OF THE REACTIONS TO PRODUCE R.D.X.

LIST OF FIGURES

Part A

NICKEL IMPREGNATED RESPIRATOR CHARCOAL

COPPER IMPREGNATED RESPIRATOR CHARCOAL

Part B

AN X-RAY INVESTIGATION OF H.M.X. CRYSTALS

FOREWORD

The author must apologize for the heterogeneous nature of the investigations to be reported.

The original problem of investigating the nature of a charcoal surface by x-ray diffraction studies failed to develop along the anticipated lines and became rather a study of the mechanism and kinetics of the decomposition of nickel carbonyl on charcoal surfaces, which, however, did not seem to be justified under existing conditions of urgency. A study to which highest priority has been conceded, namely kinetics of formation of R.D.X, was undertaken therefore, concurrently with which a study was also made x-ray diffraction pictures of H.M.X. crystals with particular reference to differences from R.D.X.

Since the investigations were entirely unrelated they have been separated into independent sections. This would necessitate some duplication in the description of the x-ray equipment used in both sections so that this has been overcome by

describing the apparatus and its adjustment and calibration separately. Thereafter only such details as are necessary to designate the steps will be described in each section.

X-RAY EQUIPMENT

The x-ray equipment may be described conveniently in three sections; the tube and its ancilliary equipment, the powder camera, and the Universal Photogoniometer.

The tube (1) was an all-steel Shearer design connected directly to an all-steel mercury diffusion pump backed by an Hyvac. The low tension end of the tube was equipped with two aluminium foil windows, one for vertical and the other for horizontal beams. Changing from the one position to the other merely required that the target and needle valve assembly be turned through ninety degrees. The targets were interchangeable but for the work reported here a copper target was used sometimes in conjunction with a nickel foil filter to remove the "beta" radiation.

With an aluminium cathode the tube is self-rectifying and is operated from a Watson transformer capable of delivering 62,000 volts (R.M.S.) at 2 K.V.A. The transformer is protected from

damage by short circuits in the tube by a 10 ampere circuit breaker. It is also protected from damage due to failure of the cooling system to the mercury diffusion pump or the target, or from failure of the D.C. current supply to the Hyvac by a relay system which must be closed manually but which opens on failure of either water supply or electrical supply.

For most of the investigations in Part A a simple powder camera was used (2,3). With the x-ray beam vertical the camera was supported in a horizontal position on a rigid stand upon which it could be moved for alignment of the beam. The pin-hole (1 mm) could be adjusted parallel to the beam by four leveling screws on the camera. The film was contained in a light-tight, flat plate holder accurately perpendicular to the x-ray beam. From a powder photograph of finely ground sodium chloride the crystal to plate distance had been found to be 30.4 millimeters.

The available Universal Photogoniometer (4) was suspected to be out of adjustment. This instrument is essentially a single circle goniometer

with pinhole and slit sources for x-ray beams, quarter plate and cylindrical cameras for x-ray investigations, a slit-collimating lens for light beams and a telescope-microscope for adjusting the instrument and setting the crystal in the crystal holder as well as for use with the instrument as an optical goniometer.

The Photogoniometer was mounted on rails so that it could be moved up to or away from the horizontal window of the x-ray tube without losing its adjustment relative to the x-ray beam. These rails were in turn mounted on a strong wooden base which could be moved about to adjust the Photogoniometer as a whole relative to the x-ray beam. Lead shields protected the film holders and the operator from stray radiation from the tube.

The standard two-arc crystal holder was adjustable in two horizontal and a vertical direction and could be rotated about its axis by a strong clockwork motor, or oscillated about its axis by the same motor using a cam and lever system.

The adjustment was carried out in the

recommended manner (4). This was greatly facilitated by the use of half-silvered and full-silvered mirrors (5) in those sections of the procedure carried out optically. A rotation picture using a slit source and a calcite needle was taken to determine whether the plate holder was normal to the x-ray beam yielded also the information that the crystal to plate distance should be corrected by 0.3 mm. A more precise determination using sodium chloride and R.D.X. crystals and a pinhole source gave 0.1 and 0.2 mm respectively so that the average correction was taken as 0.2 mm. Also using the sodium chloride and the pinhole source the radius of the cylindrical camera was found to be 30.4 mm.

The film used was Agfa Non-Screen Safety except in some preliminary work with the Photogoniometer with which Ilford Quarter Plate x-ray plates were used.

Part A

NICKEL IMPREGNATED RESPIRATOR CHARCOALS

under the supervision of

Dr. W. H. Barnes

Part A

NICKEL IMPREGNATED RESPIRATOR CHARCOAL

INTRODUCTION

During an earlier investigation Davis (6) reported that nickel carbonyl upon passing through a bed of standard respirator charcoal was decomposed quantitatively into nickel and carbon monoxide. This indicated that nickel impregnated charcoals would not be effective against carbon monoxide as had been hoped. Further study by McIntosh and Mungen (7) showed that while charcoal could be impregnated readily by tumbling in an atmosphere containing nickel carbonyl, the arsine time was not improved by such impregnation. Pierce (8) could find no relationship between the naturally occurring nickel content of the charcoals and their activity.

It occurred to Dr. McIntosh and Professor Barnes that it might be possible to determine some measure of the surface area by the use of this

technique combined with x-ray analysis as a method of obtaining a direct measure of the film thickness on the charcoal surface since a film 10 to 15 atoms thick usually will give a resolvable x-ray diffraction pattern.

Samples of impregnated charcoals containing 4.1 percent nickel (McIntosh and Mungen) and 6.52 percent nickel (Hodgins, 9) were examined by x-ray diffraction methods by Matthews (3) and failed to yield any diffraction patterns although a synthetic mixture of 5 percent nickel powder in powdered charcoal showed the characteristic nickel lines clearly. From this it was concluded that the nickel was deposited on the charcoal in such a manner as not to give a diffraction pattern or that not a sufficient thickness of film had been built up. Further it was concluded that the minimum specific surface active towards nickel carbonyl could not be less than one square meter per gram of charcoal assuming that all of the nickel was deposited in a manner detectable by x-ray analysis. It was suggested that if nickel continued to be laid down then a measure of the specific surface

could be obtained when a sufficient thickness of film had been built up.

It is obvious that only an estimate of the surface area could be obtained by this technique which precludes measuring the surface of the pores of small diameter and is based on the assumption that the nickel surface would build up uniformly to a thickness sufficient to yield a resolved diffraction pattern in the pores of sufficient size without too great a "loss" of nickel into the smaller pores. The estimate of one square meter per gram of charcoal was made on the basis of four percent nickel in the charcoal sample whereas typical surface areas of gas mask charcoal as determined by Emmett (10) using his adsorption isotherm method are tabulated in Table 1 and give values of about 1000 times greater.

TABLE 1

SURFACE AREA OF TYPICAL CHARCOALS

Charcoal	Area m^2/gm
Extruded X-6	1295
No. 1918	942
Whetlerite R.9	785
Whetlerite 17-P	941
Whetlerite 18	1278
Whetlerite 19	1338
Whetlerite VA	1220
Whetlerite VXA	990
Whetlerite VYA	1023

The estimate of the specific surface area was also calculated on the assumption that metallic nickel was laid down. This is shown to be an invalid assumption, and that the deposit would likely be nickel compounds might be inferred from a study of the properties of nickel carbonyl the essential characteristics of which follow (11).

Nickel carbonyl is a colourless liquid boiling at 43°C. In liquid form it may be stored under air-free water. It is not attacked by dilute or non-oxidizing acids, dilute or strong alkali, or solutions of salts of other metals. It may be

added to concentrated sulphuric acid without immediate effect but after a short time it explodes suddenly. It is dissolved by concentrated nitric acid and other strong oxidizing solutions, and by water or acid in the presence of air, and by chlorine and bromine. With chlorine, nickel carbonyl forms nickel chloride and phosgene, or if water is present, nickel chloride, carbon dioxide and hydrogen chloride. The vapour is not appreciably soluble in dilute acids or alkalis or in cuprous chloride solution. The liquid is soluble in organic solvents, particularly alcohol, benzene, chloroform and turpentine. It reduces ammoniacal cupric and silver solutions.

Its reactions are those of nickel and of the unsaturated carbonyl group, forming inorganic salts and organo-metallic complexes.

Exposure of the liquid to air results in the formation of carbonates whose composition varies with the hygroscopicity of the atmosphere or medium. Mixtures of the vapour and oxygen are stable but decompose slowly if some water is present and explode

if ignited, if agitated violently over mercury, or if the pressure is raised. Oxidation results in nickel salts and carbon monoxide and dioxide.

Thus it is evident that the only important reaction is that of oxidation. However it is possible thermally to decompose the carbonyl and thus liberate metallic nickel and the theoretical amount of carbon monoxide. A brief review of the studies of both the thermal decomposition and oxidation of the carbonyl is essential for the work reported here.

OXIDATION OF NICKEL CARBONYL

The oxidation of nickel carbonyl occurs very rapidly and readily but the products of oxidation are not known precisely and vary widely with the conditions of oxidation.

Berthelot (12) observed that when nickel carbonyl was added to water it remained unchanged. However if air were introduced a green precipitate formed and the nickel carbonyl vapours in contact with the moist air produced a white smoke. The composition of this white smoke was

Carbon	5.3	percent
Nickel	53.3	"
Water	40.1	"

Based upon this analysis he suggested the formula

$$Ni_3C_2O_3.10H_2O$$

This he believed to be a complex hydrate of nickel oxide and a compound

$$NiC_2O$$

produced by the oxidation of nickel carbonyl according to the equation

$$Ni(CO)_4 + \tfrac{1}{2}\,O_2 \longrightarrow 2\,CO_2 + NiC_2O.$$

The green compound formed in the water was free of carbon and seemed to be a complex hydrate of nickel oxide. Decomposition in solution might also form nickel, carbon and carbon dioxide.

Lehrer and Loos (13) observed the formation of green and brown precipitates from nickel carbonyl in solution. The amount of precipitate was increased when the solutions were exposed to air or when moist air was bubbled through the solvent. To the very complex oxidation product they ascribed the formula

$$Ni(CO)_4 \cdot 2Ni(OH)_2 \cdot 4H_2O$$

based on the analysis of the precipitates from various solvents.

Hatschek and Thorne (14) when producing metal sols in non-dissociating media such as benzene and toluene observed dissociation of the carbonyl below the boiling point to produce a greenish brown precipitate which later turned black. The nickel deposited as a coagulum, the coagulation not being inhibited by paraffin but

a uniform colloid could be obtained by using rubber as a protective colloid. The particles were both positively and negatively charged. The precipitate formed when the solutions were in contact with air. Thorne (15) analyzed the precipitates and obtained the following data:

Ni	39.63	40.11	percent
CO_2	15.92	16.21	"

They lost 22.53 percent of water on drying at 120°C and became yellow and were converted to the black oxide on ignition. No gas was evolved other than carbon dioxide on decomposition of the precipitate by hydrochloric acid. Thorne believed the substance to be a basic carbonate of nickel rather than the compound of carbonyl and hydroxide suggested by Lehrer and Loos.

Continuation of the work by Hatschek and Thorne (16) showed that careful oxidation by air produced a positively charged hydrated basic carbonate green in colour. Exclusion of air caused the production of a negatively charged black precipitate. When both precipitates were present the latter usually had the greater nickel content but both might have the same or different nickel to carbon dioxide ratios.

Mond (17) and others had observed that nickel carbonyl vapours were very unstable and exploded at 60°C producing carbon dioxide. They interpreted this as due to the decomposition of nickel carbonyl to produce nickel, carbon dioxide and carbon. This was shown to be incorrect by Dewar and Jones (18) in their studies of the vapour density. They were able to show that these explosions were due to the presence of oxygen and that in an inert atmosphere the decomposition was rapid but smooth at temperatures as high as 130°C producing nickel and carbon monoxide.

Garratt and Thompson (19) observed that the oxidation of nickel carbonyl vapours proceeded with an explosion or not at all. Below certain pressures no change would be observed in a carbonyl-oxygen mixture. A small increase in pressure would cause an explosion. The lack of reproducibility of the results and the presence of an induction period the magnitude of which depended upon the cleanliness of the reaction vessel suggested a chain reaction mechanism. As the temperature and the size of the vessel were increased the pressure

required to bring about an explosion was decreased. Possibly branching chains are involved and it is uncertain what rôle the nuclei of nickel or nickel oxide may play in the process. The erratic results and the induction period suggest that the chains are broken on the walls of the reaction vessel.

Bawn (20) observed the explosion limits also. These were surface dependent with an induction period indicating in his opinion a branching chain mechanism. He concluded that the reaction was partly heterogeneous and partly homogeneous and that both were inhibited by carbon monoxide. Most of the reaction was in the gaseous phase. On the surface of the nickel the carbon monoxide was more strongly adsorbed than the nickel carbonyl.

From all these data it is evident that the oxidation of nickel carbonyl leads to the production of complex and varied products depending upon the experimental conditions.

THERMAL DECOMPOSITION OF NICKEL CARBONYL

Dewar and Jones (18) showed that nickel carbonyl decomposed rapidly but smoothly in an inert atmosphere at temperatures as high as 130°C to produce nickel and carbon monoxide. A nickel coated tube brought about equilibrium more quickly. Dissociation increases rapidly with temperature increase. At 155°C in nitrogen it is practically complete but in undiluted carbonyl samples some trace persists even as high as 182°C. Liquid carbonyl sealed in glass tubes was heated to 200°C with only slight decomposition and the deposited nickel slowly dissolved again on cooling and standing. The presence of mercury increased the decomposition under such conditions. The reaction is readily reversible under experimental conditions which do not allow the carbon monoxide to escape. Tubes containing ten percent nickel carbonyl and ninety percent carbon monoxide were sealed off at various pressures. As the pressures increased the temperature required to bring about decomposition also increased. Also on standing the deposited nickel disappeared from the walls as the nickel carbonyl reformed.

Garratt and Thompson (19) observed that the rate of thermal decomposition at 100°C was approximately proportional to the first power of the concentration but that carbon monoxide retarded the reaction later. The activation energy of the homogeneous reaction is probably greater than 12 kilocalories. The thermal decomposition is small up to 100°C and is proportional to the concentration of the carbonyl and decreases more rapidly than given by a first order law. Packing the vessel retards the decomposition.

Mittasch (21) observed that the decomposition of nickel carbonyl in nickel coated vessels followed a first order law with the rate decreasing due to the inhibiting effect of carbon monoxide.

Bawn (20) continued similar experiments. Decomposition is very rapid at 105°C, ninety percent being decomposed in a very short time. At lower temperatures equilibria were reached. He observed that there was no loss of carbon monoxide to the nickel on the glass. The deposit of nickel

was brilliant at first then thickened and turned to a black powder at which time the rate of decomposition increased. This increase in rate was attributed to the surface reaction because a new clean reaction vessel restored the original rate. An 8.4-fold increase in the surface area by packing the bulb showed that at 118°C, twenty percent of the decomposition was due to the wall reaction.

All these data indicate that the thermal decomposition of nickel carbonyl proceeds to an equilibrium unless the carbon monoxide is removed, in which case the reaction may proceed to completion. These are the conditions by which nickel carbonyl is used to prepare metallic nickel catalysts (11). The fact that nickel carbonyl is soluble in fatty oils and that it can be so readily decomposed by heating to liberate pure nickel in extremely fine subdivision were enough to suggest this as a means of preparing hydrogenation catalysts. Among the methods of introducing the nickel carbonyl into the oils or fats may be mentioned the use of a current of oxygen-free nitrogen or carbon monoxide. This is followed by decomposing the carbonyl at

temperatures between 125 and 180°C. Since carbon monoxide is a poison to nickel catalysts in a closed system it is necessary to remove the carbon monoxide by passing a current of hydrogen through the oil at ordinary temperatures for a long time.

DECOMPOSITION OF NICKEL CARBONATE

For studies in the kinetics of the decomposition of nickel carbonyl it was necessary to know under what conditions any carbonate which might be produced could be completely decomposed into the oxide and carbon dioxide. The work of Ageno and Valla (22) indicated that the carbonate was unstable at ordinary temperatures. Srebrow (23) showed that nickel carbonate was decomposed completely at 325°C and the temperature at which the pressure of carbon dioxide reached atmospheric decreased slightly if nickel oxide were present. Thus it was assumed that complete decomposition of the carbonate could be accomplished by heating it to 325°C or slightly more.

APPARATUS

The apparatus used may be divided into two classes, continuous flow systems of which two were built, and a static system. All three were used in the studies of the oxidation of nickel carbonyl, while the static system alone was used for the adsorption studies.

The first was a continuous flow system essentially similar to that employed by McIntosh and Mungen (7). A diagram of this apparatus is shown in Figure 1. In this diagram only the essential details are shown and no attempt has been made to draw it to scale. The air entered at (A) passing through two drying towers (B) containing calcium chloride, and then through the main flow-meter (C) which contained two centimeters of one millimeter capillary tubing. This flow-meter was calibrated by connecting it in series with one calibrated previously by Arnell.

The flow was then divided the major

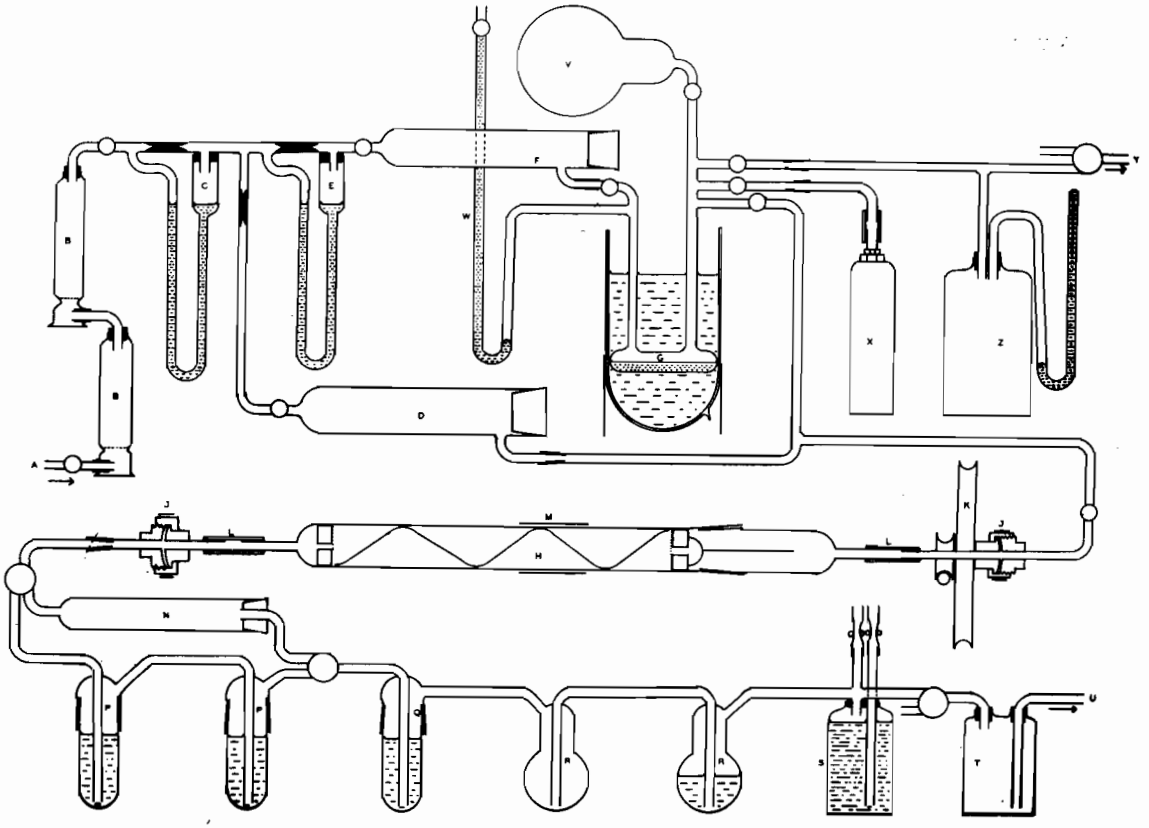


FIGURE 1 - Continuous Flow System for the Impregnation of Charcoal with Nickel Carbonyl Vapour.

portion passing through a phosphorus pentoxide drying tube (D) and the minor portion through a second flow-meter (E) which contained fifteen millimeters of thermometer tubing. The data from a similar flow-meter calibrated by Arnell was used without recalibration. The air then passed through a drying tube (F) containing phosphorus pentoxide and on to the carburettor (G). Here the air stream picked up nickel carbonyl before joining the main air stream.

The combined air streams then passed into the tumbler (H) composed of a long glass tube. The tube and the rotating wheel were so mounted that the whole assembly rotated smoothly between the two $\frac{1}{4}$" unions (J). The rotating half of one of the unions carried a large pulley (K) driven by a belt from a gear assembly so that the tumbler rotated about twice a second. The tumbler itself was connected to the unions by rubber tubing (L) to absorb the "whip" and it was supported by a glass sleeve (M). The charcoal in the tumbler (H) was confined by corks with the holes covered by brass screen, and it was kept stirred by a wire in the tube in the form of a spiral.

After passing through the tumbler the air was passed either through an Hopcalite-Calcium Chloride tube (N) to oxidize the carbon monoxide or through traps (P) containing solutions to test for the presence of carbon monoxide or nickel carbonyl. Then the air passed through a further test trap (Q) and then through a trap (R) containing dilute nitric acid (6N) to destroy any nickel carbonyl which may have been carried through. The stream then passed through a pressure regulator (S) containing water, a cushioning volume (T) and then a water aspirator (U).

The carburettor assembly was made entirely of glass and was vacuum tight. The carburettor was connected to an expansion volume (V), a manometer (W), the nickel carbonyl cylinder (X) and to the Hyvac (Y) through the cushioning volume (Z). The carburettor was charged by evacuating the system, opening the valve to the cylinder of nickel carbonyl and allowing the carbonyl to distill into the carburettor which was cooled in a dry ice - acetone mixture. The system was then returned to atmospheric pressure and room temperature before the air was allowed to flow through. The flows through the

flow-meters was adjusted so that the nickel carbonyl was present in the combined air streams in about one part per hundred.

The second flow system, Figure 2, was intended for studies of the kinetics of the decomposition of nickel carbonyl on charcoal surfaces. Although this section of the work was not carried out the flow system was found to be quite stable and some minor investigations were carried out on the apparatus. Thus it is considered of value to include it here.

Nitrogen from a cylinder entered at (A) and was kept at slightly greater than atmospheric pressure by the mercury escape manometer. It was then passed through two alkaline - pyrogallol bubblers (E) to remove oxygen and carbon dioxide, and then into the carburettor system. Air entered at (B) and passed through two bubblers (F) containing caustic to remove carbon dioxide, after which it could be diverted either to the carburettor assembly or to form the main air stream. If it were the main air stream it passed through humidifiers (G) to the

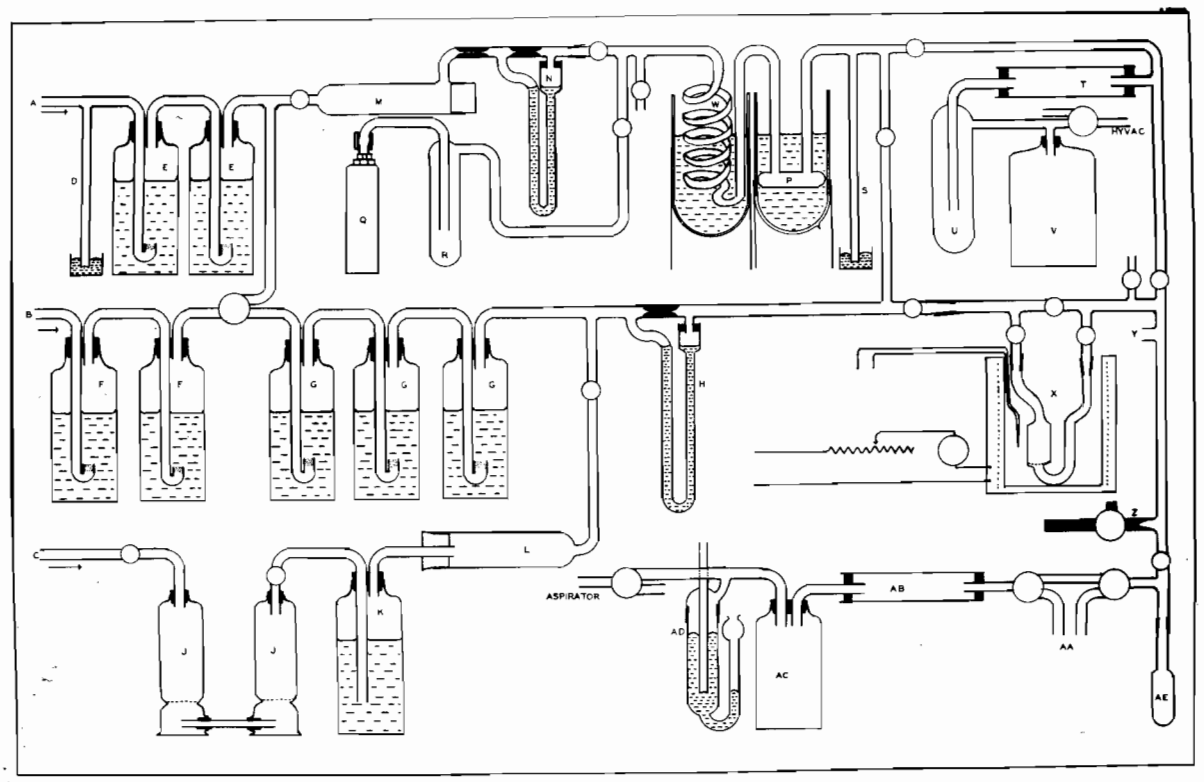


FIGURE 2 - Continuous Flow System for the Study of the Kinetics of the Decomposition of Nickel Carbonyl on the Surface of Charcoals.

flow-meter (H). Alternatively air could enter at (C) and pass through the towers (J) containing calcium chloride, the bubbler (K) containing concentrated sulphuric acid, and the tube (L) containing potassium hydroxide pellets before entering the flow-meter (H). In this way the main air stream could be composed of dry air or air of any desired humidity and free of carbon dioxide.

The flow of nitrogen from (A) or of air from (B) passed to the carburettor (P) first through a drying tube (M) containing phosphorus pentoxide, then a flow-meter (N). The carburettor was connected to the cylinder of nickel carbonyl (Q) through the trap (R) where initial purification of the carbonyl could be achieved, to a manometer (S) and to an Hyvac pump through a pyrolysis tube (T), cooling trap (U) and a cushioning volume (V). The air passed through a spiral (W) before reaching the carburettor proper to heat the air up to the operating temperature. Nickel carbonyl was introduced into the apparatus as in the previous apparatus.

The combined air flows then passed through

or by-passed as desired a cell (X) built in the form of an U and connected to the apparatus by ground glass joins. In this cell a few grams of charcoal could be supported on a brass screen so that the air stream passed through the charcoal. This cell was connected to a manometer (Y) and also to the Hyvac system. The cell was surrounded either by a constant temperature bath or a furnace, the latter for the pyrolysis of the nickel carbonyl or carbonate on the charcoal, as well as for out-gassing the charcoal. The temperature of the furnace was controlled manually with resistances and was determined by copper-constantin thermocouples.

From the cell the air passed a bleed-off (Z) leading to gas sampling, storage and analysis apparatus. The gas analysis apparatus consisted of storage bulbs and an Haldane gas analysis apparatus built in one piece with a Toepler pump. After passing the bleed-off the air passed through or by-passed as desired a gas absorbing and combustion train (AA). From this point the air stream passed through a quartz pyrolysis tube (AB) to a cushioning volume (AC) and a pressure regulator (AD) containing

mercury, to a water aspirator. Trap (AE) was introduced to catch mercury which might escape from the gas sampling system.

The third apparatus was a static system, Figure 3. The charcoal was placed in a brass screen cell in the chamber (A). This chamber was so connected to the two traps (B) and the Hyvac pump system that nickel carbonyl could be condensed in either trap and then distilled from the one trap to the other through the charcoal in the cell. This system was connected in turn to an oxygen cylinder (C) and to a carbon monoxide and hydrogen chloride generator (D) through the same trap (E) which joined the nickel carbonyl cylinder (F) to the system. Dry air could be admitted to the chamber after passing through a train composed of two towers (G) containing calcium chloride, a bubbler (H) containing concentrated sulphuric acid, and a tube (J) containing potassium hydroxide pellets. A vapour density bulb (K) was connected to the system, as was also a pyrolysis system to be described later. The whole system was evacuated through a manometer system (L), a pyrolysis tube (M), a cooling trap (N) and a cushioning volume (P) to an Hyvac.

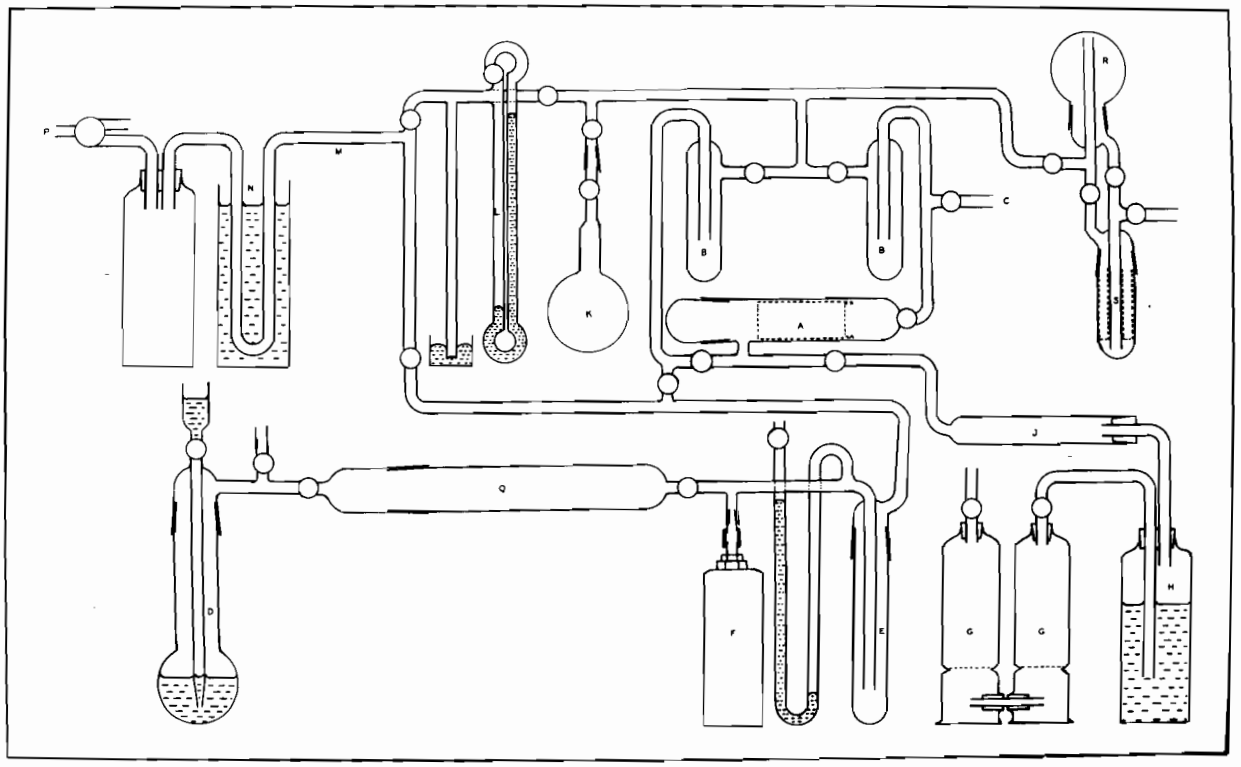


FIGURE 3 - Static System for the Study of Adsorption of Nickel Carbonyl by Charcoal.

Carbon monoxide and hydrogen chloride were prepared by dropping formic acid or hydrochloric acid respectively into concentrated sukphuric acid and passing the gas through a long tube (Q) containing calcium chloride and a trap (E) cooled by liquid air or a dry ice - acetone mixture. The nickel carbonyl was introduced by condensing it in one of the traps cooled in a dry ice - acetone mixture after the system had been evacuated. Carbon dioxide was introduced by placing dry ice in the trap (E) which was demountable and cooling it in liquid air while evacuating the system after which the trap was allowed to warm up and the pressure of carbon dioxide allowed to reach the desired value. A similar procedure was used to introduce carbon tetrachloride except that the trap was cooled in a dry ice - acetone mixture.

The pyrolysis system was a self-circulating system with an expansion bulb (R) and a trap (S). This trap contained a brass cell which held the charcoal, and it was surrounded by either a constant temperature bath or a furnace.

EXPERIMENTAL

OXIDATION OF NICKEL CARBONYL IN AN AIR STREAM OVER CHARCOAL

A sample of Standard Chemical Company activated, unimpregnated, coconut, respirator charcoal was tumbled slowly in the rotating cylinder of the first flow system, Figure 1. Dry air was used and the concentration of the nickel carbonyl in the air stream was about one part per hundred.

Periodically the charcoal was removed, weighed, and a portion removed and analyzed. The charcoal was saturated eventually with the products of decomposition as shown by venting of nickel carbonyl and by the very slow increase in weight of the charcoal corresponding to the passage of considerable amounts of nickel carbonyl past the sample.

Each sample removed was dried and the

TABLE 2

IMPREGNATION OF CHARCOAL WITH NICKEL CARBONYL IN AIR STREAM

Sample	Total Weight	Weight Charcoal	Weight Nickel	Weight Compound	Weight Water	Ratio Comp./Ni.	Percent Nickel in Compound	
SI-a	36.44	34.44			2.00			
		94.5%			5.5%			
SI-c-iA	34.96	33.04			1.92			
		94.5%			5.5%			Before
	39.26	33.04	2.63	4.57	1.65			
		84.2%	6.69%	11.6%	4.2%	1.74	57.4	After
SI-e-iC	38.01	32.00	2.54	4.42	1.60			
		84.2%	6.69%	11.6%	4.2%	1.74	57.4	Before
	39.72	32.00	3.24	6.25	1.47			
		80.6%	8.16%	15.7%	3.7%	1.92	52.2	After
SI-j-iD	37.28	30.08	3.05	5.88	1.38			
		80.6%	8.16%	15.7%	3.7%	1.92	52.2	Before
	40.89							
	41.04							
	43.59							
	44.20							
	44.34	30.08	5.98	13.27	1.04			
		67.9%	13.5%	29.8%	2.3%	2.21	45.3	After

nickel content determined. The charcoal was ashed by grinding to fine powder and heating to boiling in mixed sulphuric and nitric acids to which solid sodium chlorate was added until all of the charcoal had disappeared. The nickel was determined gravimetrically (24).

The results obtained using this sample of charcoal are given in Table 2. From these data it is evident that the amount of nickel deposited is actually about one-half the increase in weight of the charcoal. This was observed also by Hodgins (9) and the actual proportion of nickel in the deposit may be seen to vary with the amount of deposit. This result is shown also by Hodgins' data, Table 3.

TABLE 3

RELATION OF NICKEL CONTENT TO WEIGHT OF DEPOSIT

Sample	Nickel	Compound	Ratio	Percent Nickel
1	3.48 gm	6.45 gm	1.85	54.1
2	5.01	10.65	2.13	47.0
3	6.52	13.13	2.03	49.2

The other point of interest from the data shown in Table 2 is the decrease in the water content either through loss by drying or through chemical combination.

X-ray diffraction photographs of samples SI-e-iC (8.2 percent nickel) and SI-j-iD (13.5 percent nickel) showed no resolved pattern at all. The former was taken using the cellophane backed brass ring in the powder camera to hold the sample. The latter was taken by Dr. F. W. Matthews using the General Electric Multiple Unit apparatus at his disposal.

The surface of the charcoal was affected very markedly by the exposure to the nickel carbonyl vapour. Not only was saturation observed, that is that the fundamental property of the charcoal responsible for the catalytic oxidation of the nickel carbonyl disappeared eventually, but also the adsorption of carbon tetrachloride when carried out in the static apparatus by the method to be described later, was reduced from 74 cubic centimeters of the vapour per gram of charcoal for the

fresh sample to 4.0 cubic centimeters for the specimen sarurated with the decomposition products of nickel carbonyl.

It was observed that after a small amount of the nickel deposit had formed on the charcoal surface that the charcoal failed to tumble as the cylinder was rotated. This made it necessary to use the wire spiral for stirring. No visible deposit appeared upon the glass walls so this phenomenon may have been related either to a change in the nature of the surface in contact with the glass or simply to increased density of the charcoal.

The traps containing test solutions showed that carbon monoxide was passing through (palladium chloride test) and, as the charcoal approached saturation, nickel was detected by using acidified dimethylglyoxime solution. At the time of these investigations no test was made for carbon dioxide.

That the nickel surface would build up

to an appreciable thickness once it had started seems to be a sound premise if based on similar observations on glass surfaces. Explosions in the carburettor and connecting tubes started active deposits of nickel compounds. These built up very rapidly in the rich mixture from the carburettor and plugged tubing ten millimeters in diameter on occasion. Such deposits during formation glowed like burning charcoal and could not be "put out" by cooling the glass in dry ice - acetone mixtures. These deposits could be removed only by dissolving in nitric acid since they contained metallic nickel formed when the nickel carbonyl was decomposed by the heat of the reaction.

A study was made of some of the deposits laid down in the apparatus in the hope that it might lead to some information on the nature of the deposit on the charcoal. Three such deposits were studied briefly.

One deposit was laid down in the tubing leading the combined air streams to the tumbler.

At first this appeared as a thin brown stain which later pulled away from the glass and "coalesced". Eventually an opaque film built up. This adhered to the glass with varying degrees of tenacity, some flaking off easily while some was removed only with difficulty. This material was insoluble in and unaffected by water, was dry, and in the form of glistening brown leaves. It dissolved readily in six normal hydrochloric or nine normal nitric acids with effervescence in each case. Analysis showed 61.5 percent nickel and a very small trace of iron. This material failed to give any x-ray diffraction pattern.

As can be seen from Table 2, the percentage of nickel in the deposit formed on the charcoal surface drops from 57.4 to 45.3 per cent over the course of part of the experiment so that it is not inconsistent to identify the deposit removed from the glass tubing with that on the charcoal. Actually the deposit on the glass tubing was removed at a time when the nickel deposit on the charcoal assayed 52.2 percent nickel. The "age" of the deposit on the glass

was less than that on the charcoal since it did not start to form in the former case until well after the experiment had started. If it is conceded that the percent nickel in a deposit decreases with increasing "age", it is admissable to assume that the deposit on the glass is an earlier form of the similar deposit on the charcoal. One must ignore specificity of surface by such an assumption and infer from the similar chemical analyses and the fact that both deposits were laid down on surfaces and from the same air stream that they may be identical in composition. If this is true, and since the deposit removed from the glass failed to produce an x-ray diffraction pattern, then it is seen why the charcoal bearing the nickel deposit failed to show an x-ray diffraction pattern.

A second deposit was removed from the carburettor. As air passed through the carburettor a deposit of fluffy brown material settled gradually. When this dried in the empty carburettor it formed a very fine yellow powder. This was insoluble in and unaffected by water, but effervesced vigorously in six normal hydrochloric or nine normal nitric acids

and dissolved completely in either. Analysis showed 63.0 percent nickel and between 0.1 and 0.05 percent iron. An x-ray diffraction picture showed only a suggestion of nickel oxide in very finely divided state. The material was visibly heterogeneous and must have contained amorphous oxides and carbonates also.

In a large expansion volume connected to the carburettor deposits were obtained of a different character. This bulb was horizontal at first so that a layer of nickel carbonyl vapour remained in the bulb when the apparatus was returned to atmospheric pressure by the admission of air. After several days the air - carbonyl mixture exploded liberating a large amount of a very fluffy black material which settled to the bottom of the bulb like soot. Further explosions, some intentional, built this material up into an appreciable layer. Part of this was removed without mishap but some was ignited by explosions of the carbonyl still in the bulb or adsorbed on the deposit, and the material burnt vigorously, glowing like burning charcoal. These samples were insoluble in and unaffected by water. Each effervesced in six

normal hydrochloric acid and dissolved partially. Each was completely soluble in nine normal nitric acid indicating the presence of metallic nickel which dissolves in this acid but not in the hydrochloric acid.

As freshly removed from the bulb the deposits fumed violently in acids indicating the escape of nickel carbonyl from the solution with subsequent decomposition in the damp air. Small amounts of the carbonyl remained in the samples at the time of analysis, although these samples in common with the other two lost no appreciable weight on drying for six hours at 110°C. This indicated that as well as being comparatively free of carbonyl and dry at that time, the compounds themselves were stable. The unignited sample assayed 85 percent nickel and x-ray diffraction data showed the presence of finely divided nickel and nickel oxide. The ignited sample assayed 83 percent nickel and was contaminated by paper ash.

The stability of the deposits on the glass as well as that on the charcoal indicated

that these deposits were not a lower carbonyl, or a mixed metallic nickel and nickel carbonyl as had been thought possible (9).

It is of interest to note that placing the bulb vertical and keeping it at reduced pressure in the absence of air resulted in the formation of a bright metallic mirror on the surface in a period of several weeks. This is of interest in connection with the studies on the thermal decomposition to be described later.

ADSORPTION OF NICKEL CARBONYL

Until the investigations reported in the previous section had been partly completed, it was thought that the carbonyl when passed over the charcoal was decomposed into metallic nickel and carbon monoxide, although the work of Hodgins had indicated that this was probably not so. The present results show conclusively that metallic nickel is not deposited, but possibly an amorphous oxide - carbonate mixture. Thus it would seem probable that the charcoal acts as an oxidation catalyst rather than one catalyzing decomposition. This could be shown more clearly by carrying out the adsorption in the absence of air. Thus samples of charcoal were placed in the brass screen basket of the chamber of the static apparatus, Figure 3, for adsorption studies.

The apparatus and charcoal specimen were evacuated and the chamber containing the charcoal isolated from the rest of the apparatus. Then the rest of the apparatus was brought to a known pressure with the gas to be adsorbed and then connected to the

chamber. The pressure after equilibrium was read, and the amount by which it was less than that for some unadsorbed material such as air was obtained and the volume of the gas adsorbed calculated from the volumes of the chamber and apparatus. The volumes were calculated by measuring the pressure change accompanying the adsorption of a given weight of material. Thus the values are to be considered relative rather than absolute. It was only desired to obtain some idea of the adsorption of various vapours at room temperature in an effort to understand better the adsorption of nickel carbonyl and the composition of the solid product left after the decomposition of the carbonyl. The results obtained, while numerically not entirely satisfactory, clarified the problem very well and so justified the time spent thereon.

In the absence of air, dry charcoal adsorbed nickel carbonyl very strongly without decomposition and with the liberation of considerable heat. Nickel carbonyl was distilled from one trap (B) to the other in the static apparatus until the charcoal was saturated at the pressure of the

nickel carbonyl. Then the sample was removed and weighed very quickly to determine the adsorbed nickel carbonyl. Similar results were obtained using carbon dioxide, carbon tetrachloride, oxygen and carbon monoxide. The results are tabulated in Table 4, and compared with results obtained when the fresh sample of charcoal was replaced by one which was saturated with the decomposition products of nickel carbonyl. This latter sample contained 14 percent nickel and the weight of the deposit amounted to 26 percent of the weight of the specimen.

TABLE 4

ADSORPTION BY UNIMPREGNATED AND NICKEL IMPREGNATED CHARCOALS

Vapour	Pressure	Boiling Point	Unimpreg. cc/gm	Impregnated cc/gm
Carbon Monoxide	363 mm	-192°C	1.6	1.1
Oxygen	331	-183	.0	.8
Carbon Dioxide	342	-78.5	30	17.8
Nickel Carbonyl	323	43	74	6.5 to 10
Carbon Tetrachl.	77	77	90	1.3 to 4.0

Some results were obtained also using C.W.2, a copper impregnated Whetlerite charcoal. These data are given in Table 5.

TABLE 5

ADSORPTION BY C.W.2

Vapour	Pressure	Boiling Point	Adsorption cc/gm
Nickel Carbonyl	309 mm	43°C	79
Carbon Tetrachlor.	77	77	95
Water (calc. from 12 percent water)		100	174

From these data and from the fact that the nickel carbonyl is not decomposed it is evident that the adsorption of nickel carbonyl is not specific, and that the charcoal does not catalyze the decomposition of the carbonyl into nickel and carbon monoxide. The actual adsorption isotherms from which some of the above data were taken are shown in Figures 4 and 5. The data recorded in Tables 4 and 5 represent the maximal adsorption at the indicated pressures, and the steps in the process of reaching the maximum are those shown in Figures 4 and 5.

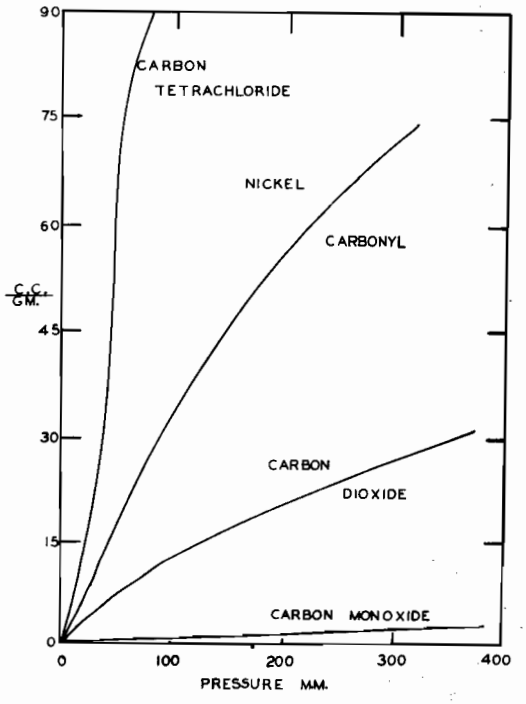


FIGURE 4 - Adsorption by an Unimpregnated Charcoal

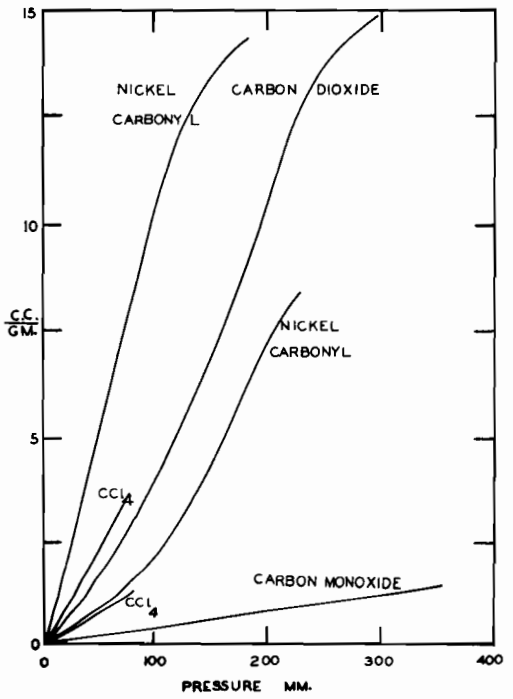


FIGURE 5 - Adsorption by a Nickel Impregnated Charcoal.

Figure 4 shows the adsorption of nickel carbonyl, carbon dioxide, carbon monoxide and carbon tetrachloride by a sample of unimpregnated charcoal while Figure 5 shows similar results obtained when charcoals which had been saturated with nickel carbonyl and the carbonyl oxidized were used.

From Figure 4 it is evident that the adsorption follows typical isotherms, and the amount adsorbed follows the same order as the boiling points. Figure 5 shows that the adsorption is reduced greatly but is of the same general form. The relative order of magnitudes of the results shown in Figure 5 may not be correct since it was necessary to use different samples of nickel impregnated charcoal. The reduction of the amount of carbon tetrachloride adsorbed relative to the amounts of carbonyl adsorbed might be explained by the blocking effect of large molecules as observed by Emmett (25). The greatly increased adsorption of carbon dioxide may represent the formation of nickel carbonate.

From Figure 6 the effect of saturation of

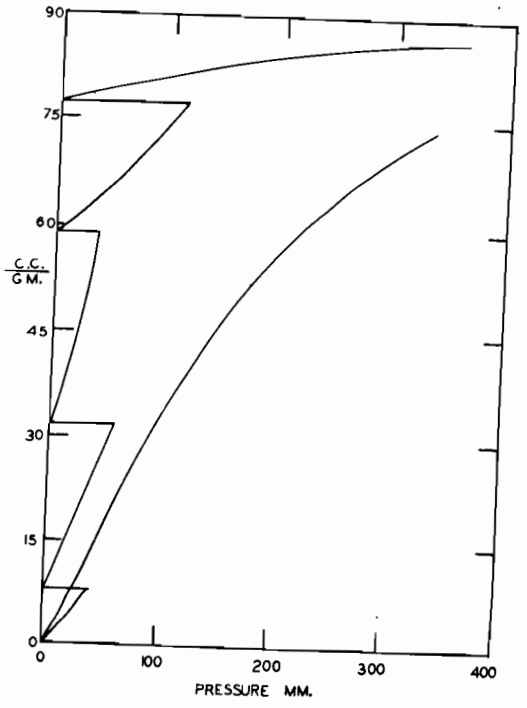


FIGURE 6 - Adsorption of Nickel Carbonyl in One or Several Steps.

the charcoal with nickel carbonyl followed by oxidation of the carbonyl may be compared with the results obtained when the charcoal is partially saturated with nickel carbonyl, the carbonyl oxidized, and the procedure repeated to saturation. This is of interest only in that it illustrates that the amount adsorbed is quite constant and the rate of increase of the pressure and the amount adsorbed would seem to be independent of whether the nickel carbonyl is present as such or as oxidized to carbonate and oxide.

The nickel carbonyl is adsorbed quite firmly since exhausting the sample for four hours under Hyvac failed to remove a residue of 48 cubic centimeters of nickel carbonyl per gram of charcoal.

OXIDATION OF ADSORBED NICKEL CARBONYL

When exposed to oxygen the charcoals which had been saturated with nickel carbonyl brought about the rapid but smooth decomposition of the carbonyl into a nickel deposit, carbon monoxide and carbon dioxide.

One sample of the charcoal was saturated with nickel carbonyl at 254 millimeters pressure. The sample adsorbed 73.5 cubic centimeters of the vapour per gram of charcoal, or 0.425 cubic centimeters of liquid carbonyl per gram of charcoal. The carbonyl was then oxidized after which the resulting deposit represented 25.6 percent of the total weight of the sample. The nickel content was 14.4 percent. It was this sample which was used in most of the investigations shown in Table 4 and Figure 5.

The amount of deposit produced in this way and the nickel content may be compared with similar specimens in which the adsorption and oxidation were continuous, Table 2. In this latter sample the

deposit amounted to 30 percent of the weight of the charcoal, but was only 13.5 percent nickel. This difference is not considered significant since these would be expected from the fact that the adsorption in the latter case was made at partial pressures of the nickel carbonyl not exceeding ten millimeters.

Another specimen was not completely saturated but nickel carbonyl was adsorbed and oxidized alternately until saturation was complete. The amount of deposit was increased to over 30 percent by weight of the final specimen. Thus the results are essentially the same regardless of the method by which the charcoal is impregnated. The results are summarized in Table 6. Oxidation did not seem to be complete in every case since after many days exposure to air very slight amounts of nickel carbonyl remained on the charcoal. This showed up as the characteristic white fumes when acid was added to the charcoal.

TABLE 6

EFFECT OF PROCEDURE ON ADSORPTION

Sample	Weight gm	Treatment	X/M	Deposit percent	Nickel Percent	Ratio
SI	30.08	continuous		29.8	13.5	2.21
SII	10.55	pumped off	47.9	23.3	13	1.79
SIII	11.39	saturated	73.5	25.6	14.4	1.78
SIV	6.76	stepwise	77	25.9	14.2	1.82
SV	5.66	stepwise	80	27.7	15.2	1.82
CW2	5.33	saturated	78	28.4	14.8	1.92

The ratio of the weight of the deposit to the weight of the nickel is about two as shown from Tables 2 and 6. While variable, from 1.74 to 2.21, it is relatively constant. The high value of 2.21 was exhibited by the deposit on a dried, phosgene saturated charcoal. The formula which corresponds most closely with a ratio of 1.83 is

$$NiCO_3.5NiO.$$

Writing the formula this way does not need to imply a compound formed with that composition but may mean that the carbonate and oxide occur together in about that ratio.

The products of oxidation other than solids are of interest, particularly since the solid phase seems to be an amorphous oxide - carbonate mixture rather than metallic nickel. Nickel carbonyl was adsorbed on the charcoal and a definite amount of oxygen flowed in and the pressure changes noted. Taking the initial pressure of the oxygen as the reference pressure, there was an instantaneous rise of about 10 to 30 percent in pressure (mean 17 percent). This was followed by a slow rise lasting for approximately five minutes at which time the maximum would represent an increase of about 20 to 50 percent (mean 36 percent) after which the pressure fell to an equilibrium value about 10 to 45 percent higher than the initial pressure (mean 28 percent).

The pressures tended to be higher if the nickel carbonyl exploded around the charcoal instead of decomposing entirely on the charcoal. Such conditions favour the formation of metallic nickel and the oxide. The equilibrium atmosphere contained from 14 to 37 percent carbon dioxide (mean 21 percent), the content rising as equilibrium is reached. These and other approximate analyses were made by dividing

the gases into three groups. One group was uncondensable in liquid air cooled traps (oxygen, nitrogen and carbon monoxide), a second group was condensable in dry ice - acetone mixture cooled traps (nickel carbonyl, water, phosgene, and carbon tetrachloride), and a third group was uncondensable in dry ice - acetone mixture cooled traps but condensable at liquid air temperatures (carbon dioxide and hydrogen chloride). In addition to the carbon dioxide in the gas phase considerable amounts could be pumped off the charcoal after oxidation of the carbonyl. The results are summarized in Table 7.

TABLE 7

PRESSURE CHANGES DURING OXIDATION

No.	Percent of Volume of Oxygen			Percent Carbon Dioxide at Equilibrium
	First	Maximum	Equilibrium	
1	106	122	122	
2	112	144	133	14.1
3	111	137	132	
4	125	147	144	
5	146	165	148	22.2
6	124	140	124	16.1
7	129	137	136	19.0
8	115	130	111	37.1
9	118	129	121	16.5

It seemed possible that a known amount of carbonyl could be oxidized and all the carbon dioxide collected to give a carbon dioxide to nickel carbonyl ratio. The results were variable but roughly 3.5 volumes of carbon dioxide were liberated for 4.5 volumes of carbonyl oxidized. Estimating the amount of carbon dioxide necessary to explain the weight of the solid deposit, the amount of carbon dioxide produced by 4.5 volumes of carbonyl was of the order of 6.9 volumes. This crude estimate indicated that at least one mole of carbon dioxide is produced per mole of nickel carbonyl oxidized, the other products being nickel oxide and carbon monoxide. The data are summarized in Table 8.

TABLE 8

CARBON DIOXIDE PRODUCED BY OXIDATION

	Volumes of Nickel Carbonyl	Volumes of Carbon Dioxide
	1.52	1.00
	1.25	1.38
	1.75	1.18
calculated from Carbonate		3.31
Total	4.52	6.87

It was possible that the carbon dioxide was produced by the oxidation of carbon monoxide on the nickel impregnated charcoal. This possibility was eliminated when it was observed that both wet and dry carbon monoxide - oxygen mixtures produced no carbon dioxide on prolonged exposure to the charcoal.

THERMAL DECOMPOSITION OF NICKEL CARBONYL ON THE SURFACE OF CHARCOAL

While the decomposition of nickel carbonyl in the absence of air is very slow at room temperature, it is practically complete and instantaneous at temperatures above 100°C. It was observed that by adsorbing a known amount of nickel carbonyl and decomposing it at 150°C the theoretical amount of carbon monoxide was liberated. This procedure was repeated several times until a deposit amounting to 16.5 percent of the weight of the final sample was built up on a charcoal sample in Trap (S) of the static apparatus, Figure 3.

While the metallic nickel was visible, it was decided to confirm its presence by an x-ray diffraction photograph. The presence of metallic nickel and no other distinguishable material was confirmed. The photograph is shown in Figure 7. Unfiltered copper radiation and a crystal to plate distance of 4.52 centimeters was used, and the charcoal was ground to a fine powder and molded into a rod about one millimeter in diameter. This

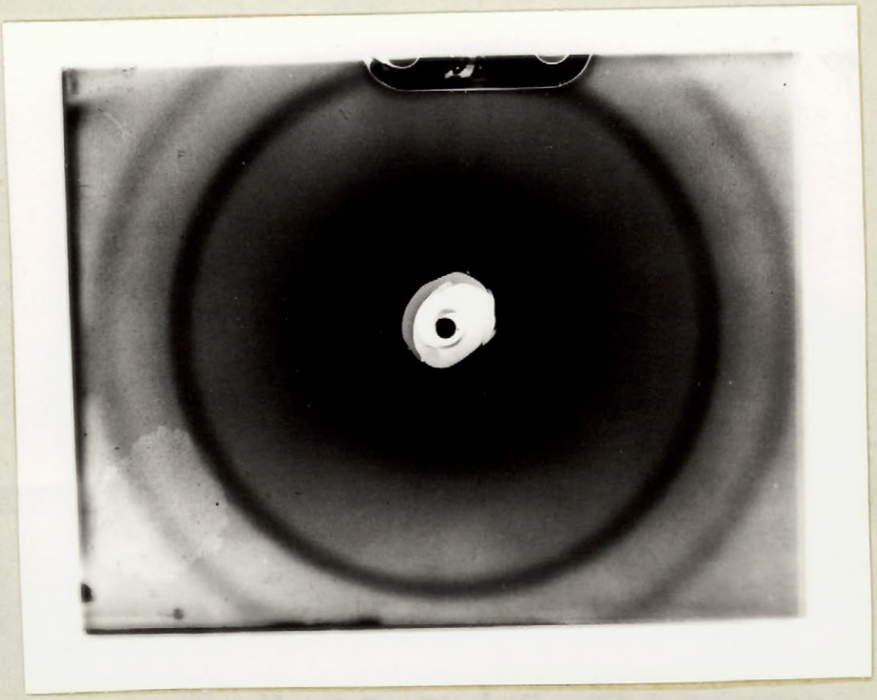


FIGURE 7 - X-Ray Powder Photograph of Charcoal bearing Deposit of Metallic Nickel. Copper Radiation. Crystal to Plate Distance 4.52 Centimeters.

rod was mounted vertically in the crystal holder of the Universal Photogoniometer and rotated continuously during the exposure.

The two prominent nickel lines corresponding to spacings of 2.03 and 1.76 Angstroms are shown clearly. It is not known whether the nickel was deposited throughout the charcoal or just on the surfaces where the heat reached the charcoal first.

ADSORPTION OF NICKEL CARBONYL BY CHARCOALS EXPOSED PREVIOUSLY TO OTHER GASES

That the previous history of the charcoal affects the adsorption of nickel carbonyl is indicated in Table 4. Some further data may be of interest. A sample of charcoal which had been saturated with nickel carbonyl at 324 millimeters pressure was exposed to air until oxidation was complete. On saturation again at 188 millimeters pressure the sample adsorbed only 10 cubic centimeters of the vapour per gram of charcoal as compared with the 74 cubic centimeters of the original adsorption. Repetition of the above procedure caused the amount adsorbed to be reduced to only 6.5 cubic centimeters per gram of charcoal.

Oxidation of the carbonyl was carried out and then the resulting sample adsorbed only 1.3 cubic centimeters of carbon tetrachloride vapour at 76 millimeters pressure per gram of charcoal. The same charcoal not previously treated with nickel carbonyl adsorbed 90 cubic centimeters of carbon tetrachloride per gram of charcoal. When this

sample so saturated with carbon tetrachloride was exposed to nickel carbonyl vapour at 280 millimeters pressure, it adsorbed but 8.2 cubic centimeters of the vapour per gram of charcoal.

Saturation of the charcoal with nickel carbonyl involves the adsorption of about 0.425 milliliters of the liquid per gram of charcoal, and when carbon tetrachloride is used the volume is 0.385 milliliters.

During a study of arsine service times of some copper impregnated charcoals a sample of C.W.2 adsorbed 119 cubic centimeters of arsine per gram of charcoal. There was no indication whether this sample was saturated or not. On exposure of this charcoal to nickel carbonyl vapour at 313 millimeters pressure it adsorbed 34 cubic centimeters of the vapour per gram of charcoal, much reduced from the original 79 cubic centimeters at 309 millimeters pressure for the original C.W.2. Similarly at 77 millimeters pressure the adsorption of carbon tetrachloride was reduced from 95 to 49 cubic centimeters per gram of charcoal.

A sample of charcoal had been run to service time with phosgene in an air stream of 100 percent relative humidity and at a phosgene concentration of one part in two hundred, was then run to saturation. This sample was dried at 110°C for several hours. Exposure of this charcoal to nickel carbonyl at 319 millimeters pressure resulted in the adsorption of 33 cubic centimeters of nickel carbonyl vapour per gram of charcoal. The adsorption of carbon tetrachloride by a similar sample was 46 cubic centimeters at 77 millimeters pressure per gram of charcoal. Undried samples adsorbed a much smaller amount of nickel carbonyl or carbon tetrachloride. Other results with dried and wet samples which had been run at various humidities are shown in Table 9. The word charcoal in the case of both the arsine and phosgene tested samples is considered to include the weight of the deposit on the charcoal before this investigation was begun, so that the results are low by an amount equivalent to the deposit on the charcoal. This amount was not known exactly but was estimated at about 30 percent in the case of the arsine tested samples.

TABLE 9

ADSORPTION ON PHOSGENE SATURATED CHARCOALS

Relative Humidity percent	Adsorption Nickel Carbonyl	Adsorp. Carbon Tetrachloride
Wet Specimens		
0	43.2 cc	24.4 cc
40	24.3	28.7
80	20.5	13.0
100	20.0	16.2
Dried Specimens		
0	43.2	24.4
40	59.2	61.9
80	50.9	72.6
100	33	46

The phosgene tested samples caused some decomposition of the nickel carbonyl. Thus it was of interest to determine the cause. It is not due to water alone or to water and carbon dioxide since wet charcoals with or without carbon dioxide failed to do so. The presence of hydrogen chloride seems to cause decomposition but it seems to be slight. No attempt was made to study the effect of chlorine or of phosgene itself so that the exact cause is uncertain.

DECOMPOSITION OF NICKEL CARBONATE

A sample of Kahlbaum Nickel Carbonate (green) was used to test whether the carbonate on the charcoal could be decomposed at a reasonable temperature or not. The compound was heated at 110°C to drive off water, then at 325°C to drive off carbon dioxide. The analysis is shown in Table 10.

TABLE 10

ANALYSIS OF NICKEL CARBONATE

Water	0.296 grams or	9 percent
Carbon Dioxide	0.884	27
Nickel Oxide	2.125	64

In the absence of any data on the division of water between adsorbed and molecular, and due to the fact that the value for carbon dioxide may represent water of constitution as well as carbon dioxide, no formula is suggested for this sample. The results show that this complex carbonate may be decomposed into the black oxide under the experimental conditions specified.

It was observed that the nickel oxide tended to revert to a yellow compound, probably a carbonate, on exposure to air. Consequently it is probable that the deposit on the charcoal if originally nickel oxide would be converted to the carbonate in the atmosphere rich in carbon dioxide.

The vapour pressure, Table 11, of nickel carbonate shows that at the temperatures used to decompose nickel carbonyl, 150°C, it would be expected that an appreciable amount of carbon dioxide would be liberated from the nickel carbonate. This factor would complicate the kinetic study.

TABLE 11

VAPOUR PRESSURE OF NICKEL CARBONATE

Temperature	Vapour Pressure
20°C	6 mm
80	25
90	31
100	35
110	42
120	47
130	59
140	70
150	86

ABSORPTION OF GASEOUS NICKEL CARBONYL

Because the analysis of gas streams in the proposed study of the kinetics of the decomposition of nickel carbonyl on charcoal surfaces involved the absorption of the carbonyl carried through, the flow-system, Figure 2, was used to determine whether turpentine which had been reported as an excellent absorber of the gas would do. It was found that the nickel carbonyl content of an air stream containing one part per hundred of the carbonyl and flowing at a rate of 250 cubic centimeters per minute was reduced practically to zero but the carbonyl was not removed entirely. The absorbing train was composed of two Geissler and two Gombar bulbs in series. Since this was a rather long train and not entirely effective in removing the carbonyl, some more certain method for the absorption of nickel carbonyl must be developed before the study can be carried out.

DISCUSSION

The oxidation of nickel carbonyl proceeds in two different manners. In a deficiency of air the products are nickel and nickel oxide while in an excess of air it is inferred in the absence of direct data that the solid product is an amorphous oxide - carbonate mixture whose percentage composition varies but seems to average about 55 percent nickel. On this basis an average formula might be

$$NiO.5NiCO_3.$$

It would seem probable from the data given that the composition would vary from pure oxide to pure carbonate depending upon the conditions of formation. The gaseous products are understandable on the basis of the equation

$$Ni(CO)_4 + O_2 \longrightarrow NiO + CO_2 + 3CO,$$

and the formation of the carbonate on the basis of

$$NiO + CO_2 \longrightarrow NiCO_3.$$

Since the adsorption of nickel carbonyl seems to be non-specific for the charcoal surface it might be possible to estimate a surface area by assuming a monomolecular layer of molecules. Such

an estimate for the unimpregnated charcoal gives an area of 858 square meters per gram of charcoal which is in good agreement with the results of Emmett (25). He showed that as the molecular weight of the adsorbate increased the indicated area decreased. He reported results with molecules ranging from water which gave an area of 1830 square meters per gram to octane which gave an area of only 922 square meters per gram of the same charcoal. Since nickel carbonyl is still heavier than octane the indicated area should be still lower.

None of the other adsorptions were carried out sufficiently close to the boiling point of the adsorbate to be of any use although the use of similar calculations gave an area of 857 square meters per gram of charcoal when carbon tetrachloride was used. While this result agrees very well with that obtained using nickel carbonyl this can be only a coincidence since the carbon tetrachloride was used well below its boiling point, and the molecular weight is less than that of nickel carbonyl. These two opposing factors must have balanced fortuitously in this case.

If one assumes that the nickel carbonyl is adsorbed in a monomolecular film then one can see readily why oxidation failed to leave a product which could give a resolvable x-ray diffraction picture. The thickness of the film necessary for a pattern is about 10 molecules and this is impossible if the initial adsorption is monomolecular and subsequent adsorption fails to take place. Also it can be seen that activated adsorption of carbon dioxide would be very likely and the formation of carbonate also would be extremely easy with such finely divided oxide. Thus the data obtained in this investigation may be explained on that basis.

The observations that the adsorption of one vapour prevented the adsorption of another to a considerable extent is explained on the basis of Emmett's work (25). In his experiments the use of toluene, a large molecule, blocked off whole capillary systems to the entry of nitrogen so that there was a net reduction in the surface area as measured by this method. In the same way the adsorption of carbon tetrachloride, the decomposition products of

nickel carbonyl, phosgene and arsine, all seem to block the systems to the entry of nickel carbonyl to varying degrees. Also the adsorption of nickel carbonyl quite effectively blocks the entry of carbon tetrachloride molecules. It should be noted that the results reported here were not obtained under conditions comparable with those used by Emmett but it has been considered probable that his conclusions would apply at least qualitatively.

COPPER IMPREGNATED RESPIRATOR CHARCOAL

INTRODUCTION

Matthews identified copper and cuprous oxide in Canadian Whetlerite and observed that when the impregnant was reduced by hydrogen the arsine time of the wet sample was not greatly altered but that that of the dry sample was reduced. On the other hand Johnstone (26) reports that the American Whetlerite contained only cupric oxide and that the arsine time was much greater when the crystal size was very small.

It was reported later (27) that under the conditions of the American test the Canadian Whetlerite had an arsine time of only 3.5 minutes as compared with an American Whetlerite with a service time of 105 minutes (dry sample). It was considered that a comparison of the arsine service times of these charcoals at 60 percent relative humidity, and dry, under the standard Canadian test conditions might explain the differences observed.

APPARATUS

For the preparation of arsine, calcium arsenide prepared by F. Lossing was used at first. Only a poor yield was obtained from this old material, and considerable hydrogen was produced. For most of the investigations aluminium arsenide was produced by igniting a mixture of 65 parts of powdered arsenic and 35 parts of aluminium powder in a crucible. This mixture ignited readily and fused violently with the destruction of the crucible, and the production of dense white fumes. The reddish brown mass from the inner part was ground to a powder easily but beads of the material were fused to the crucible parts so that the parts of the crucible had to be broken up also. The powdered product was stored thus till use.

The arsine was produced by the action of water or dilute sulphuric acid on the calcium or aluminium arsenide in the apparatus shown in Figure 8. The arsenide was placed in the generator (A) and the water or acid added from the dropping funnel (B) after the entire apparatus had been evacuated. The

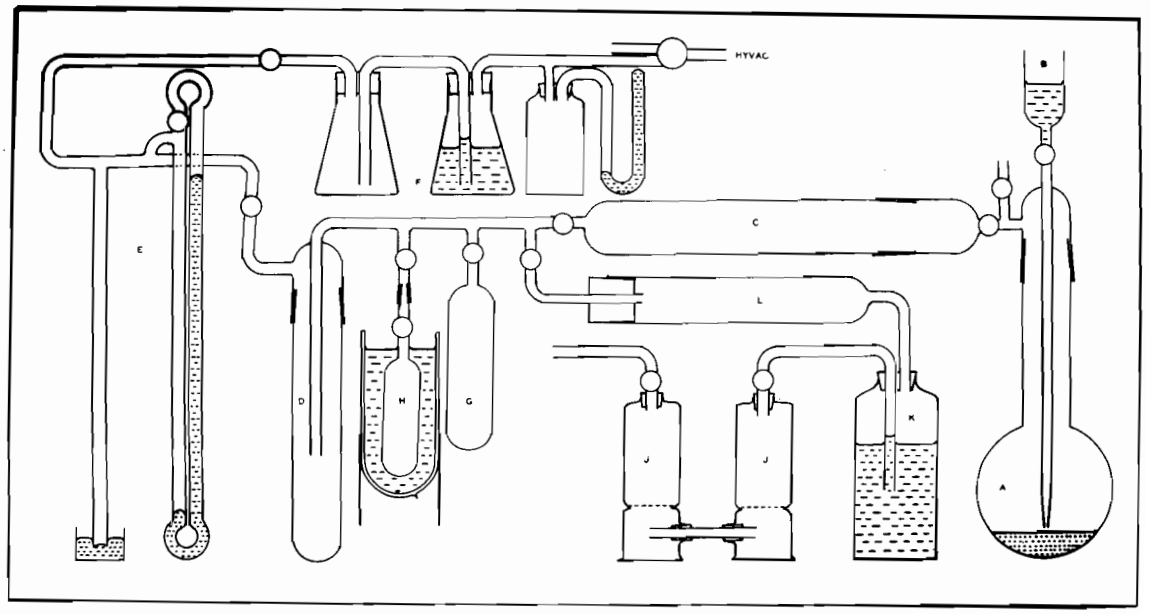


FIGURE 8 - Arsine Generator.

arsine passed through the drying tower (C) and was condensed in trap (D) cooled with liquid air. The escape from the trap connected to the manometer (E) and the pumping system. The pumping system contained sulphuric acid traps (F) to decompose uncondensed arsine.

The earlier samples of arsenide produced arsine and hydrogen instantly, the hydrogen being removed by continuous pumping of the system. The fresh aluminium arsenide had a pronounced and unsuspected induction period so that with its use arsine was produced violently after considerable water had been added. The apparatus as designed failed to cope with this leading to the escape of considerable quantities of arsine and the termination of the investigations.

The arsine condensed in trap (D) was redistilled twice from carbon dioxide snow - acetone mixture temperatures to liquid air temperatures using in turn bulbs (G) and (H). This latter storage bulb was connected to the apparatus by a

ground glass joint so that it could be removed and later connected to the service time apparatus. The arsine was stored in this bulb till use, and was kept at liquid air temperatures.

The entire apparatus was of glass to prevent decomposition of the arsine and to minimize leaks. The arsine stored at liquid air temperatures and under its own vapour pressure showed no decomposition within a week.

The arsine service times were determined using the apparatus the essential parts of which are shown in Figure 9. It was built by J. Davis and is essentially a storage volume and flow-meter assembly connected to the apparatus described by him (28).

The arsine storage bulb (A) was connected to the apparatus and the storage volume (B) and manometer (C) evacuated. Connection was made to the arsine which was allowed to warm up till the pressure just exceeded atmospheric. The vapour was then drawn through the flow-meter (D) and joined the main air

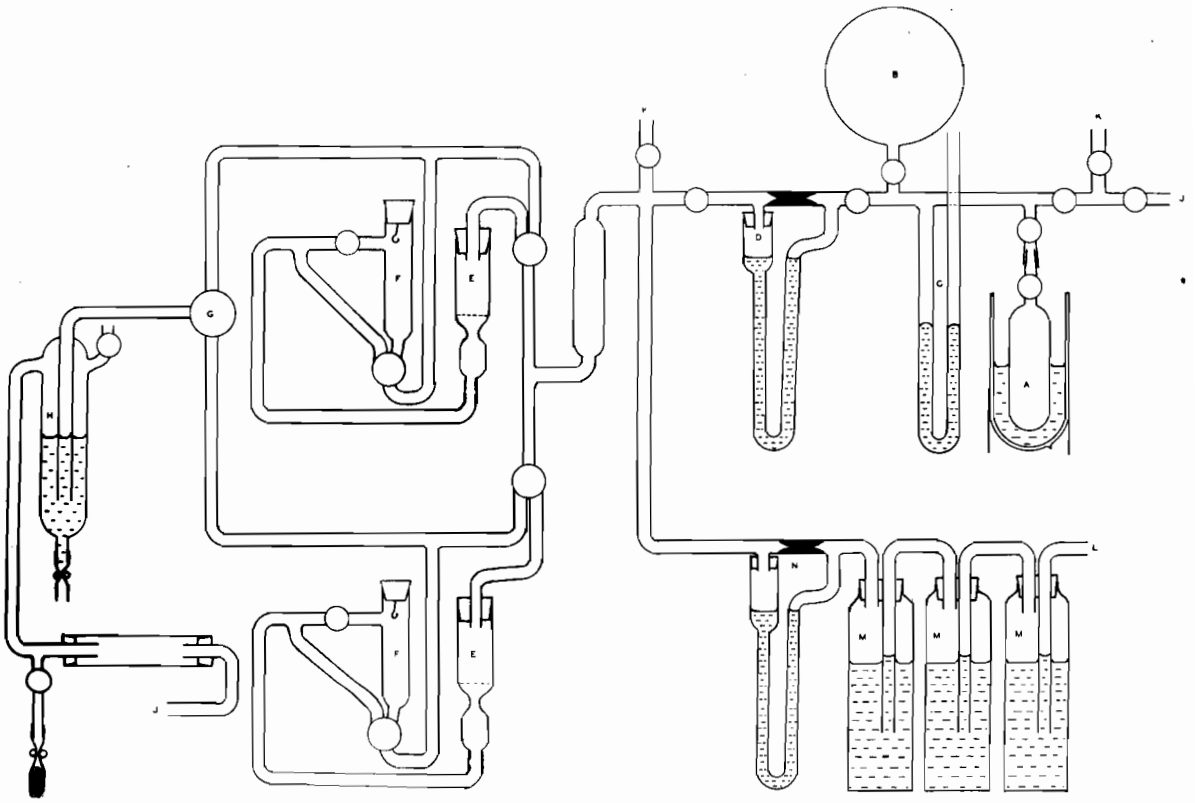


FIGURE 9 - Arsine Service Time Apparatus.

stream which had entered at (L) and had been brought to the desired humidity by the bubblers (M). The flow of the main air stream was measured by the flow-meter (N). The combined stream flowed through the two cells (E) and the test paper chambers (F) alternately as the rotating valve (G) connected them alternately with the pressure regulating system (H) and the exhaust system (J). Other systems were connected at (K).

The test cells were one square centimeter in cross-sectional area and the charcoal bed five centimeters deep. The cells were filled and packed according to the standard technique, and were weighed before and after the passage of the arsine through the charcoal.

RESULTS

It was confirmed that an American Whetlerite CWSE-I-TE-I showed only the diffraction pattern of cupric and cuprous oxides, in contrast with the Canadian Whetlerite C.W.2 which showed the presence of iron, copper and cuprous oxide. These patterns were obtained using finely ground specimens of the charcoal mounted in cellophane backed brass ring cells one millimeter deep placed normal to the x-ray beam defined by a one millimeter pinhole.

The American Whetlerite contained only 0.76 percent moisture as compared with the 12 percent present in the Canadian Whetlerite when determined under identical conditions.

In attempting to obtain arsine service times on these charcoals it was observed first that the test papers failed to respond to the arsine. In an effort to save the determinations a test was tried using the method of heating the glass tubing in the pressure regulating system and watching for the

appearance of a mirror. No mirror formed in any of the determinations attempted so that the service times may be in error considerably. The first two determinations were terminated by failure of the arsine supply, the third voluntarily after two hours. The results are tabulated in Table 12.

TABLE 12

ADSORPTION OF ARSINE

Weight Before Grams	Weight After Grams	Weight Gain Grams	Weight Arsine Grams	X/m cc/gm	Time Minutes
CWSE-I-TE-I, Arsine 1/100, Relative Humidity 0.					
5.3493	7.6446				
5.5259	6.9738				
10.8752	14.6184	3.7432	3.58	78.5	103
C.W.2. Dry, Arsine 1/100, Relative Humidity 0.					
4.9384	6.4722				
5.1291	6.1878				
10.0675	12.6600	2.5925	2.89	62.0	83
C.W.2. Wet, Arsine 1/100, Relative Humidity 60 %.					
5.6234	6.8728				
5.7187	7.1288				
11.3421	14.0016		4.17	119	120

The determinations were without incident.

Considerable heat developed during the determinations and some white material distilled out of the charcoal (arsenious oxide ?) and in the case of the wet sample of C.W.2 the heat was sufficient to dry the sample completely so that one was dealing with dry charcoal essentially. Drying the specimens at 110°C for several hours resulted in a negligible loss in weight as shown by Table 13.

TABLE 13

DRYING OF CHARCOALS EXPOSED TO ARSINE

	Weight Before Grams	Weight After Grams	Loss Grams
CWSE-I-TE-I	7.015	6.954	0.061
C.W.2,Dry	6.226	6.176	0.050
C.W. 2,Wet	7.210	7.169	0.041

The close relationship between the amount of arsine used (calculated) and the increase in the weight of the charcoal suggested that arsenic might be the product laid down. This is in disagreement with previous investigations. The error must be attributed to failure to reach a test, that is

considerable arsine or its decomposition products must have passed the charcoal bed without showing a test during these investigations. However it was considered worth while to attempt to identify the decomposition products on the charcoal in spite of the failure of similar attempts when nickel carbonyl was used. In the case of the charcoals exposed to arsine the increase in weight is such that the arsenic compounds represent 20 percent of the weight of the sample, a value considerably higher than that used by Matthews (3) when he observed no change in the x-ray diffraction pattern of C.W.2 containing perhaps five percent of arsenic compounds. The report of Danby, Davoud, Everett, Hinshelwood and Lodge (29) refers to the production of arsenite and arsenate in a silver impregnated charcoal while Johnstone (30) reports the production of arsenious oxide in a dry charcoal under test.

The two specimens, CWSE-I-TE-I and C.W.2 containing the arsenic compounds were ground to a fine powder and the x-ray diffraction patterns obtained by Dr. Matthews. These patterns showed lines

additional to those characteristic of the impregnant. These are listed in Table 14 together with the lines to be expected from arsenic and its oxides.

TABLE 14

DIFFRACTION PATTERN OF CHARCOALS EXPOSED TO ARSINE

CWSE-I -TE-I	C.W.2	Copper	Cupric Oxide	Cuprous Oxide	Arsenic	As_2O_3	As_2O_5
3.24						3.18	3.21
2.88							
2.58			2.51			2.53	2.62
	2.47			2.45			
2.37			2.31				2.34
2.16						2.24	2.20
	2.14						2.18
				2.12		2.12	
2.09	2.09	2.08					2.10
2.03	1.97				2.04	1.95	2.02
	1.82	1.81	1.85		1.88		1.84
	1.74		1.70		1.77		1.77
							1.71
	1.58		1.57	1.51	1.56	1.59	
1.52	1.52		1.50			1.54	
	1.285	1.28	1.30	1.28	1.30		
			1.26		1.27		
	1.180		1.16		1.20	1.21	

The results show the probable presence of both arsenic and its oxides. The glass parts of the service time apparatus were coated with a black mirror of arsenic so that it seems possible that the charcoal might be coated similarly.

DISCUSSION

Since the investigations reported here were inconclusive and the apparatus has been dismantled or converted to other uses thus preventing further work along these lines, it is not proposed to discuss the subject exhaustively.

No new information has been obtained on the subject of the relationship of the impregnant or of the water content on the arsine service time.

That arsenic oxides appear to be the principal products of decomposition of arsine on the charcoal seems to be certain. It had been reported that arsine was adsorbed and desorbed (31) without decomposition in the absence of air. However the greater ease with which arsine decomposed to liberate the metal would lead one to expect that this type of reaction would be more prevalent when arsine is used than when nickel carbonyl is used. On the other hand the oxidation reaction of nickel carbonyl seems to be very rapid even on clean glass surfaces so that one would expect this reaction to predominate.

The differences in the ease of oxidation are shown by the fact that unimpregnated charcoals have essentially zero arsine service times showing that the catalytic action of the impregnant is necessary, while no appreciable differences were noted in the ability of unimpregnated and impregnated charcoals to catalize the oxidation of nickel carbonyl. The velocity of the oxidation reaction of nickel carbonyl is very great in either case.

The direct decomposition of nickel carbonyl or arsine to produce nickel or arsenic do not seem to be catalized by the charcoals.

The weight of the deposit on the American Whetlerite would indicate a greater adsorption of the arsine which might be used to infer that the American Whetlerite had a superior arsine service time under the experimental conditions used here.

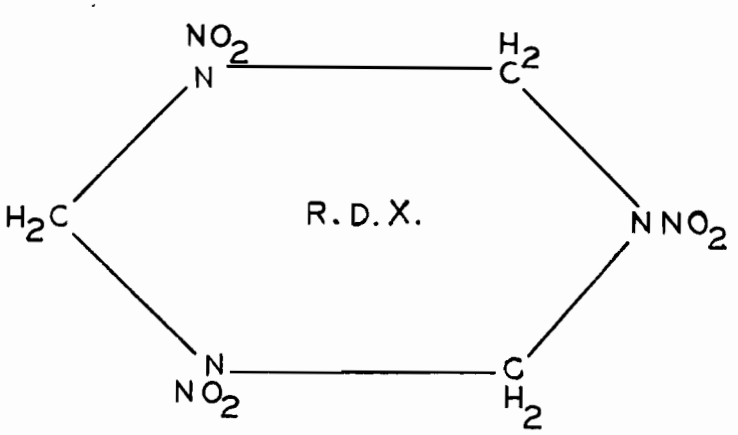
Part B

AN X-RAY INVESTIGATION OF H.M.X. CRYSTALS

under the supervision of

Dr. W. H. Barnes

Henning's original method involved the conversion of hexamine to hexamine dinitrate followed by nitrolysis of the dinitrate to R.D.X. in cold concentrated nitric acid. von Herz was able later to convert hexamine directly to R.D.X. without the isolation of the intermediate, hexamine dinitrate, and he was able to suggest the formula for R.D.X. which is still most probable.



A very extensive investigation of the reaction of nitric acid on hexamine was made by the Research Department at Woolwich Arsenal (see 33). Their work was not confined to increasing the yield and stabilizing the process, but included also a study of the nitration products of formaldehyde,

P_1 and P_2, which were responsible for the "fume-off". Continuous processes were developed at Woolwich and by Whitmore, and also a process by Wright to recover the formaldehyde as a by-product. The disadvantages of these processes were the large quantity of comparatively pure (95 to 100 percent) nitric acid required, and the loss of potential R.D.X. in the unused or destroyed formaldehyde.

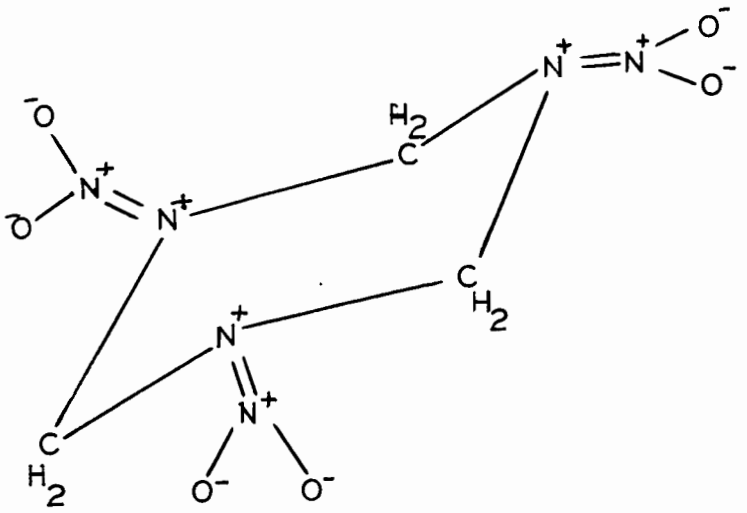
A new method was developed by Schiessler and Ross at McGill University which method involved the use of paraformaldehyde and ammonium nitrate heated to 70°C in acetic anhydride. The R.D.X. was precipitated by addition of water to the reaction mixture. The yields in this process were not good when calculated on a formaldehyde basis, but the reaction suggested that it should be possible to utilize the formaldehyde liberated in the nitrolysis process by such a method. This led to the Bachmann or Combination process. In this method hexamine or hexamine dinitrate, ammonium nitrate and nitric acid are allowed to react in an acetic acid - acetic anhydride medium. Very excellent yields, up to

ninety percent, have been obtained in this process calculating on the formaldehyde conversion, or carbon conversion. In this process there appeared for the first time the compound H.M.X. which proved to be a tetramer of the same unit of which R.D.X. is the trimer, and melted about 278°C. The structure of this compound was uncertain.

The work reported here is concerned with two distinct phases of the study of these explosives. The first is a study of the structure and x-ray diffraction patterns of H.M.X. crystals. The other began as a study of the mechanism of the Ross Reaction or McGill Process, a continuation of the work of A. Gillies (34), but when the mechanism of the Ross Reaction proved to be similar to that for the Bachmann Process, the latter became the main problem for investigation.

STRUCTURE OF R.D.X. AND H.M.X.

Present data on x-ray measurements (35) and dipole moments (36) indicate that R.D.X. is a six membered ring with an equilibrium existing between the chair and boat forms, the former predominating. The structure favoured also has the double bonds between the amino and nitro nitrogens.



Crystallographical studies of R.D.X. were made by Terpstra (37), Hultgren (38) and Cox (35). It is orthorhombic with cell dimensions and density as shown in Table 15.

TABLE 15

X-RAY DATA FOR R.D.X.

	Terpstra	Hultgren	Cox
a_o	11.64 A	11.5 A	11.52 A
b_o	13.25	13.2	13.16
c_o	10.80	10.6	10.64
density	1.77	1.83	1.83

(density determined by von Herz was 1.82)

The space group is Q_h^{15} (Pcab). There are eight molecules to the unit cell and there can be no symmetry within the molecule in the crystalline state. Further work by Cox awaits more favourable circumstances for its interpretation.

At the time the present investigations were begun there were no similar data on H.M.X. so that it was proposed to obtain information on H.M.X. analagous to that which existed for R.D.X. It was recognized that progress beyond that point would be too long and tedious to warrant such an investigation at this time. When most of the results had been obtained data for H.M.X. were reported by Cox (39) whose results checked those presented here very closely.

STRUCTURE OF H.M.X.

RESULTS

The Universal Photogoniometer was adjusted and mounted so that it could be used with the horizontal window of the x-ray tube. Unfiltered copper radiation was used, and the crystals were set optically and adjusted by x-ray methods.

While there was every reason to believe that H.M.X. differed from R.D.X. to a recognizeable extent it was considered of value to have comparison photographs of R.D.X. Therefore three Laue photographs, one along each of the principal axes with the other two respectively horizontal and vertical were obtained. These are shown in Figures 10 to 12.

When a good Laue photograph had been obtained along the a-axis the crystal was rotated through 90 degrees and a good setting along the b-axis obtained similarly. When the two good Laue photographs were obtained at 90 degrees apart the

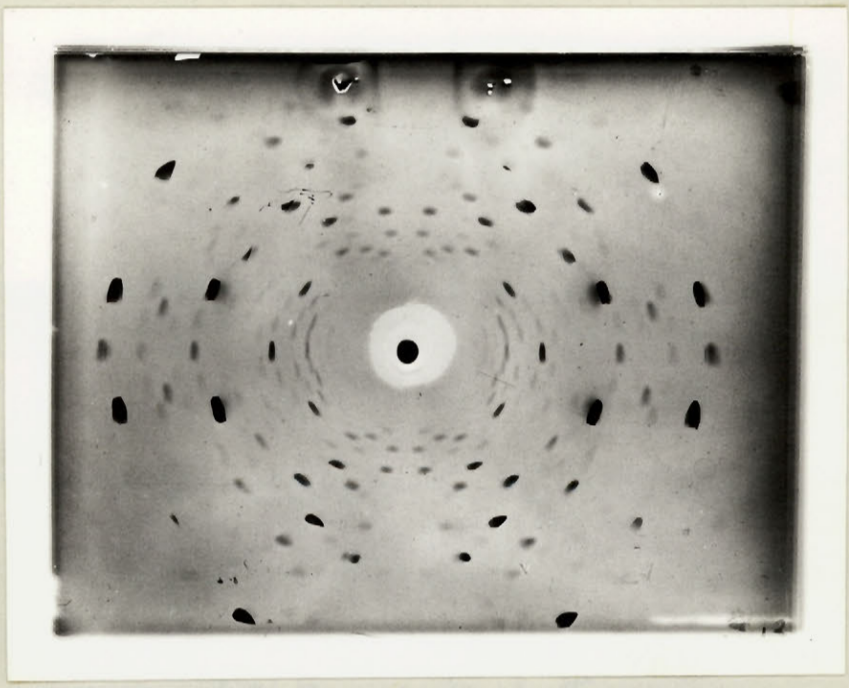


FIGURE 10 - Laue Photograph of R.D.X. Crystal, along a-axis, c-axis vertical. Copper Radiation. Crystal to Plate Distance 4.52 Centimeters.

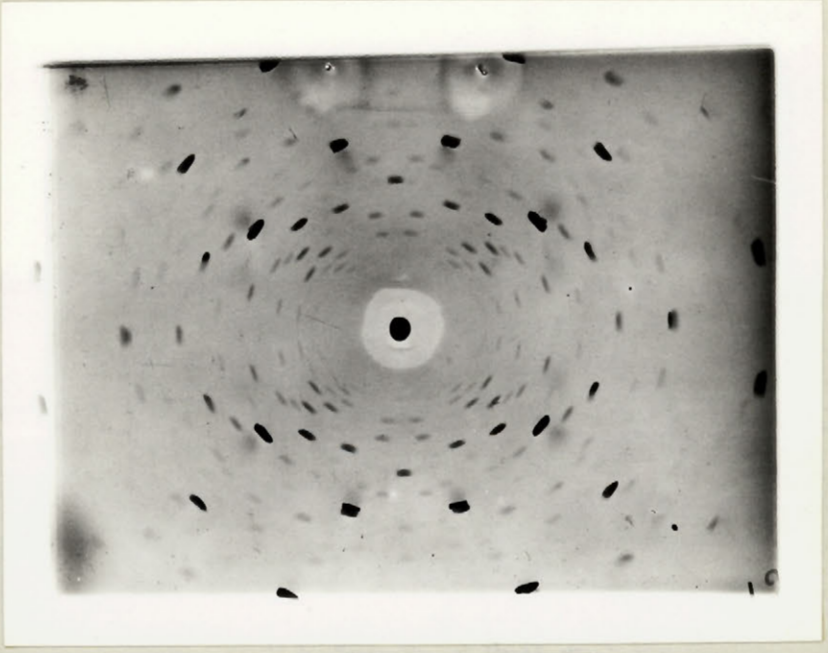


FIGURE 11 - Laue Photograph of R.D.X. Crystal, along b-axis, c-axis vertical. Copper Radiation. Crystal to Plate Distance 4.52 Centimeters

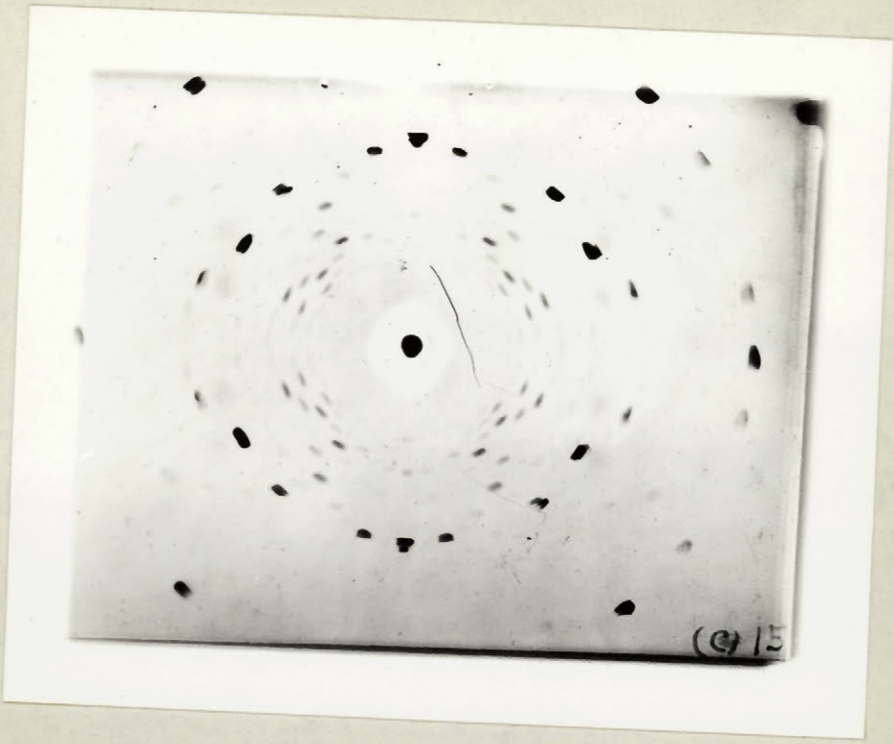


FIGURE 12 - Laue Photograph of R.D.X. Crystal, along c-axis. Copper Radiation. Crystal to Plate Distance 4.52 Centimeters.

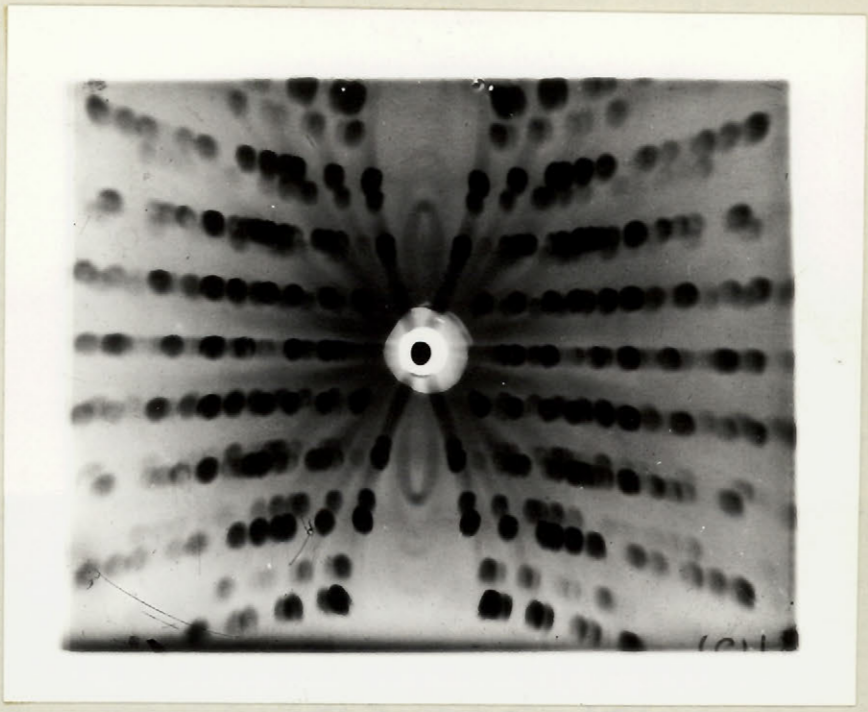


FIGURE 13 - Rotation Photograph of R.D.X. Crystal about c-axis. Copper Radiation. Crystal to Plate Distance 4.52 Centimeters.

crystal was rotated about the c-axis to obtain the rotation picture. This is shown in Figure 13, previous page. Calculations of the value of c_o from the rotation photograph gives a value of 10.64 Angstroms in exact agreement with the work of Cox.

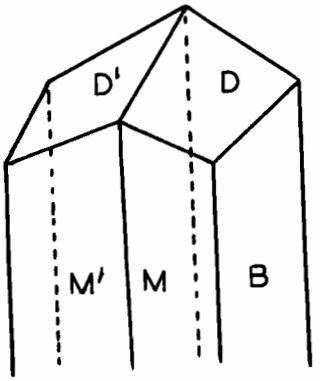
Small but satisfactory crystals of H.M.X. were prepared by J. T. Edward. The H.M.X. was produced by using a procedure which gave a high proportion of that product in the yield followed by destruction of the R.D.X. in boiling one percent solution of sodium carbonate. The H.M.X. was recrystallized from acetone - water solution from which the acetone evaporated slowly at room temperature. This yielded crystals which have been assumed to be of the "beta" form.

The crystals were monoclinic with a beta angle of about 100 degrees. Laue photographs taken along what was presumed to be the three principal axes fully confirmed this. Dr. Graham determined the angles between the faces and his data are summarized in Table 16, in which the lettering is

identical with that used in the diagram of the H.M.X. crystal. The crystal lies in the holohedral class of maximum symmetry.

TABLE 16

CRYSTALLOGRAPHY OF H.M.X.

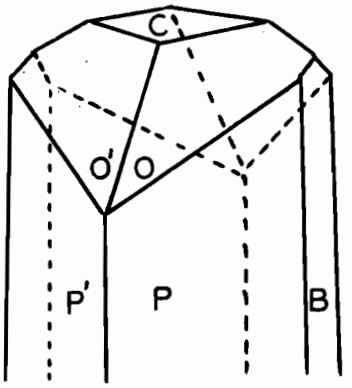


MM'	66° 40'
MB	56° 40'
DD'	60° 00'
BD	60° 00'

For comparison the similar data obtained by Terpstra for R.D.X. is included and given in Table 17.

TABLE 17

CRYSTALLOGRAPHY OF R.D.X.



BP	29° 39'
PP'	120° 42'
CO	50° 57'
BO	59° 8'
OO'	61° 42.5'

Laue photographs of H.M.X. crystals are shown in Figures 14 to 17. The Laue photograph along the a-axis with the b-axis horizontal is shown in Figure 14. It is characterized by a vertical plane of symmetry but no horizontal plane of symmetry. The Laue photograph along the b-axis with the c-axis vertical, Figure 15, shows only a center of symmetry as does the Laue along the b-axis with the a-axis vertical, Figure 16. The Laue photograph along the c-axis with the b-axis vertical shows a horizontal plane of symmetry, Figure 17. These agree with the

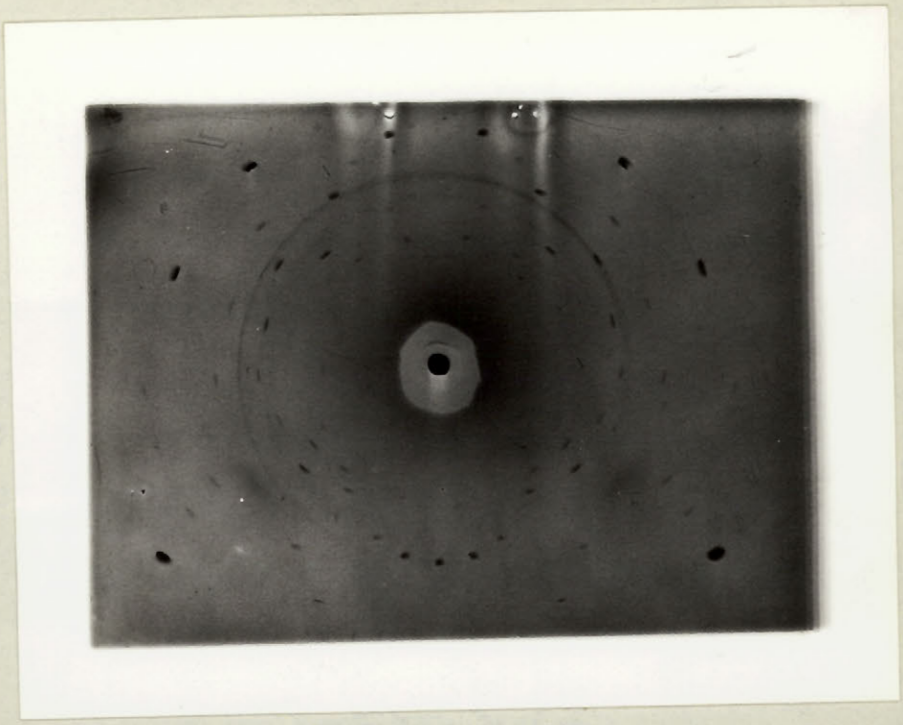


FIGURE 14 - Laue Photograph of H.M.X. Crystal, along a-axis with b-axis vertical. Copper Radiation. Crystal to Plate Distance 4.52 Centimeters.

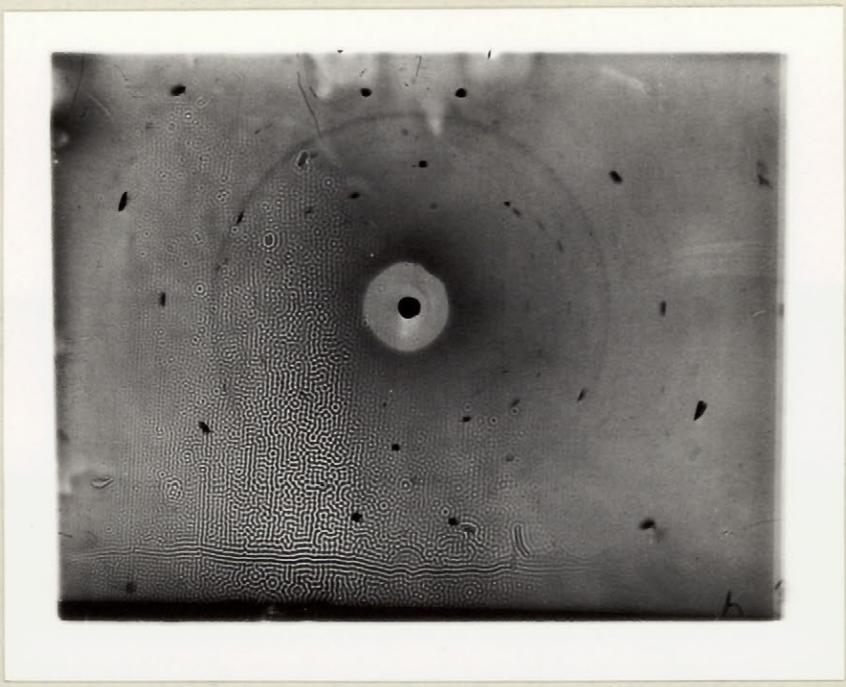


FIGURE 15 - Laue Photograph of H.M.X. Crystal, along b-axis with c-axis vertical. Copper Radiation. Crystal to Plate Distance 4.52 Centimeters.

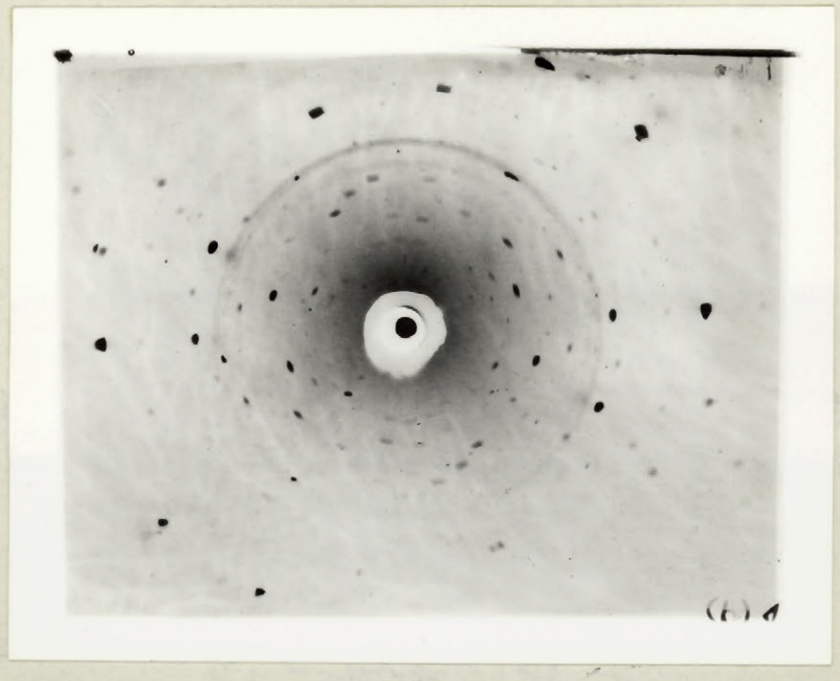


FIGURE 16 - Laue Photograph of H.M.X. Crystal along b-axis with a-axis vertical. Copper Radiation. Crystal to Plate Distance 4.52 Centimeters.

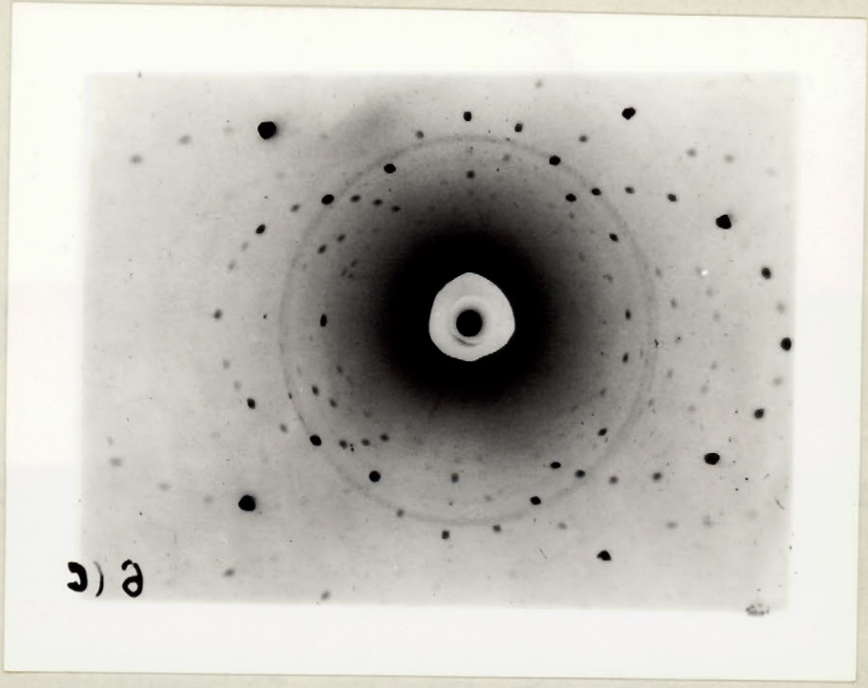


FIGURE 17 - Laue Photograph of H.M.X. Crystal along c-axis with b-axis vertical. Copper Radiation. Crystal to Plate Distance 4.52 Centimeters.

fact that the crystal is monoclinic with a plane of symmetry enclosing the b- and c-axes and a center of symmetry.

Adjustment of the crystal for rotation photographs was difficult. The initial settings were made optically, then Laue photographs were taken. Calculating from the distances from the edge of the film, or the distances of the spots from the center or axis of symmetry based on two Laue photographs taken along one axis and at 90 degrees from that axis, it was possible to correct the settings on the arcs and circle to get reasonably good settings for rotation photographs. The long slim nature of the crystals made the spots rather large and ill-shaped for accurate measurement but the following results were obtained:

The rotation photographs about the a-, b- and c-axis respectively are shown in Figures 18, 19 and 20. The average values of a_o, b_o and c_o calculated from these photographs together with the deviations are shown in Table 18.

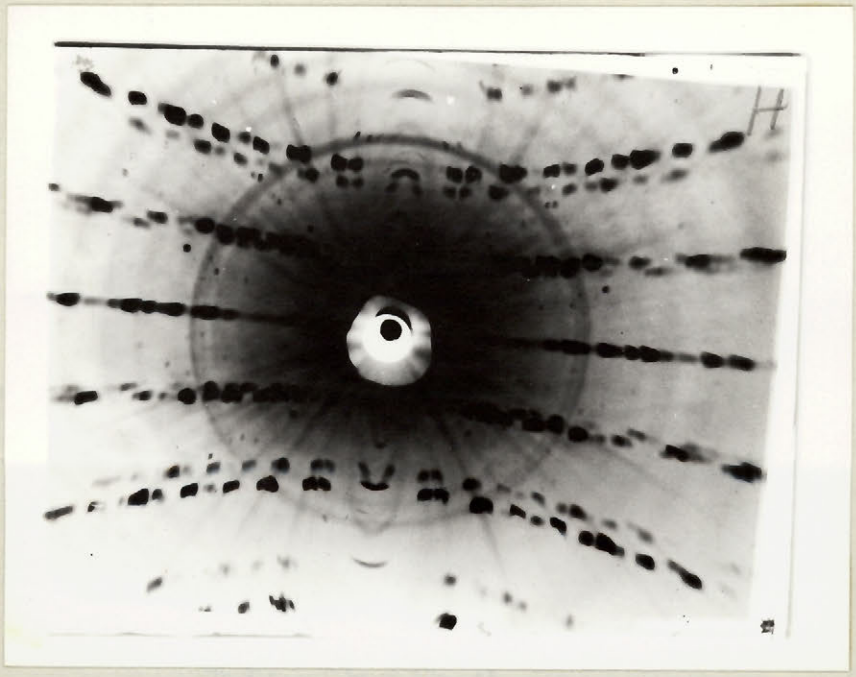


FIGURE 18 - Rotation Photograph of H.M.X. Crystal, about a-axis. Copper Radiation. Crystal to Plate Distance 4.52 Centimeters.

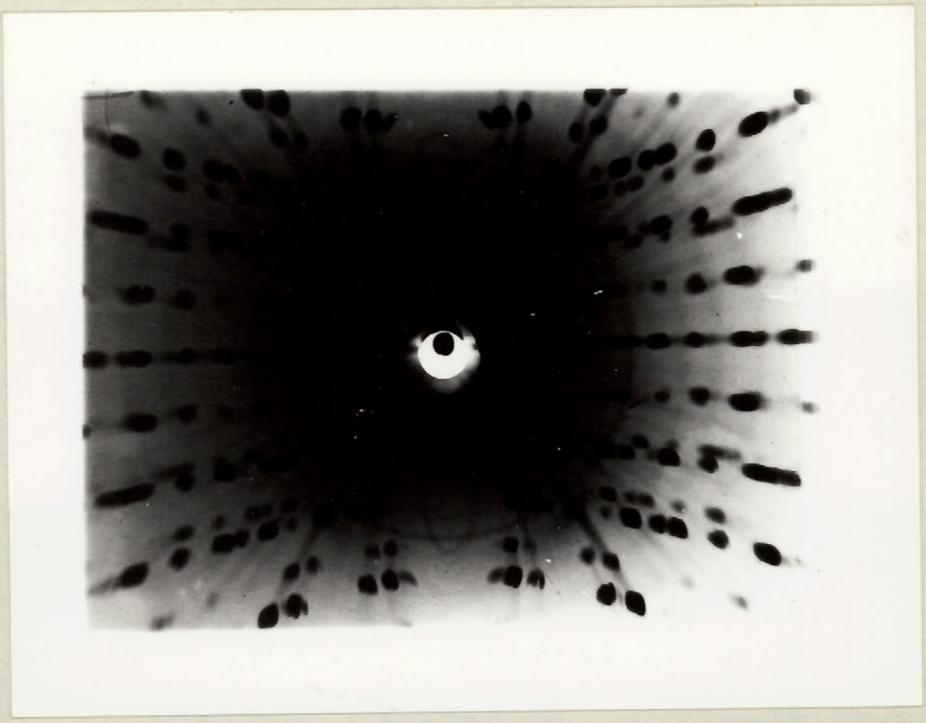


FIGURE 19 - Rotation Photograph of H.M.X. Crystal, about b-axis. Copper Radiation. Crystal to Plate Distance 4.52 Centimeters.

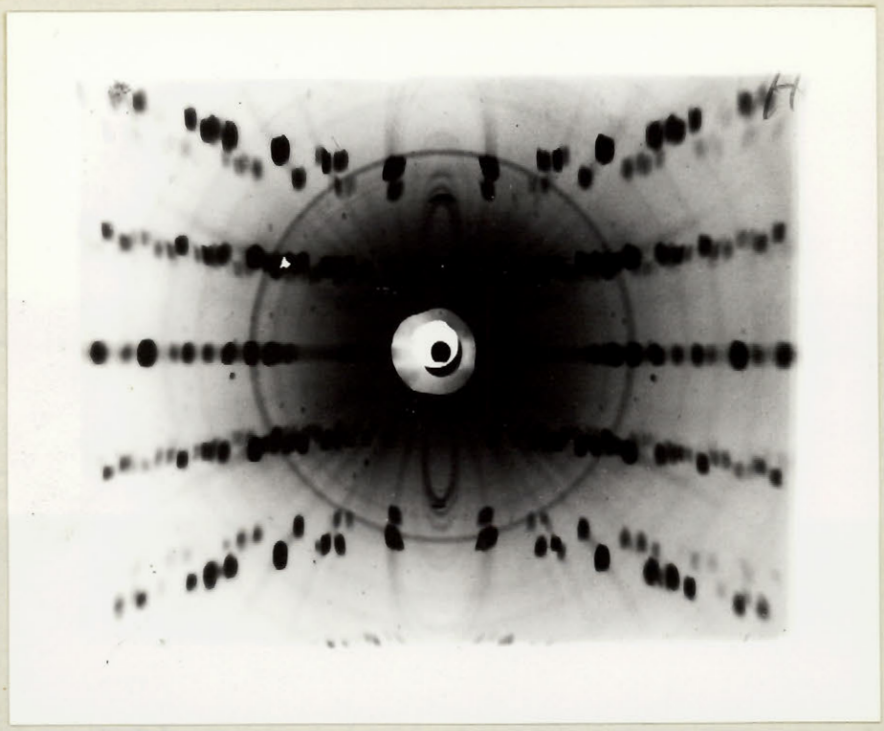


FIGURE 20 - Rotation Photograph of H.M.X.
Crystal about c-axis. Copper Radiation.
Crystal to Plate Distance 4.52 Centimeters.

TABLE 18

DIMENSIONS OF UNIT CELL OF H.M.X.

a_o	7.35 ± 0.01 A
b_o	11.27 ± 0.02 A
c_o	6.50 ± 0.02 A

To calculate the number of molecules per unit cell it was necessary to know the molecular weight, the density, and the beta angle. The experimental molecular weights seem to indicate that H.M.X. is a tetramer of the unit of which R.D.X. is a trimer and this was used to calculate a theoretical molecular weight of 296 grams per mole.

The density was determined by suspending good crystals of H.M.X. in a mixture of methylene iodide and benzene and adjusting the specific gravity of the mixture by adding benzene or methylene iodide until the crystals floated suspended in the mixture for an appreciable time without showing any tendency to rise or fall. The specific gravity of the medium was determined then in a pycnometer calibrated previously with water at a known temperature. The results are shown in Table 19.

TABLE 19

DENSITY OF H.M.X.

1	1.8923
2	1.9006
3	1.9054
4	1.9005
average	1.900 ± 0.004

Attempts to measure the beta angle using the single circle photogoniometer were discouraging. The first accurate estimate was made by preparing the gnomonic projection of the Laue photograph shown in Figure 16. This gnomonic net is shown in Figure 21. The construction and theory of this method of analysis may be found in Wyckoff (40). Suffice to say that each point on it represents the intersection of the normal of the plane responsible for the corresponding spot on the Laue photograph, projected on the plane of the net at a distance from the crystal equal to the crystal to plate distance. The lines drawn then join points whose indices are the same in one co-ordinate other than the b for which it is constant and equal to one for a projection of a Laue photograph taken along the b-axis. These lines which are parallel for a properly drawn net from a perfect Laue photograph

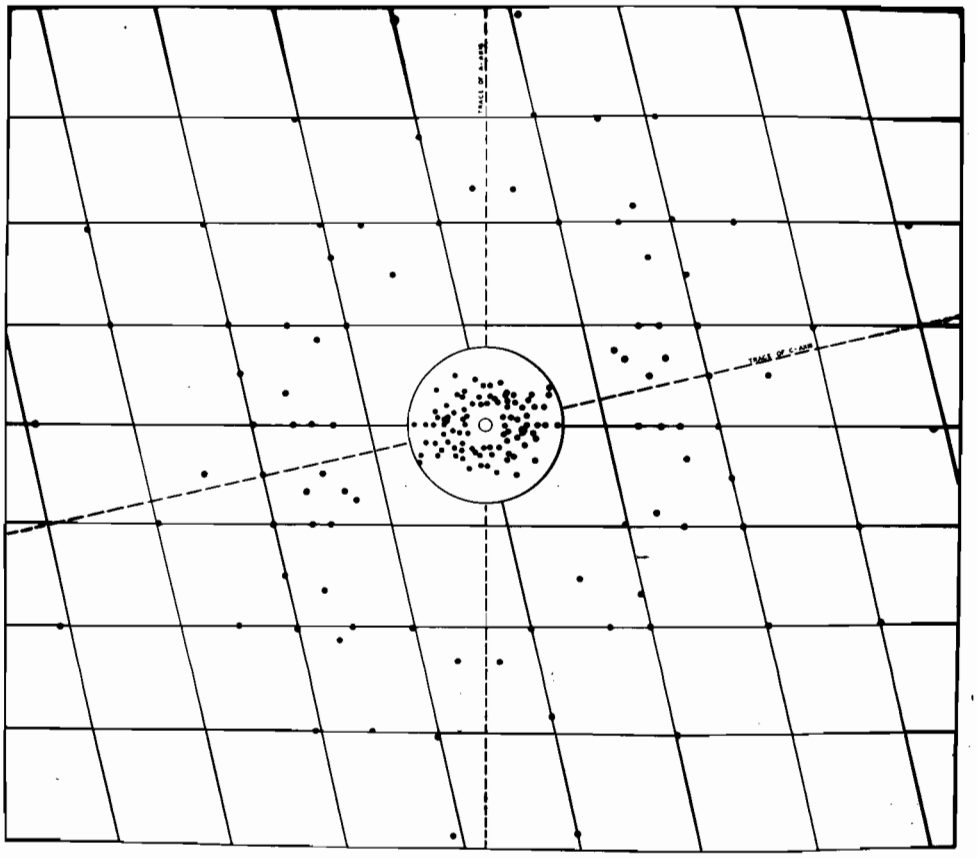


FIGURE 21 - Gnomonic Projection of the Laue Photograph shown in Figure 16. H.M.X. Crystal along the b-axis with the a-axis vertical.

make angles with each other equal to the beta angle. Using a protractor the beta angle was measured at many intersections and the angle was found to be 103°. With these data and the fact that the a-axis was vertical, the trace of the c-axis was drawn in as shown.

Another property of this projection is that the distances along the traces of the axes between consecutive intersections with the net are proportional to the ratios of b/c and b/a. When the distance along the trace of the a-axis is divided by the crystal to plate distance it gives the ratio of b/a. Similarly the distances along the trace of the c-axis give the ratio of b/c when divided by the crystal to plate distance. If one assumes the values of a_o, b_o and c_o as determined from the rotation photographs then one can calculate the values of these ratios. These are shown in Table 20 together with the values obtained from the gnomonic projection.

TABLE 20

RATIO b/a AND b/c FOR H.M.X.

	calculated	from projection
b/a	1.533	1.520
b/c	1.734	1.734

The agreement is very good and indicates that the net as drawn is correct and hence that the beta angle is correct. Also conversely the unit cell must be of the dimensions found from the rotation photographs and not some multiple of these in which the alternate orders of the layer lines have been suppressed.

The volume of the unit cell was calculated and from the density and molecular weight there must be two molecules to the unit cell. The investigations were at this stage when the results of Cox (39) became available. It was decided to discontinue the study since its aim to determine the space group was attained by Cox who reports it to be C^5_{2h}. His other data are tabulated in Table 21 and compared with the present data.

TABLE 21

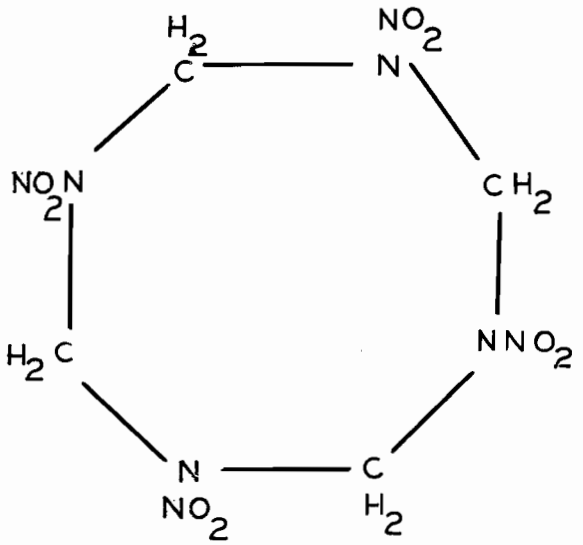
COMPARISON OF X-RAY DATA FOR H.M.X.

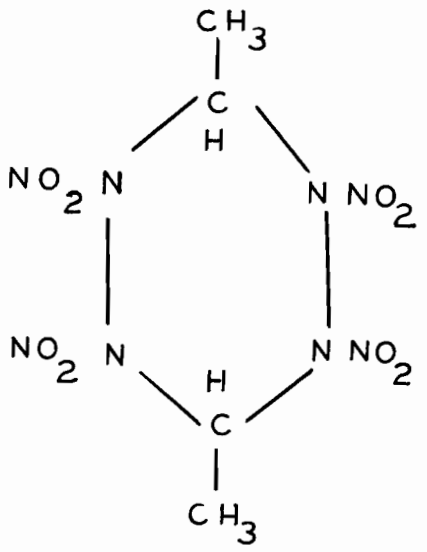
	Present Data	Cox' Data
density	1.91	1.90
a_o	7.32 A	7.35 A
b_o	10.93 A	11.27 A
c_o	6.50 A	6.50 A
beta angle	103^o	103^o 04'
b/a	1.533	1.493
b/c	1.734	1.683

The deviations between the results may not be significant due to the experimental errors involved.

DISCUSSION

From the space group as determined and the fact that there are two molecules to the unit cell it is evident that the molecule itself must have a center of symmetry in the crystalline state. Two structures were proposed by Cox based on this, of which the more probable and the accepted structure is the eight-membered ring. This and the other structure may be represented:





Both of these structures satisfy the requirements that the molecule must have a center of symmetry.

The other data of this investigation were fact-finding and need no discussion. The molecular weight must be considered to be 296 if the empirical analyses are correct.

Part C

THE KINETICS OF THE REACTIONS TO PRODUCE R.D.X.

under the supervision of

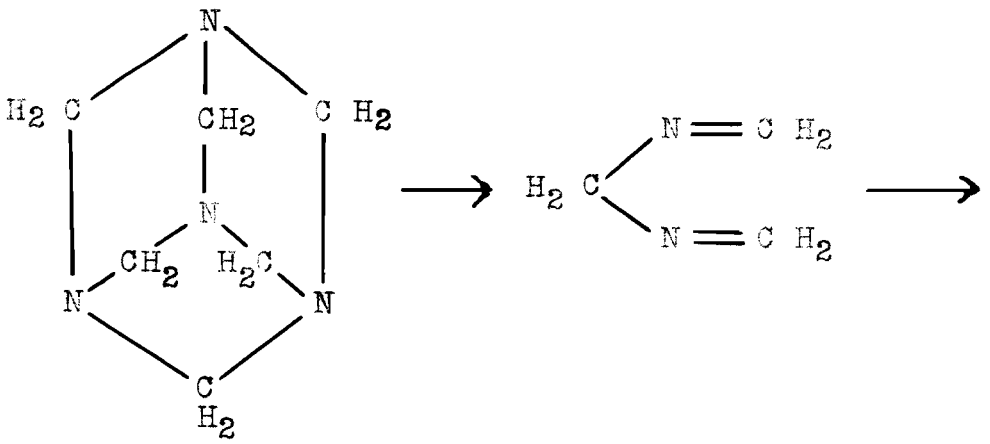
Dr. C. A. Winkler

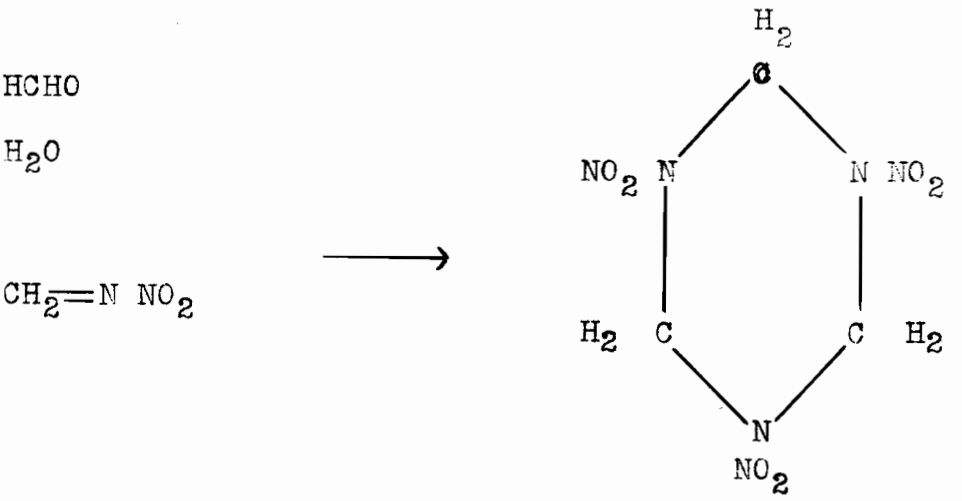
KINETICS OF THE PRODUCTION OF R.D.X.

INTRODUCTION

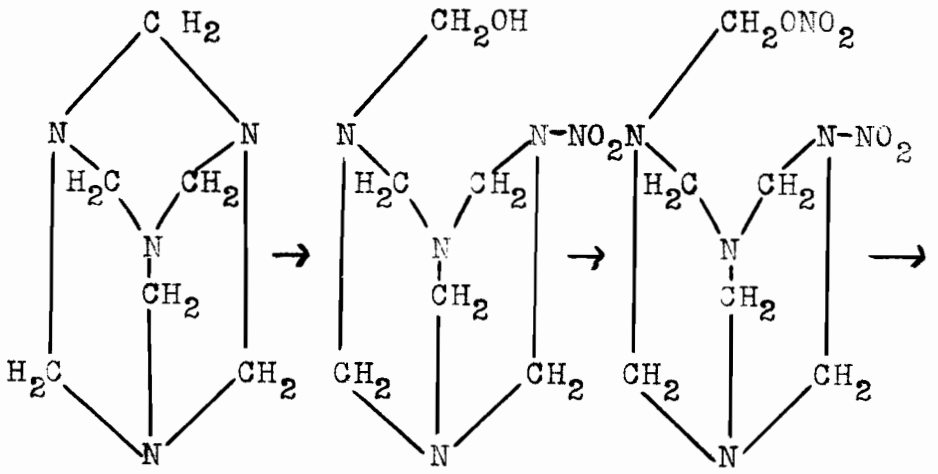
The mechanisms proposed by which hexamine is converted to R.D.X. by direct nitrolysis using absolute nitric acid are two in number. It is obvious from a comparison of the formulae and structures of hexamine and R.D.X. that fundamental and far reaching changes are made in the molecules.

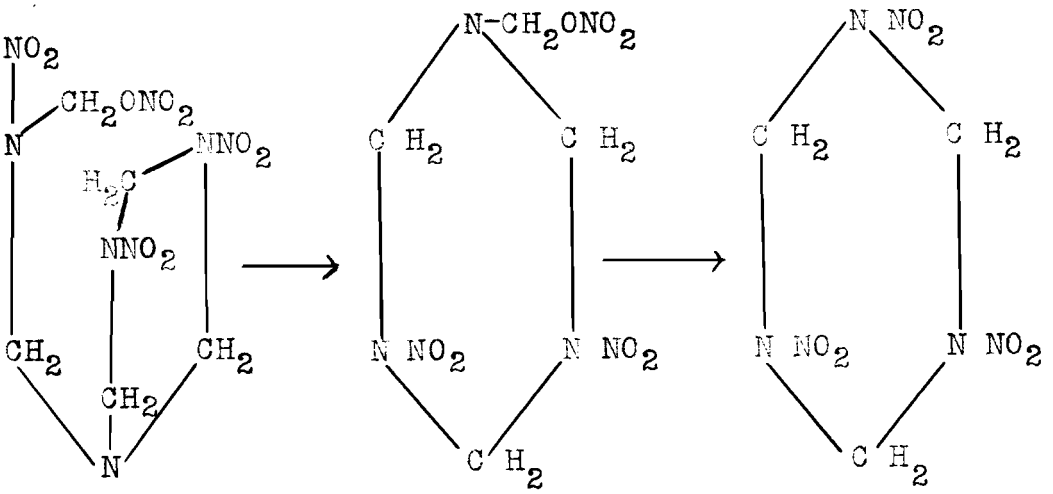
The first mechanism is the depolymerization hypothysis. By this the hexamine is broken down into simpler units which then rebuild to form R.D.X. This is illustrated below:



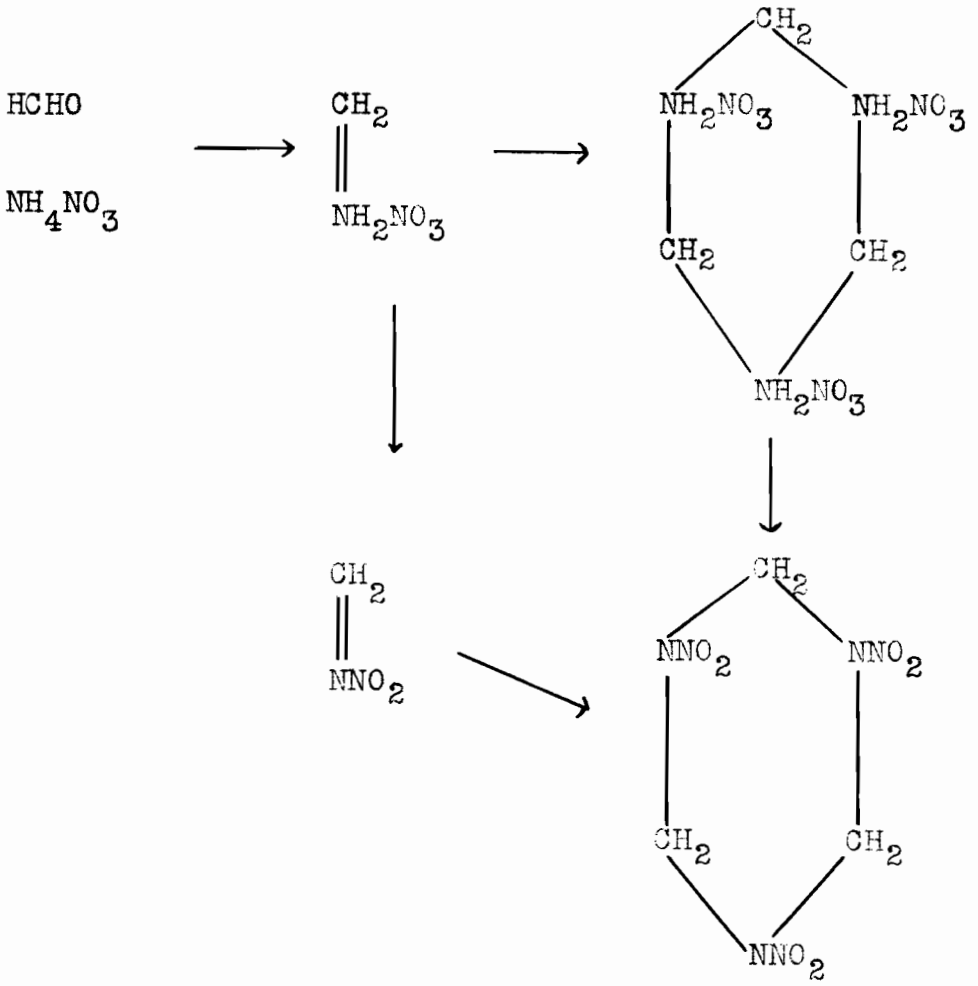


The second mechanism is the ring hypothysis by which the hexamine remains intact but loses its "center" in a stepwise fashion with the conversion of the amine groups to nitramine groups. This may be illustrated in principle as below:





The mechanisms by which ammonium nitrate and paraformaldehyde were condensed in acetic anhydride to give R.D.X. were suggested to be very much like the depolymerization mechanism for the nitrolysis reaction. It was suggested that the depolymerized formaldehyde condensed with the ammonium nitrate in a molar ratio and gave an unsaturated base. This base either polymerized first and then dehydrated to produce R.D.X., or was dehydrated first and then trimerized to give R.D.X. The dehydration might involve an acetylation. The mechanisms are outlined below:



When the combination process was developed it was recognized that it could consist essentially of the other two processes carried on together. Thus the mechanism by which hexamine was converted to R.D.X. was suggested to be the direct action of the nitric acid in the acetic anhydride upon the hexamine. This could occur by either the depolymerization or

ring hypothyses. Then the extra formaldehyde combined with the ammonium nitrate to yield R.D.X. by the Ross Reaction, by whichever of the suggested mechanisms, if any, might be correct.

The preliminary work on the mechanism of the Ross Reaction may be summarized briefly. In the reaction between paraformaldehyde and ammonium nitrate in acetic anhydride to give R.D.X. it is evident that there must be intermediates formed, and these might be evident by the presence of an induction period. This was found in fact, and is quite long when the reaction is carried out at 40°C. While not all of the formaldehyde could be accounted for in the unused and used formaldehyde, no other product was isolated to account for the discrepancy. The induction period decreased as the temperature was raised so that it was comparatively short at the optimal temperature of 70°C.

Gillies (34) was able to show that the intermediate whose formation was responsible for the induction period was in solution in the acetic

anhydride and was formed only in the presence of all three reagents. When fresh acetic anhydride lengthened the induction period it was suggested that the acetic acid present in the older material in some way lowered the induction period. Investigation of this point showed that small amounts of acetic acid added to the anhydride shortened the induction period and larger amounts appeared to increase the rate of conversion of the intermediate into R.D.X. Fresh paraformaldehyde reduced the induction period and increased the rate of conversion to R.D.X. With gaseous formaldehyde the induction period was reduced suggesting that part of the induction period at least was due to the depolymerization of the paraformaldehyde. Trichloroacetic acid seemed to reduce the induction period when this acid was added to the anhydride, but hydrochloric and nitric acids did not. In the latter two cases no R.D.X. was produced.

His study of the formation and decomposition of the intermediate prepared in acetic anhydride led Gillies to estimate the energy of activation of the conversion of this intermediate into R.D.X. to be between 17 and 20 kilocalories per mole.

The intermediate was prepared in acetic acid medium in later work and as thus prepared the induction period for the conversion to R.D.X. was eliminated. The energy of activation for this conversion was calculated to be 19.4 kilocalories per mole.

It was observed that propionic anhydride would replace acetic anhydride in the process, but that the former was much less effective than the latter.

APPARATUS

The apparatus was all of standard design and simple so that most of it will be self-evident from the procedures employed.

The reactions were carried out in 125 milliliter Erlenmeyer flasks which were shaken in a constant temperature bath. Unless otherwise stated the temperature employed was 35°C and the temperature was controlled to better than 0.1°C. On completion of the reaction water was added, the mixture brought to boiling and allowed to boil for five minutes after which it was cooled and diluted to the neck of the flask, that is to 125 milliliters.

After standing for several hours the solids were filtered off with suction using sintered - glass ware and the solids dried at 100°C for several hours after which the weight was obtained.

Melting points were obtained using a double oil bath and removable capillaries. The melting points are all uncorrected.

EXPERIMENTAL

THE ROSS REACTION OR McGILL PROCESS

The investigation of the kinetics and mechanism of the McGill Process was begun by utilizing what might be called a two-step process. The intermediates were prepared in some solvent such as acetic acid, nitromethane or petroleum ether. This was accomplished by shaking ammonium nitrate and paraformaldehyde in an appropriate amount of the solvent until the maximal amount of intermediate had formed. To this solution was added acetic or propionic anhydride, or such other dehydrating agents as might be under test. The amount of R.D.X. produced under the conditions laid down was then determined. The R.D.X. included all "water-insolubles" so that the values as obtained must be considered to include the weight of possible impurities.

An insoluble intermediate which was later identified as hexamine dinitrate will be referred to as such even in those investigations in which it was not in fact isolated from the mixture.

EFFECT OF THE RATIO OF PARAFORMALDEHYDE TO AMMONIUM NITRATE

(a) Effect on the Yield of R.D.X.

The effect of the ratio of ammonium nitrate to paraformaldehyde on the yield of R.D.X. has been studied using two solvents, acetic acid and nitromethane, in which to prepare the intermediates. The ammonium nitrate and paraformaldehyde were shaken in the appropriate solvent for 20 to 22 hours at 35°C. Then acetic anhydride was added in volume equal to the volume of the solvent used for preparing the intermediate and representing normally three moles for each mole of formaldehyde. The reaction was allowed to proceed for two hours and the yield of R.D.X. determined by stopping the reaction with water, bringing the mixture to the boiling point and boiling for five minutes, cooling and diluting to precipitate the R.D.X. which was later filtered off and weighed. The results are shown in Figure 22. There the yield of R.D.X. calculated as a percentage of the potential carbon conversion is plotted against the mole ratio of ammonium nitrate to formaldehyde.

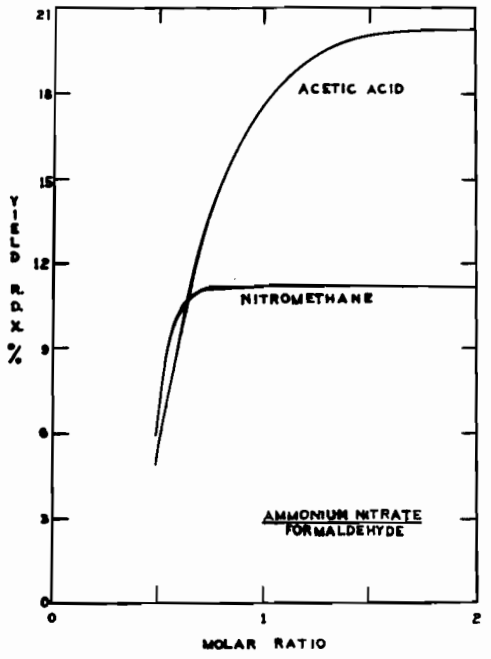


FIGURE 22 - Effect of the Ratio of Ammonium Nitrate to Formaldehyde on the yield of R.D.X. at 35°C.

When acetic acid is used as solvent in which to prepare the intermediate it can be seen that above a mole ratio of 1.0 the percentage conversion of the formaldehyde to R.D.X. is practically constant. Thus the addition of further ammonium nitrate tending to raise the ratio does not force the reaction beyond a certain limit determined by the formaldehyde present. On the other hand the percentage yield should fall to zero only when the mole ratio reaches zero. It appears to reach zero before that stage is reached, that is the efficiency of the conversion of the formaldehyde to R.D.X. falls off faster than it is limited by the amount of ammonium nitrate present.

When nitromethane is used as the solvent in which to prepare the intermediates the yield of R.D.X. is constant over a wider range of mole ratios. Above a ratio of 0.62 the further increase in the amount of ammonium nitrate does not increase the yield while a decrease in the ratio causes the yield to fall off very sharply just as in the case of the intermediates prepared in acetic acid.

From work to be reported later it would seem that the amount of ammonium nitrate present as such affects not only the yield but rate of production of R.D.X. from the intermediate also. Thus the flat portion of the curves represents the efficiency of the conversion of the intermediates to R.D.X., the amount of intermediate formed per mole of formaldehyde being constant. The lower ratios of ammonium nitrate to formaldehyde give lower yields because as the ammonium nitrate disappears its effect on the conversion of the intermediates disappears; in the absence of ammonium nitrate these intermediates are not converted to R.D.X.

(b) Effect on the Visible Course of the Reaction

The course of the reaction between paraformaldehyde and ammonium nitrate in acetic acid medium varies in appearance according to the ratio of the reactants, and also the appearance after the acetic anhydride is added is different.

If the ratio of formaldehyde to ammonium nitrate is one mole to two (0.6 grams of paraformaldehyde, 3.2 grams of ammonium nitrate in six

milliliters of glacial acetic acid) the reaction follows the following course: The cloudiness due to the paraformaldehyde disappears gradually in about three hours to give a clear solution with the excess ammonium nitrate on the bottom of the flask. As shaking is continued there is no change observed for another two hours or so, then the mixture becomes cloudy very quickly. This precipitate always appears for this mole ratio of reactants and persists even if the mixture is shaken for several days longer, but seems to fade slightly. This white precipitate was later identified as hexamine dinitrate.

When acetic anhydride is added to this mixture it clears up within a few minutes and then the mixture clouds again with precipitated ammonium nitrate.

If on the other hand the ratio of formaldehyde to ammonium nitrate is one mole to one the mixture generally fails to become cloudy again after the initial clearing up. Upon the addition of acetic

anhydride approximately the same percent yield of R.D.X. is produced as shown from Figure 22, and the R.D.X. is produced at the same rate as with the larger ratio of ammonium nitrate to formaldehyde as will be shown in Figure 23. Less ammonium nitrate is precipitated by the acetic anhydride.

If the ratio of formaldehyde to ammonium nitrate is two moles to one then the mixture again fails to become cloudy after the initial clearing up. No ammonium nitrate is precipitated on the addition of acetic anhydride and the amount of R.D.X. produced is much reduced in yield from that expected from the amount of formaldehyde or ammonium nitrate present as can be seen from Figure 22.

The course of the reaction when nitromethane, hexane or heptane are used as the solvent in which to prepare the intermediate resembles the second example when acetic acid is used. The solution fails to become cloudy after the initial clearing up, and the excess ammonium nitrate remains on the bottom of the flask overlayered with droplets of aqueous

solution. The addition of acetic anhydride causes the water droplets to disappear and a very dense precipitate to appear, clouding the mixture and adhereing to the bottom of the flask. This precipitate is water soluble and may consist largely of ammonium nitrate.

The interesting fact which can be observed directly is the appearance of the precipitate after the initial clearing up of the mixture when the molar ratio of formaldehyde to ammonium nitrate is one to two. This precipitate of hexamine dinitrate also appears in those mixtures whose molar ratios are as much as one to one and a quarter, and very rarely when the ratio is one to one. The precipitate seems to be more easily deposited in the presence of ammonium nitrate or possibly of nitrate ion.

(c) Effect on the Rate of Conversion of Intermediate to R.D.X.

When the intermediate was prepared at 35°C in glacial acetic acid using two moles of ammonium nitrate to one of formaldehyde the precipitate of hexamine dinitrate formed but was not formed as a

rule, if the ratio was one to one. It was of interest to determine whether the rate of conversion of the intermediate to R.D.X. differed on this account, that is to determine whether the same intermediate was involved. The results are shown in Figure 23.

These data show that while the initial rate is virtually the same, there is a slightly lower final yield for the lower ammonium nitrate to formaldehyde ratio. This falling off of yield and rate is attributed to the disappearance of ammonium nitrate the presence of which is necessary for the production of R.D.X. and the concentration of which greatly affects the rate of conversion of hexamine dinitrate to R.D.X. as will be shown in a later section.

Taking this into account it is evident that there can be little or no fundamental difference in the two reactions unless the rates at 35°C were fortuitously very nearly equal. It is concluded that the appearance of the hexamine dinitrate as a precipitate need not occur but that under certain experimental conditions it may remain in solution.

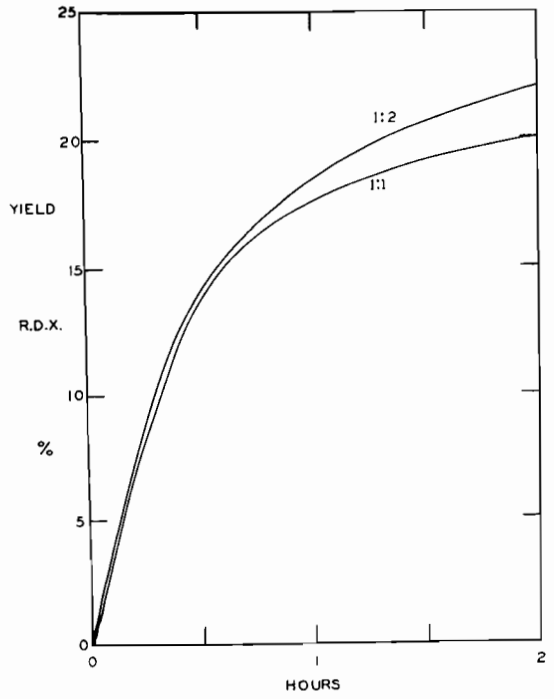


FIGURE 23 - Effect of the Ratio of Formaldehyde to Ammonium Nitrate on the Rate of Conversion and Yield of R.D.X. from the Intermediates Prepared in Glacial Acetic Acid at 35°C.

SEPARATION AND IDENTIFICATION OF HEXAMINE DINITRATE

If paraformaldehyde and ammonium nitrate are shaken for various lengths of time at 35°C in glacial acetic acid before acetic anhydride is added and the reaction to produce R.D.X. allowed to proceed for two hours, the yield of R.D.X. is that shown in Figure 24, upper curve. This shows the yield of R.D.X. plotted as a function of the time for which the ammonium nitrate and paraformaldehyde are shaken in the acetic acid before the anhydride is added. On the other hand if the mixtures are filtered before the anhydride is added to the filtrate then the yield of R.D.X. is that shown in the lower curve. The solids removed by filtration do not give R.D.X. with acetic anhydride by themselves except those removed during the first few hours which are essentially ammonium nitrate and paraformaldehyde and hence would produce a little R.D.X. in the two hour period with acetic anhydride at 35°C.

Thus it is evident that the process of filtering markedly lowered the yield of R.D.X. if

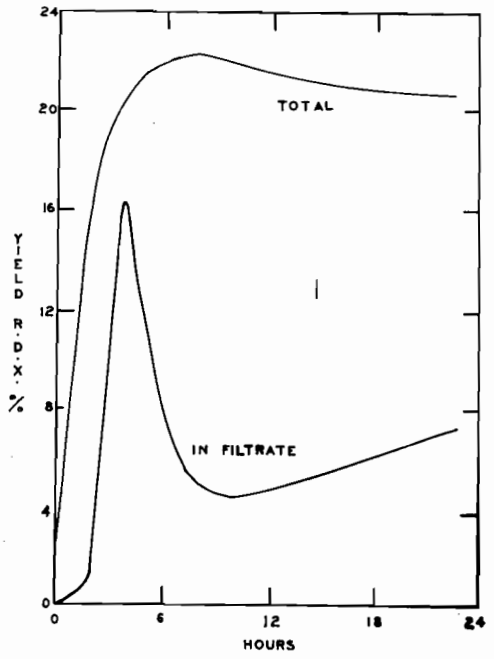


FIGURE 24 - Yield of R.D.X. from Unfiltered and Filtered Preparations of Intermediate.

the filtration were carried out after the solids had been shaken for about five hours in the glacial acetic acid, that is after the appearance of the precipitate of hexamine dinitrate, as it was later identified to be. This suggested that the intermediate in the Ross Reaction must be among the solids filtered off, or else that the mere mechanical separation of solid from liquid by suction filtration had removed something that was volatile or labile. That this latter possibility was not so may be seen from Table 22.

TABLE 22

EFFECT OF FILTERING INTERMEDIATE

Unfiltered	19.9	percent	yield
Filtrate	5.5	"	"
Solids Returned to Filtrate	17.2	"	"
Solids Returned to Activated Filtrate	27.7	"	"

The activation of the filtrate involves the addition of acetic anhydride to the filtrate before the solids are returned to it, and this will be discussed in a later section.

While there is a slight reduction in R.D.X. yield when the solids are filtered off and then returned to the filtrate it is of such a small magnitude that it could be more than accounted for by losses during handling. Thus it must be concluded that the removal of the solids results in a genuine loss in the R.D.X. producing power of the mixture and that the solids must contain an essential intermediate in the Ross Reaction.

Only two solids were known to be present on filtering, excess ammonium nitrate and the white precipitate which came down after the ammonium nitrate and paraformaldehyde had been shaken together for five hours.

The most satisfactory method of separating the ammonium nitrate and the intermediate was found to be as follows: Sixteen grams of ammonium nitrate and three grams of paraformaldehyde were shaken at 35°C in 30 milliliters of glacial acetic acid for about five hours. During that time the mixture clears up and then becomes cloudy again with the precipitated intermediate. A further three grams of paraformaldehyde

are added to dissolve the remaining ammonium nitrate and the shaking continued for another three to five hours at 35°C. After this period the precipitates from six such batches are filtered off, sometimes washed with a small amount of cold glacial acetic acid but usually just washed with two or three portions of acetone sufficient to cover the precipitate. The precipitate is sucked dry and dried in a vacuum descicator. Heating the material at 100°C for several hours destroys it. The crude yield is about 24 to 26 grams, about 50 percent.

In all of the experiments in the study of the Ross Reaction except those involving the analyses for the identification of the intermediate the crude material was used as removed. This crude material melts from 154° to 164°C uncorrected, with about a two or four degree melting range about the melting point.

Some of the material was recrystallized by Pickard using glacial acetic acid as solvent and the material melted quite sharply at 161°C corrected. The melting point was the same when mixed with

hexamine dinitrate prepared by Friedman. Pickard showed that there were no acetyl groups, and that there were two nitrate groups.

Elemental analysis gave the following data, Table 23.

TABLE 23

ANALYSIS OF INTERMEDIATE

	Intermediate*		Hexamine Dinitrate
Carbon	27.4	27.5%	27.1 %
Hydrogen	5.3	5.4	5.3
Nitrogen	30.7	30.8	31.6
Oxygen			36.1

It is evident that the material has the same empirical formula as hexamine dinitrate.

The solubilities of the two materials are similar: the intermediate is very soluble in water,

---

*Appreciation is expressed to Dr. G. F. Wright of the University of Toronto for these analyses.

ethanol, methanol, glycerine and pyridine. It is slightly soluble or insoluble in the following solvents either cold or boiling: acetone, acetic acid, acetic anhydride, ethyl acetate, chloroform, propionic acid, diethyl ether, nitromethane, carbon tetrachloride, benzene and dioxane.

Later it will be shown that when the intermediate is removed from the filtrate and replaced by hexamine dinitrate that the yields are very similar.

Some of the purified intermediate was used to obtain a powder photograph by x-ray diffraction. This is shown in Figure 25 together with a powder photograph of hexamine dinitrate obtained with hexamine by Friedman. The identity of the two patterns is obvious.

The intermediate by itself is not converted into R.D.X. by the addition of acetic anhydride, or by the addition of acetic anhydride with either ammonium nitrate or paraformaldehyde

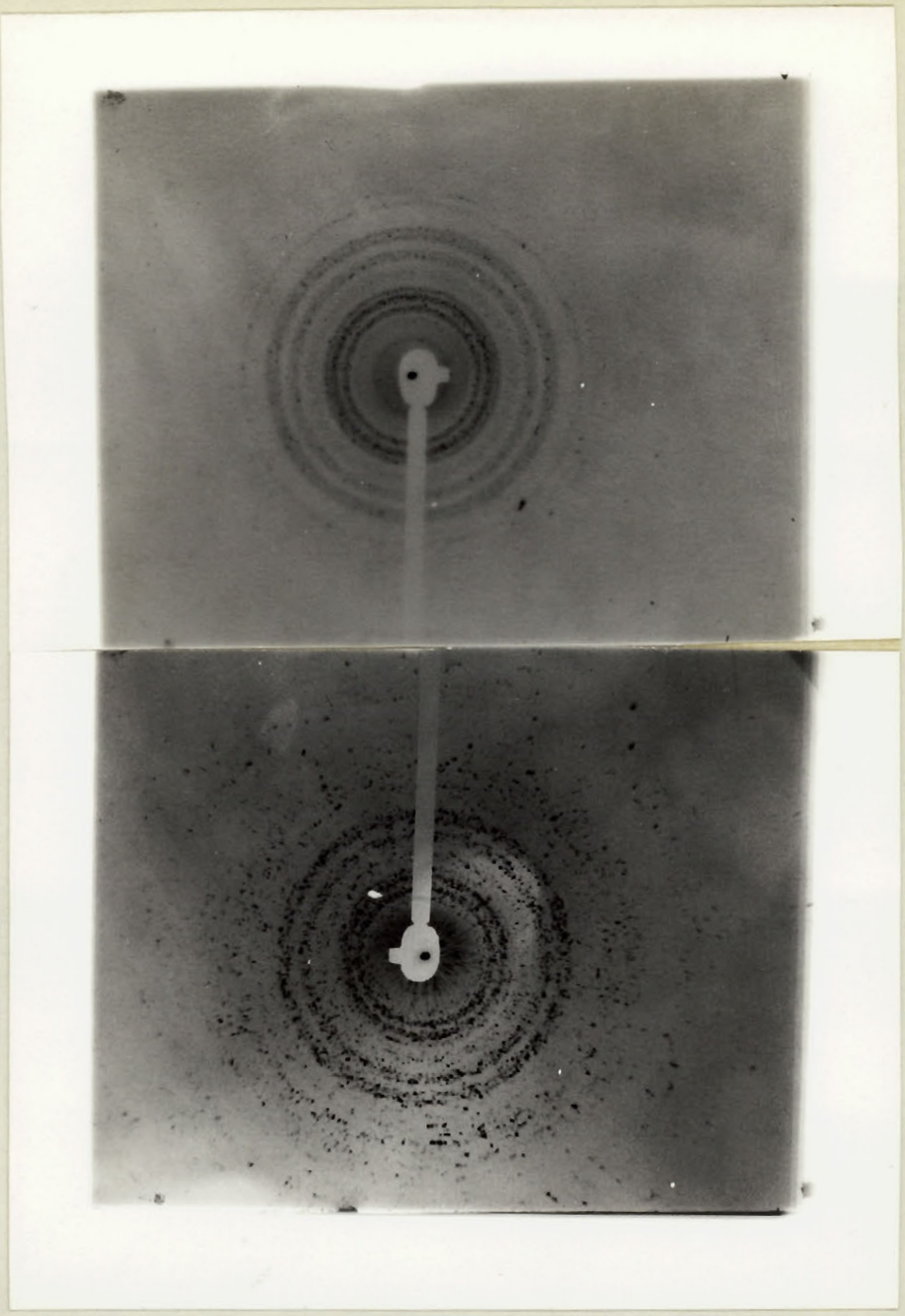


FIGURE 25 - X-Ray Powder Photographs of Intermediate in Ross Reaction (Upper) and of Hexamine Dinitrate (Lower). Copper Radiation. Crystal to Plate Distance about 3 centimeters.

even if in any of the three cases a very small amount of nitric acid was added. However when the material was identified as hexamine dinitrate the experiments were repeated using larger amounts of nitric acid. The nitric acid was mixed with enough acetic acid to make six milliliters and then six milliliters of acetic anhydride was added followed in about 15 minutes by the intermediate. Small amounts of R.D.X. were obtained after two hours at 35°C even in this preliminary experiment as shown from Table 24.

TABLE 24

REPLACING FILTRATE BY NITRIC ACID

	R.D.X. Yield
0.5 ml of 70% Nitric Acid	84 mg
1.0	69
2.0	57

This shows that the nitration of the intermediate does proceed under the conditions specified and much further work was done to establish the proper conditions as will be shown later in the sections on the study of the Bachmann

Process. Pickard nitrated the intermediate directly in the cold by the method usually employed in the nitration of hexamine dinitrate to produce R.D.X. and obtained some R.D.X.

Thus there can be no doubt that this solid is not only an essential intermediate in the McGill Process at 35°C, but that it is also hexamine dinitrate.

Two questions arose naturally from this, whether hexamine dinitrate was formed and stable at 70°C at which temperature the McGill Process produces its optimal yield, and whether the intermediate formed when the ammonium nitrate to formaldehyde ratio is one mole to one is hexamine dinitrate which does not precipitate out under those conditions.

Hexamine dinitrate is quite stable at 70°C. One gram of the material largely but not completely dissolves in 12 milliliters of glacial acetic acid at 70°C and 67 percent of this material is recovered on cooling this mixture to room temperature after one

hour at 70°C. This loss does not indicate any very great destruction since there must have been some solubility losses and there was some ammonium nitrate present in the hexamine dinitrate used in this test.

Hexamine dinitrate is exceedingly soluble at 70°C in the filtrate from which it was removed originally at 35°C. Three grams of the material dissolved completely in 10 milliliters of the filtrate. In common with the phenomenon observed at 35°C when the intermediate is prepared at that temperature with no or little excess of ammonium nitrate the rate of crystallization of the hexamine dinitrate from this medium proceeds quite slowly with the formation of large crystals. This slow crystallization may be related to the water content of the filtrate as well as to the lower ammonium nitrate content, since the crystallization from glacial acetic acid is quite rapid.

The intermediate forms very rapidly at 70°C, the solution becoming clear in a few minutes. Leaving the mixture at 70°C for one hour does not

cause the precipitation of hexamine dinitrate in keeping with the great solubility of this material in the filtrate at this temperature.

To establish the identity of the intermediate prepared at 70°C several procedures were followed. A large batch of the intermediate was prepared by heating 16 grams of ammonium nitrate and 4.8 grams of paraformaldehyde in 40 milliliters of glacial acetic acid for 15 minutes at 70°C. Six milliliter portions of this solution were cooled rapidly to 35°C and six milliliters of acetic anhydride added. The amount of R.D.X. produced at various times thereafter are shown in Figure 26, lower curve. The upper curve shows similar data when the intermediate is prepared normally at 35°C.

Since the rates and yields are quite closely identical it seems evident that the same reaction is involved in each case, that is that the intermediates are the same. There is no induction period in the conversion of either intermediate to R.D.X. indicating that the

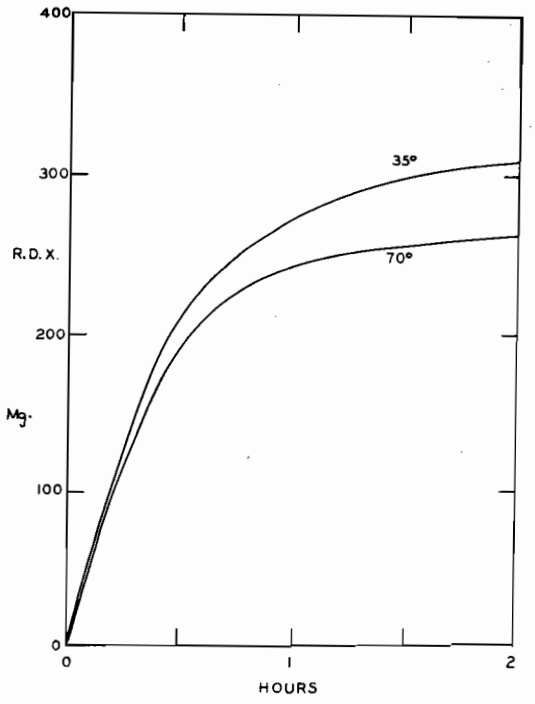


FIGURE 26 - Rate of Conversion and Yield of R.D.X. from Intermediate prepated at 35°C (Upper) and at 70°C (Lower).

intermediate was present as such in either case when the reaction was started by the addition of acetic anhydride. In the case of the intermediate prepared at 70°C this reaction was started within a few minutes of the preparation of the intermediate.

In any attempt to confirm the presence of hexamine dinitrate by separation in the solid form it was expected that difficulty would be experienced in separating it from the ammonium nitrate. The melting point of a reasonably pure fraction might be expected to lie within the range 154° to 158° (uncorrected). The presence of hexamine dinitrate in any appreciable amount in the precipitated solids may be confirmed by the following test: A mixture of three milliliters of the filtrate from which the hexamine dinitrate has been removed in the preparation of the intermediate at 35°C and six milliliters of acetic acid is treated with three milliliters of acetic anhydride at 35°C for 30 minutes. If hexamine dinitrate is then added, R.D.X. is produced after two hours at 35°C whereas hexamine, or ammonium nitrate and paraformaldehyde together do not.

The intermediate was prepared by heating ammonium nitrate and paraformaldehyde together in glacial acetic acid for 10 to 15 minutes at 70°C. The ratio of ammonium nitrate to formaldehyde was either one and a quarter moles to one or two to three, with three moles of acetic acid for each mole of formaldehyde. The resulting clear solution was poured into about 10 volumes of ether. A precipitate appeared immediately as it did also when a synthetic mixture of the filtrate of the preparation at 35°C and hexamine dinitrate were similarly treated. These precipitates produced R.D.X. under the experimental conditions laid down above showing the presence of hexamine dinitrate.

Similarly, using mixtures in which the molar ratios of ammonium nitrate to formaldehyde were one and a quarter to one, one to one, or two to three, the solutions were poured into acetone, from one to ten volumes, and the precipitate collected. Precipitation of the solids from acetone tended to be slow particularly when the excess of ammonium nitrate was reduced. The excess ammonium

nitrate was precipitated first and it could be removed by cooling the mixture and filtering before pouring the filtrate into acetone to precipitate the hexamine dinitrate. All of the solid fractions precipitated by acetone gave R.D.X. under the experimental conditions laid down showing the presence of hexamine dinitrate.

Both of the above methods gave fractions often grossly contaminated by ammonium nitrate, and only a fraction of the solids present were precipitated. Cooling the mixture to 35°C for 15 minutes or cooling to 0°C for two to five minutes was found to precipitate most of the ammonium nitrate usually without any appreciable loss of hexamine dinitrate which normally is much less rapidly crystallized. The method finally adopted for the preparation of pure fractions was to collect the total crop of crystals produced by cooling the solution of intermediate to 35°C for about 30 minutes. Then the solids were filtered off and suspended in glacial acetic acid to which some paraformaldehyde was added, and the mixture heated again at 70°C for about five

minutes. The solution was then cooled quickly to room temperature and filtered immediately. From 0.5 grams of this crude material was obtained 0.126 grams of R.D.X. as compared with 0.171 grams of R.D.X. from the same weight of hexamine dinitrate. The once purified material gave 0.180 grams of R.D.X. under the same conditions.

The yields obtained with the various fractions are shown in Table 25 omitting those fractions which produced s yield so low that the purity of the material must have been very poor, and also omitting a great many which were observed qualitatively to give a good yield of R.D.X. but the quantity of the latter was not determined.

TABLE 25

R.D.X. FROM HEXAMINE DINITRATE - RICH FRACTIONS

Fraction	Yield R.D.X.
Hexamine Dinitrate	0.177 gm
Intermediate Prepared at 35°C	0.158 0.171
Intermediate Prepared at 70°C	
After Cooling to 35°C for 30 minutes	0.126
Above purified	0.180 0.196
Cooling to 35°C for 15 minutes	0.210
Precipitated by Acetone	0.113 0.189

The once purified fraction was used to obtain an x-ray diffraction powder photograph. Only the characteristic pattern of hexamine dinitrate was observed as can be seen from Figure 27, when this is compared with Figure 25.

The melting point of this and other relatively pure fractions was within the range obtained normally with crude hexamine dinitrate contaminated with ammonium nitrate, that is 154° to 158°C, uncorrected.

Thus there seems to be no doubt as to the formation and stability of hexamine dinitrate at 70°C, and on the basis of the investigations carried out at 35°C it would seem likely that it is the essential intermediate in the McGill Process at 70°C also. No quantitative estimation of the amounts of hexamine dinitrate produced at 70°C has been attempted since all of the methods used so far have resulted in only partial precipitation of the solids present. The completion of this work awaits the development of reliable means of determining hexamine quantitatively.

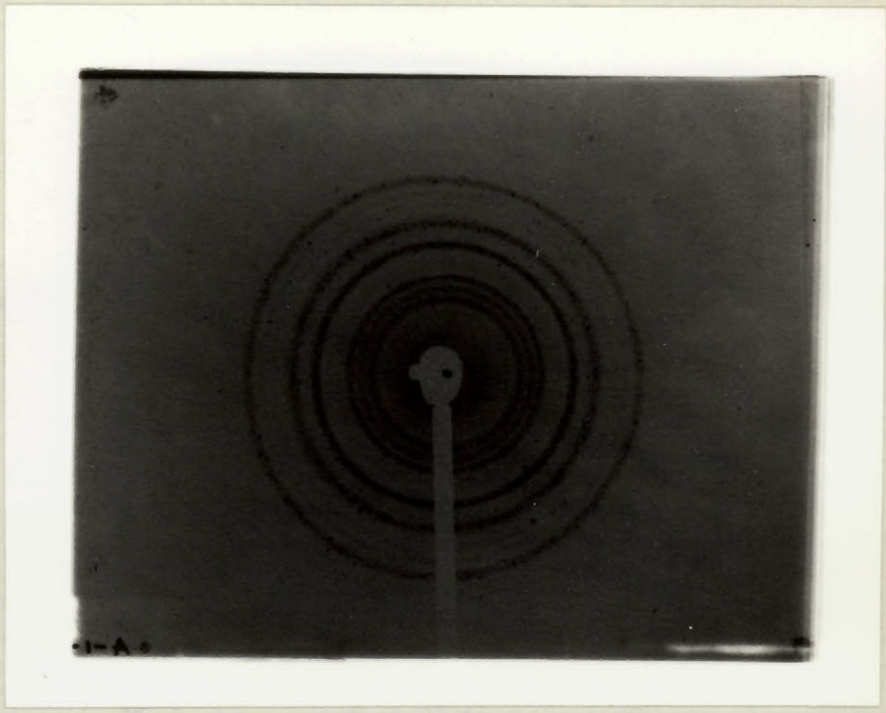


FIGURE 27 - X-Ray Powder Photograph of Hexamine Dinitrate isolated from the Preparation of the Intermediate at 70°C. Copper Radiation, Crystal to Plate Distance 30.4 millimeters.

Mention has been made that when the ratio of formaldehyde to ammonium nitrate is one mole to one or greater hexamine dinitrate does not precipitate out. It was of importance to determine whether this mixture would yield hexamine dinitrate on concentration. The mixtures were fractionated by cooling and concentrating in vacuo in turn. Three solid fractions were obtained. The first, but not the other two, gave some R.D.X. when tested by the technique used to identify the presence of hexamine dinitrate. Fractionation of a second batch yielded three fractions all of which were quite rich in hexamine dinitrate. It was concluded that most of the solid fractions were very heterogeneous and might or might not show the presence of hexamine dinitrate, and that while hexamine dinitrate was not precipitated when the intermediate was prepared using the initial ratios of formaldehyde to ammonium nitrate indicated, hexamine or hexamine dinitrate was formed so that the latter was precipitated on cooling and concentration of the solution. Some typical yields of R.D.X. from these solid fractions are shown in Table 26 together with some data obtained using hexamine dinitrate.

TABLE 26

INTERMEDIATE SEPARATED BY FRACTIONATION

Fraction	R.D.X. Yield
Hexamine Dinitrate	0.177 gm
Fraction One	0.160 0.185 0.155
Fraction Two	0.225
Fraction Three	0.045

Later work will show the ease with which hexamine is converted to the dinitrate under conditions very close to those prevailing in the McGill Process so that it matters little whether the intermediate is considered to be hexamine or hexamine dinitrate.

EFFECT OF THE ADDITION OF FURTHER AMOUNTS OF AMMONIUM NITRATE OR PARAFORMALDEHYDE UPON THE YIELD OF R.D.X.

If the McGill Process proceeds in steps then it might be suspected that addition of further reactants at different times after the reaction to produce the intermediate had started should indicate if certain of these steps were affected. Thus the reaction was started in glacial acetic acid with a given ratio of formaldehyde to ammonium nitrate and then at stated time intervals further reactants was added to change that ratio to some other value. Then at the end of 23 hours from the start of the reaction at 35°C acetic anhydride was added and the yield of R.D.X. at the end of two hours at 35°C was determined. The results are shown in Figure 28.

Curve 1 was obtained when the initial ratio of the number of moles of ammonium nitrate to formaldehyde was two to one, that is 3.2 grams of ammonium nitrate to 0.6 grams of paraformaldehyde in six milliliters of glacial acetic acid. At various

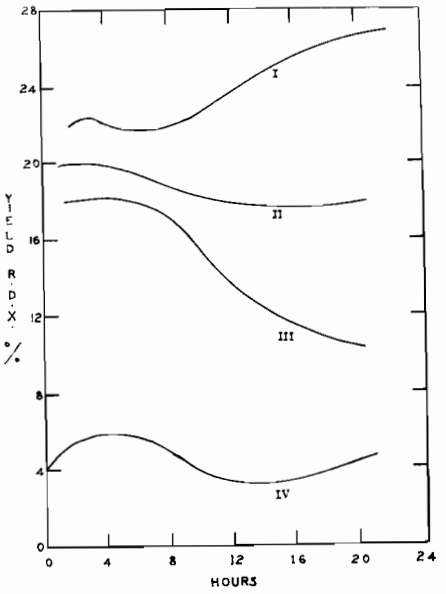


FIGURE 28 - Effect of adding further Reactants at various times after the Reaction to produce Intermediate has been started.

	Formaldehyde to Ammonium Nitrate Ratio	
	Initial	Final
I	1 : 2	1 : 1
II	1 : 1	1 : 2
III	2 : 1	1 : 1
IV	1 : 1	2 : 1

times after the reaction was started a further 0.6 grams of paraformaldehyde were added to bring the ratio to one mole to one. The mixture was shaken for the remainder of the 23 hours at 35°C after which time six milliliters of acetic anhydride were added and the R.D.X. determined after two hours at 35°C. The addition of the paraformaldehyde has little apparent effect in the first few hours. The solution remains clear with no precipitation of hexamine dinitrate just as one would expect from the fact that the ratio of formaldehyde to ammonium nitrate is in effect one mole to one. However, if addition of more paraformaldehyde is made after about five hours the precipitate of hexamine dinitrate does appear and does not disappear with the additional paraformaldehyde. Concurrently the yield seems to increase. The yields are calculated on the basis of the total formaldehyde added except for the last point on the curve. This value is uncertain since the paraformaldehyde was added just before the acetic anhydride so that some of the paraformaldehyde must have existed as such throughout the reaction time. As shown in Figure 28 it is assumed that none of the

paraformaldehyde added has entered into the reaction so that the value is most likely high. This decision is based on the fact that the two hours for which the reaction was allowed to proceed is less than the induction period for the conversion of paraform-aldehyde and ammonium nitrate to R.D.X. at 35°C. The effect of intermediate already present, or of condensation products of ammonium nitrate and formaldehyde may invalidate this assumption.

Curve II of Figure 28 was obtained similarly starting with a mixture whose molar ratio was one to one, 1.6 grams of ammonium nitrate, 0.6 grams of paraformaldehyde in six milliliters of acetic acid, and adding a further 1.6 grams of ammonium nitrate at various times thereafter to bring the ratio to two moles to one. As would be expected from the results shown in Figure 22 the yield is not altered material by the addition of the ammonium nitrate at any stage. The amount of hexamine dinitrate precipitated is reduced as the addition of ammonium nitrate is delayed. Thus the reaction proceeds more and more like one in which the molar ratio

remains one to one throughout. This effect is greater than can be accounted for by merely "summing" the effect of two consecutive reactions at the two different ratios for the appropriate times. In all cases except the last point for which the ammonium nitrate was added just before the acetic anhydride, the time during which the molar ratio was two to one was sufficiently long for the maximum amount of hexamine dinitrate to be formed if it were going to do so. No reason for this effect is suggested by other investigations.

Curve III shows similar data for a mixture which was originally one mole of ammonium nitrate (0.8 grams) to two of formaldehyde (0.6 grams) and ammonium nitrate (0.8 grams) was added to bring the ratio to one mole to one. As in the case of Curve I, additions early in the reaction give yields essentially the same as if the ratio were always one mole to one. However after seven hours the addition of ammonium nitrate fails to maintain the yield even though sufficient time is allowed after the addition of the ammonium nitrate and before the addition of the

acetic anhydride for the maximal amount of intermediate to be formed except in the case of the last point at which the ammonium nitrate was added just before the acetic anhydride. Thus there must be side reactions after seven hours which reduce the formaldehyde available for the production of R.D.X., that is that there is no longer the possibility of producing the maximal amount of intermediate from the added ammonium nitrate. Only in one case, when the ammonium nitrate was added after three hours, did hexamine dinitrate precipitate in this series.

Curve IV similarly shows the results when a mixture which was originally one mole (1.6 grams of ammonium nitrate) to one (0.6 grams of paraformaldehyde) had enough paraformaldehyde (0.6 grams) added to bring the ratio to two to one. The yield is uniformly low. Since for the last few points at least there must have been as much intermediate as gave the results shown in Curve II, the inference is that the presence of the excess paraformaldehyde over ammonium nitrate inhibits the conversion of already existing intermediate into R.D.X., or

promotes the conversion of intermediates into by-products. Later investigations showed that the effect might be due to tying up of the ammonium nitrate which is necessary for the conversion of hexamine dinitrate to R.D.X. under comparable experimental conditions.

INTERMEDIATE IN OTHER SOLVENTS

(a) Solvents

In an effort to obtain media other than glacial acetic acid and nitromethane in which to study this reaction, ammonium nitrate and paraformaldehyde were shaken in various solvents at 35°C in most cases with a small amount of sulphuric acid added, for about 20 to 24 hours. Six milliliters of the solvent were used and the molar ratio of reactants was two moles of ammonium nitrate (3.2 grams) to one of formaldehyde (0.6 grams). Then six millliliters of acetic anhydride were added and the amount of R.D.X. produced after two hours at 35°C was determined.

Positive results were obtained using hexane and heptane as solvents. Negative results were obtained under these conditions with acetone, chloroform, pyridine, ethyl acetate, dioxane, diethyl ether, toluene, benzene, propionic acid, malonic ester, chlorobenzene, chloroacetic ester, pentachloroethane, isobutanol, butyl nitrite, butyl ether, methanol and carbon tetrachloride. It is possible that under

other conditions these solvents would permit the formation of intermediate as well. If one accepts the view that the intermediate is hexamine dinitrate then certain of the solvents must be excluded. They must not only have the property of permitting the formation of hexamine dinitrate but also must form effective nitrating media for its conversion to R.D.X. when acetic anhydride is added.

(b) Rate of Formation of Intermediate Prepared in Different Solvents.

The fact was observed by Gillies that the rate of conversion of, and yield from, the intermediate in nitromethane were less than those for the intermediate prepared in acetic acid. Since the intermediate in each solvent had been prepared by shaking the reactants for the same length of time, that is about 24 hours, it seemed possible that the differences in behaviour might be explained on the basis of great differences in the rate of formation of the intermediate in the two solvents.

In Figure 29 are shown the data for the

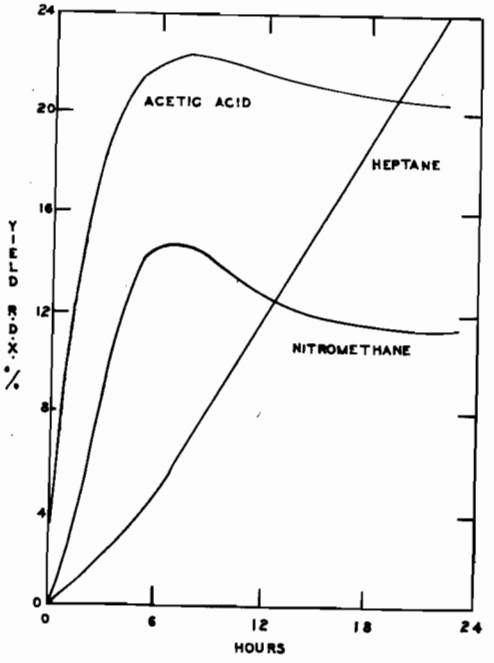


FIGURE 29 - Rate of Formation of the Intermediate at 35°C.

rate of formation of the intermediate in the two solvents. In six milliliters of the solvent were suspended 3.2 grams of ammonium nitrate and 0.6 grams of paraformaldehyde, molar ratio two to one, and these mixtures were shaken at 35°C for the times indicated. Then six milliliters of acetic anhydride were added and the yield of R.D.X. determined after a further two hours at 35°C. These graphs show that the amount of intermediate increases with time to a maximum at about eight hours after which there is a slow decline. When heptane was used, however, the few values obtained seemed to indicate that the yield was still increasing steadily after 20 hours. Thus it is evident that the differences observed in the yield of R.D.X. must be explained either on the basis of less intermediate formed in nitromethane, or on a less efficient conversion of the intermediate to R.D.X. with nitromethane present. That the latter is probably the case is shown later in a section dealing with the rates of conversion and yields from hexamine dinitrate in various solvents.

(c) Localization of the Intermediate in Other Solvents

By decanting the liquids from the solids when the intermediate was formed in nitromethane it was determined that all of the potential R.D.X. was in solution. The solids were inactive and non-essential for the production of R.D.X. from the intermediate. The same procedure when heptane was used as solvent showed that the liquid phase and solid phase were each inactive when separated. The solids failed to give R.D.X. with the filtrate obtained after filtering off the hexamine dinitrate from the acetic acid preparation of the intermediate and the solution gave very little R.D.X. with added hexamine dinitrate. This investigation was terminated before the cause of this was elucidated. Heptane tended to form systems with two liquid phases.

EFFECT OF ADDED ACID OR ALKALI

The study of the effect of added acid or alkali, and of the pH of the system has been handicapped by the lack of a reliable means of measuring the pH. The effect of acid may be divided into two phases (a) the effect on the rate of conversion to and yield of R.D.X. when acetic anhydride is added to the solution containing the intermediate and (b) the effect upon the rate of formation and amount of intermediate produced in the initial solvent before acetic anhydride is added.

(a) Effect on the Conversion of the Intermediate to R.D.X.

The intermediate was prepared by shaking 3.2 grams of ammonium nitrate and 0.6 grams of paraformaldehyde in six milliliters of glacial acetic acid for approximately 24 hours. The amount of intermediate formed at that time is quite reproducible, the amount present actually falling off very slowly with time. When the acetic anhydride is

added to the mixture and the amount of R.D.X. produced in various times thereafter is determined the yields are those shown in Curve I of Figure 30. If just before the acetic anhydride is added, two drops of concentrated sulphuric acid are added, the results are as shown in Curve II. Replacing the sulphuric acid by one-half milliliter of a mixture of one volume of 60 percent perchloric acid and four volumes of acetic anhydride, the results are shown in Curve III. From these it is evident that the addition of acid increases the initial rate of conversion of the intermediate to R.D.X. and also increases the yield to a less marked extent.

(b) Effect on the Production of Intermediate.

If the acid is added to the acetic acid at the very beginning then the resulting yield of R.D.X. after the acetic anhydride is added will depend upon the effect of the acid on the formation of the intermediate as well as upon the effect on the conversion of a given amount of intermediate to R.D.X. Sulphuric and trichloroacetic acids in the amounts shown in Table 27 were added to the usual

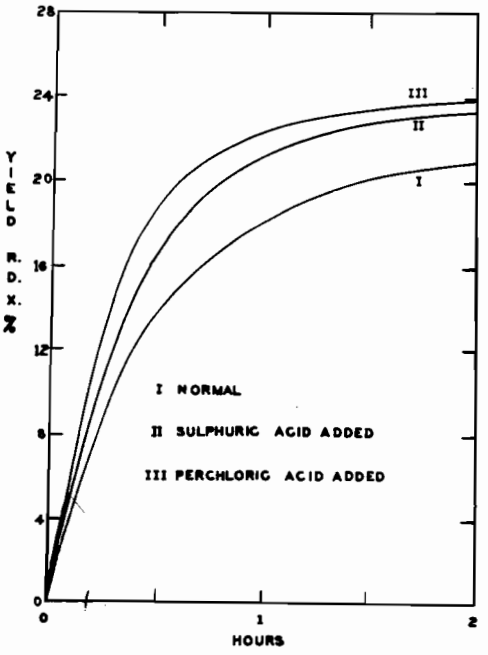


FIGURE 30 - Effect of added Acid on the Rate of Conversion to and Yield of R.D.X. from the Intermediate formed in Glacial Acetic Acid at 35°C

amounts of reactants and after about 24 hours at 35°C, acetic anhydride was added and the reaction continued for another two hours. The effect on the yields of R.D.X. are shown in Table 27.

TABLE 27

EFFECT OF ACID ON YIELD OF R.D.X.

No Acid Added		21 %
Sulphuric Acid	(2 drops)	34.8
	(4 drops)	28.8
Trichloroacetic Acid	(0.3 grams)	28.5
	(0.6 grams)	26.1
	(0.9 grams)	24.9

From Figure 30 it might be concluded that an increase in the yield from 21 to 24 percent would be accounted for by the effect of the added acid on the conversion of the intermediate into R.D.X. The higher values shown in Table 27 may be considered, therefore, to indicate that the presence of acid in small amounts favoured the formation of the intermediate. It is interesting to note that the precipitation of hexamine dinitrate does not occur from the more strongly acid solutions.

In an effort to measure the pH of the solutions of reactants and products in acetic acid and acetic anhydride the halochromic compounds of Conant and Hall (41) were tried. These are a series of carbinols, acetones and acetophenones which form highly coloured salts with inorganic acids in acetic acid medium. Those used were benzalacetophenone, triphenylcarbinol, diphenyl-alpha-naphthylcarbinol, dipiperonylacetophenone, anisolcinnamalacetone, dipiperonylacetone and dianisolacetone. They were used as directed, the indicator being M/50 in glacial acetic acid and added in the required number of drops to five milliliters of the solution under test.

The results showed that the pH of the acetic acid was not altered by the addition of paraformaldehyde, ammonium nitrate or acetic anhydride either alone or in any possible combination. However the addition of as little as one drop of concentrated sulphuric acid caused to pH to drop to below -3. If the mixture contained acetic anhydride as well then the pH fell even lower, to a value below -3.2. However, if ammonium nitrate were

present as well as the acid and acetic anhydride then the colour of the indicator faded rapidly and the indicator was destroyed eventually. The acidity of the solution remained "super acid" because the addition of further indicator restored the colour momentarily. Thus it is evident that the indicators were being destroyed by the combination of acid, acetic anhydride and ammonium nitrate. It is interesting to note that all three compounds are necessary also for the conversion of hexamine dinitrate to R.D.X. Such a medium is a powerful acetylating, nitrating and dehydrating system. Indicators seemed to function satisfactorily under other conditions. Other indicators such as o-nitraniline (42) are acetylated easily to produce colourless compounds (43) and their use was not attempted. It would seem probable that the electrometric method of Russell and Cameron (44) might be applied to measuring the pH of this system.

An attempt was made to follow the pH of the reaction mixture using the indicators at hand and by glimpsing the colour momentarily before it

faded. By this technique after the initial phases had been passed no difference in pH could be detected between the normal reaction and one to which acid had been added. The normal reaction mixture started out with a pH of about zero on the Conant and Hall pH(HAc) scale and became more acid as the paraformaldehyde disappeared until the pH was about -3 when the mixture was clear and when the precipitate of hexamine dinitrate appeared. The addition of acetic anhydride left the solution very strongly acid. On the other hand the same experiment to which two drops of concentrated sulphuric acid had been added was strongly acid (-3) to start with and the acidity was indistinguishable from that of the normal reaction thereafter. The rate of conversion of the intermediate and yield of R.D.X. are shown in Figure 31. Thus while the indicators failed to show more than the fact that acid was formed as the reaction to produce intermediate went on, the yield of R.D.X. and the rate of conversion of the intermediate to R.D.X. were increased. This may be explained on the basis of work to be reported later; the added acid brings the nitric acid concentration more nearly optimal for the conversion of hexamine dinitrate to R.D.X.

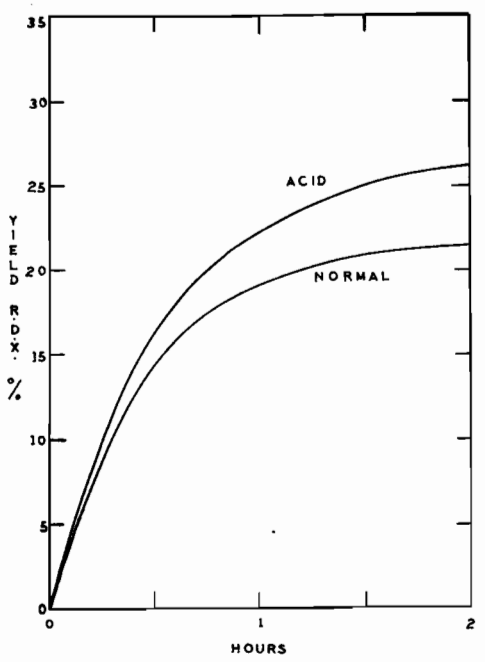


FIGURE 31 - Effect of added Acid on the Rate of Conversion of Intermediate to R.D.X., indicators present.

Some information has been accumulated on the effect of pH on the formation of the intermediate in nitromethane and heptane. When nitromethane was used as the initial solvent and made more acid or alkaline by the addition of sulphuric acid or pyridine respectively, the results shown in Table 28 were obtained.

TABLE 28

EFFECT OF pH ON YIELD OF R.D.X. IN NITROMETHANE

	R.D.X. Yield 1 hour	3 hours
Sulphuric Acid Added	13.4 %	16.7 %
Neutral	7.6	11.2
Pyridine Added	3.9	13.6

While the results are far too sketchy for a complete analysis, it seems evident that the presence of acid both increases the yield of R.D.X. and the rate of production of R.D.X. over the normal yield and rate. The results when pyridine was added are less consistant in that while indicating a lower rate the final yield was greater than normal. The amount

of pyridine added (3 drops) is not likely to have affected the pH to the same extent as the two drops of concentrated sulphuric acid added to the mixture to be acidified.

When heptane is used to prepare the intermediate the effect of acid on the rate of production of the intermediate may be summarized as in Table 29. The times indicated are the times before acetic anhydride is added, and the R.D.X. yield was determined two hours after the anhydride was added. The entire reaction was carried out at 35°C with the normal amount of reactants and solvents.

TABLE 29

EFFECT OF ACID ON YIELD OF R.D.X. IN HEPTANE

	Hours	Yield
No Acid	19	9.1 %
	22	9.6
Sulphuric Acid, One Drop	19	12.3
Sulphuric Acid, Two Drops	15	11.9
Sulphuric Acid, Three Drops	11	10
	14	10.5
	22	24

In this case also the addition of acid seems to have a beneficial effect on the yield. No study has been made of the rate at which the intermediate is converted to R.D.X. in heptane so that it is impossible to state whether this increased yield is due to increased production of intermediate, or to increased efficiency of conversion to R.D.X., or to a combination of the two.

In general the small amount of data accumulated shows that a thorough study of the rôle and relation of pH to the mechanism of the reactions to produce R.D.X. should be of interest.

ATTEMPTS TO ISOLATE THE FILTRATE FACTOR

While hexamine dinitrate can be converted to R.D.X. by nitric acid, or by nitric acid with acetic anhydride and ammonium nitrate, it is worth recording the attempts to isolate a "filtrate factor" which in the presence of acetic anhydride combined with hexamine dinitrate to give R.D.X., even though the fact that the intermediate was hexamine dinitrate was not known when these investigations were attempted.

It was ascertained that the filtrate factor was present both before and after the addition of acetic anhydride to the filtrate, and it appeared that this factor was quite stable in solution.

When hexamine dinitrate is filtered off the preparation of the intermediate and acetic anhydride added to the filtrate the amount of precipitate which was normally thrown down by the acetic anhydride was increased. It was inferred

that this might be the material which normally combined with the hexamine dinitrate, but under these conditions was precipitated. It was filtered off but failed to give any R.D.X. with acetic anhydride and hexamine dinitrate. It looked like, and gave all the tests of ammonium nitrate.

By alternately cooling the filtrate to 0°C and concentrating it in vacuo at 30° to 40°C, six other solid fractions were obtained. Four dry fractions gave no R.D.X. with acetic anhydride and hexamine dinitrate, but the two very wet fractions did give a little R.D.X. However, when these latter two fractions dried they failed to give any R.D.X. either. Meantime the ability to produce R.D.X. with hexamine dinitrate and acetic anhydride remained in the filtrate and became greater with concentration of the filtrate as indicated by an increasing yield of R.D.X. for a given amount of the concentrated filtrate, acetic anhydride and hexamine dinitrate.

Drying the filtrate at any stage caused

disappearance of the activity. Thus the activity must be assumed to be present only in solution, and to be lost by drying. Several independent fractionations amply confirm these data, and filtrates were used which had been prepared with different initial ratios of reactants, although in all cases by appropriate addition of ammonium nitrate or paraformaldehyde the filtrate corresponded finally to one with a molar ratio of reactants of one to one under the conditions used to prepare hexamine dinitrate. If the final ratio of reactants was two moles of formaldehyde to one of ammonium nitrate this solution failed to give any appreciable amount of R.D.X. with acetic anhydride and hexamine dinitrate. This solution was not fractionated, therefore.

All of the above fractionations were carried out with acetic anhydride present, and it seemed possible that this might be destroying the filtrate factor on concentration. Therefore, the addition of acetic anhydride was omitted and the fractionation of the filtrate as it was after the

removal of hexamine dinitrate was undertaken. The final ratio of formaldehyde to ammonium nitrate was always adjusted to be one mole to one. Replicate fractionations were made.

Cooling the filtrate caused a considerable amount of ammonium nitrate to crystallize, an amount equivalent to about 20 percent of the amount added originally. Concentration and cooling produced six solid fractions the first two of which were completely inactive while the last four, obtained wet, were slightly active, giving some R.D.X. with acetic anhydride and hexamine dinitrate. As before most of the activity remained in the filtrates and disappeared when these were dried. The wet fractions above were suspended in acetic acid and refractionated. In all cases three solid fractions were obtained which were dry and inactive. The small amount of activity originally present in the wet fractions remained in solution and disappeared on drying.

With the filtrate factor evanescent it was decided to study the conditions of its formation

and to determine whether it was present in preparations of the intermediate in other solvents in order that attempts might be made to isolate it from them using such techniques as low temperature fractionations.

The criterion for the identification of the filtrate factor was that the addition of hexamine dinitrate increased the yield. When the intermediate was prepared in acetic acid the normal amount of R.D.X. produced by the addition of acetic anhydride wasaabout 260 milligrams. However, the addition of hexamine dinitrate raised the yield to 424 milligrams. When the same technique was applied to the preparation of the intermediate in heptane the yield rose from 176 to 231 milligrams indicating the probable presence of the filtrate factor. No attempt was made to isolate the factor from such a medium.

The observation that this filtrate factor was present in good amounts in the solution of the intermediate in acetic acid prepared when the molar

ratio of the reactants was one to one suggested that this material might be an unstable compound between the two reactants, and that it might be produced early in the reaction. This latter was found to be the case as can be seen from Table 30. The second column shows the normal amount of R.D.X. produced after two hours at 35°C if the acetic anhydride is added to the acetic acid solution at the times indicated after the reaction to produce intermediate has started. The third column shows the effect of adding 0.5 grams of hexamine dinitrate at the start of the reaction along with the 0.6 grams of paraformaldehyde and 1.6 grams of ammonium nitrate in six milliliters of acetic acid. The fourth column shows the effect of adding 0.5 grams of hexamine dinitrate just before the six milliliters of acetic anhydride. The results show that the material which reacts with hexamine dinitrate in the presence of acetic anhydride is produced very early in the reaction between ammonium nitrate and paraformaldehyde.

TABLE 30

PRODUCTION OF FILTRATE FACTOR IN ACETIC ACID

Time Before Acetic Anhydride Added	Hexamine Dinitrate Added		
	None	Added at Start	Added with Anhydride
0 hours	41 mg	201 mg	201 mg
1	157	216	211
2		236	201
3	268	317	261
4			351
15	251		423

Although any attempt to learn whether this filtrate factor was produced from the very start of the reaction meant trying to determine very small amounts of R.D.X. with consequential unreliability of the results, it was decided to carry out similar experiments in which the time of reaction in the presence of acetic anhydride was reduced to periods of less than two hours. The solids, ammonium nitrate, paraformaldehyde and hexamine dinitrate, were mixed in acetic acid to which on occasions as noted some sulphuric acid was added, and then acetic anhydride and the amount of R.D.X. produced at various times thereafter determined as shown in Figure 32.

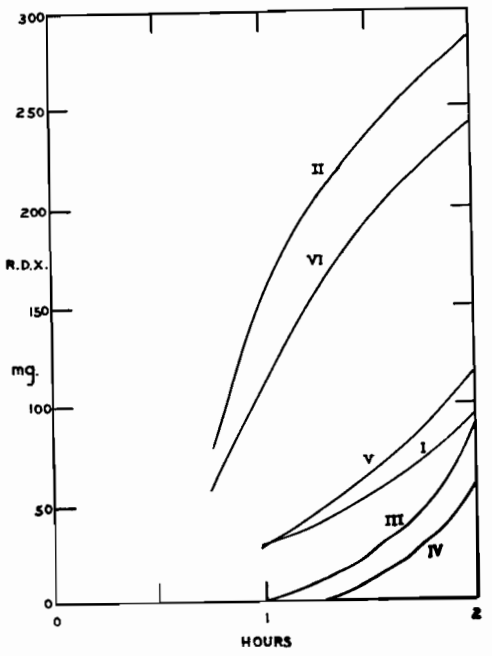


FIGURE 32 - Formation of Filtrate Factor from Ammonium Nitrate and Paraformaldehyde in Glacial Acetic Acid.

I 1.6 gm ammonium nitrate, 0.6 gm paraformaldehyde

II same acidified

III unacidified, hexamine dinitrate added after one hour

IV same acidified

V 3.2 gm ammonium nitrate, 1.2 gm paraformaldehyde

VI same acidified

Curve I shows the amount of R.D.X. produced with time when 1.6 grams of ammonium nitrate, 0.6 grams of paraformaldehyde and 0.5 grams of hexamine dinitrate are used with six milliliters of acetic acid and six milliliters of acetic anhydride, while Curve II is the same mixture to which two drops of concentrated sulphuric acid have been added. Together they seem to indicate that there is an induction period, and that the formation is favoured by acid. To overcome the induction period the same mixture of solids was shaken for one hour in the acetic acid before the acetic anhydride was added. This gave the results shown in Curve III which shows that there is still an acceleration of the reaction. Similar results (Curve IV) were obtained with the acetic acid mixture acidified and the acetic anhydride added after 75 minutes. It is evident that the induction period must be in that phase of the reaction which involves the acetic anhydride since the R.D.X. production under these conditions is roughly independent of the times before which the acetic anhydride is added.

Doubling the amount of ammonium nitrate and paraformaldehyde added with all the other conditions the same gave the results shown in Curve V. The same mixture acidified gave the results shown in Curve VI. These show that the amount of R.D.X. produced increases with the amount of reactants used. It is concluded that while the filtrate factor is formed early in the reaction and that while its formation or utilization is markedly affected by the addition of acid, there still remains the possibility that its formation is characterized by an induction period. It is known that as the amount of R.D.X. to be recovered is decreased, the percentage recovered on dilution decreases and this may account for the induction period, but there are other explanations possible. Since it will be shown later that R.D.X. yields are affected by the ratio of hexamine dinitrate to filtrate factor, and keeping in mind that paraformaldehyde is used and so must be depolymerized, the presence of the induction period is not surprising. As the ratio of hexamine dinitrate to filtrate factor decreases the rate of conversion of

the dinitrate to R.D.X. increases and this would give the curves in Figure 32 their convexity upwards. Then too the presence of formaldehyde inhibits the formation of R.D.X. so that its disappearance would also give the curves that convexity. On the other hand if it is conceded that the active filtrate factor is nitric acid then the fact that the addition of sulphuric acid markedly increases the yield of R.D.X. is understood readily, and the convexity downward of Curves II and VI can be explained by the normal falling off of the production of R.D.X. as the hexamine dinitrate is used up.

To minimize the effect of the variation in the ratio of the amount of hexamine dinitrate to filtrate factor the following experiment was conducted: The amount of R.D.X. produced by 0.5 grams of hexamine dinitrate and three and four milliliters of the filtrate was determined by making the respective volumes of filtrate up to six milliliters with glacial acetic acid, and then adding six milliliters of acetic anhydride and allowing the reaction to proceed for 30 minutes at 35°C. Then in addition

to the paraformaldehyde and ammonium nitrate as used in the previous investigations, three milliliters of the filtrate was used and the mixtures shaken for various lengths of time. Then acetic anhydride was added and the R.D.X. produced in 30 minutes at 35°C determined. The results are shown in Table 31.

TABLE 31

FORMATION OF FILTRATE FACTOR

Anhydride Added	Yield R.D.X.
0 min.	71 mg
30	76
60	121
3 ml Filtrate Alone	56
4 ml Filtrate Alone	101

These data may be interpreted as showing the amount of filtrate factor present at the times indicated. Again the induction period is apparant. This must indicate that the induction period is real, that is that the filtrate factor is not the first step in the reaction, or else that the

induction period is falacious and due to the depolymerization of the paraformaldehyde or to the difficulty in recovering small amounts of R.D.X. The effect cannot be due to the acetic anhydride because of the constant length of time in the presence of that reagent in all cases. It would seem that in 60 minutes the ammonium nitrate and paraformaldehyde produce an amount of filtrate factor equivalent to one milliliter of the filtrate used for comparison, but that this amount appears largely in the latter half of the experiment.

EFFECT OF RATIO OF HEXAMINE DINITRATE TO FILTRATE FACTOR

If various amounts of hexamine dinitrate are used with a constant amount of the filtrate and acetic anhydride the amounts of R.D.X. produced within two hours at 35°C after the addition of the anhydride are those shown in the second column of Table 32. In the third column are shown similar values in which the six milliliters of filtrate was replaced by six milliliters of acetic acid and 1.6 grams of ammonium nitrate and 0.6 grams of paraformaldehyde. In both cases it is shown clearly that the amount of R.D.X. produced does not increase in proportion to the hexamine dinitrate added. If it is conceded that the filtrate factor is nitric acid, then these variations from a linear relationship are in line with later investigations on the effect of acid concentration on R.D.X. yield from hexamine dinitrate.

TABLE 32

EFFECT OF RATIO OF HEXAMINE DINITRATE TO FILTRATE FACTOR

Hexamine Dinitrate	With Filtrate	With Reactants
0.1 gm	171 mg	46 mg
0.2	246	126
0.4	356	131
0.6	381	156
0.8	471	171
1.0	496	146

If on the other hand the amount of hexamine dinitrate is kept constant (0.5 grams) and the amount of filtrate added is varied, the yields after acetic anhydride has been added and the reaction allowed to proceed for 15 minutes at 35°C are those shown in Table 33. The amounts of filtrate indicated in the first column were made up to a volume of six milliliters with acetic acid before the addition of six milliliters of acetic anhydride.

TABLE 33

EFFECT OF RATIO OF HEXAMINE DINITRATE TO FILTRATE FACTOR

Filtrate	Yield R.D.X.
3 ml	0 mg
4	36
5	127
6	185

These data may be compared with those in Table 34. In this case the filtrate has been replaced by acetic acid containing 1.6 grams of ammonium nitrate and 0.6 grams of paraformaldehyde, and one-half and one-quarter of these amounts. To these solids with 0.5 grams of hexamine dinitrate present in six milliliters of acetic acid was added six milliliters of acetic anhydride and the R.D.X. produced in two hours at 35°C determined.

TABLE 34

EFFECT OF RATIO OF HEXAMINE DINITRATE TO REACTANTS

Reactants	R.D.X. Yield
1/4 Quantity	40 mg
1/2 Quantity	106
Full Quantity	156

When the filtrate is used the yield of R.D.X. falls off much faster than the decrease in the amount of filtrate should indicate. A later section will show that this is true also when nitric acid is used with ammonium nitrate and acetic anhydride to bring about the nitrolysis of hexamine dinitrate. When

as shown in Table 34, ammonium nitrate and paraformaldehyde are used instead of the filtrate, the yield of R.D.X. is much more nearly proportional to the amounts of these used. However, the probable production of extra hexamine dinitrate complicates the analysis of these results.

EFFECT OF ACETIC ANHYDRIDE ON HEXAMINE DINITRATE

The study of the final phase of the reaction to produce R.D.X., that is the reaction between hexamine dinitrate, the filtrate factor and acetic anhydride was of importance in attempting to explain the rôle of the acetic anhydride. The formation of hexamine dinitrate takes place spontaneously in acetic acid medium, but that the full effectiveness of the filtrate depends upon it being treated with acetic anhydride, and that the final union of hexamine dinitrate and the filtrate factor seems dependent upon the presence of acetic anhydride, will be shown in later sections.

In the reaction between hexamine dinitrate, the filtrate factor and acetic anhydride there are three possible reactions which could determine the rate of the reaction, the effect of acetic anhydride on hexamine dinitrate, the effect of acetic anhydride upon the filtrate, or the reaction between hexamine dinitrate and the filtrate factor. Attempts were made to determine which of these three was rate determining.

The effect on hexamine dinitrate of shaking in acetic anhydride is shown in Table 35. The yields of R.D.X. recorded are those produced by the addition of six milliliters of the filtrate to 0.5 grams of hexamine dinitrate which had been shaken with six milliliters of acetic anhydride for the times indicated at 35°C. After the filtrate was added, the reaction was allowed to proceed for 15 minutes at 35°C.

TABLE 35

EFFECT OF ACETIC ANHYDRIDE UPON HEXAMINE DINITRATE

Time With Anhydride	R.D.X. Yield
0 minutes	190 mg
15	170
30	170
60	155
90	135
120	115

Instead of showing that the action of acetic anhydride upon hexamine dinitrate was the rate determining step in the production of R.D.X., that is that the yield of R.D.X. goes up with increasing time of treatment of the hexamine

dinitrate with acetic anhydride, the reverse is true. The amount of R.D.X. produced has fallen off about 40 percent in the two hour treatment. This rate of destruction may have some effect upon the efficiency of the conversion of hexamine dinitrate to R.D.X. Possibly acetyl derivatives are formed which are converted to R.D.X. very slowly or not at all, in keeping with the observations of Linstead (45). If dinitropentamethylene tetramine (D.P.T.) is formed at an appreciable rate at this temperature, its conversion to H.M.X. as will be shown later is of such a magnitude that its formation in this case would not affect the yield of R.D.X. when the latter is considered, as normally, to include H.M.X.

EFFECT OF ACETIC ANHYDRIDE UPON THE FILTRATE

From the previous section it is obvious that the effect of acetic anhydride upon hexamine dinitrate is not the rate determining step in the production of R.D.X. Thus the rate determining step must be either the effect of acetic anhydride upon the filtrate factor, or on the reaction between hexamine dinitrate and the filtrate factor.

A preliminary experiment showed that acetic anhydride had a considerable effect upon the filtrate. The following mixtures were shaken for one hour at 35°C:

(i) 0.5 grams of hexamine dinitrate and six milliliters of the filtrate

(ii) 0.5 grams of hexamine dinitrate and six milliliters of acetic anhydride

(iii) six milliliters of filtrate and six milliliters of acetic anhydride.

Then to (i) was added six milliliters of acetic anhydride, to (ii) six milliliters of filtrate, and to (iii) 0.5 grams of hexamine dinitrate. The amount of R.D.X. produced within the next ten minutes at 35°C was determined, and were (i) 135 milligrams,

(ii) 125 milligrams and (iii) 235 milligrams. The lower yield of (ii) relative to (i) is to be expected from the effect of acetic anhydride upon hexamine dinitrate, but the increased yield of (iii) is very marked. This observation prompted a more thorough investigation.

In all of the experiments in this section the total volume was kept at 12 milliliters by adding glacial acetic acid to make the volume while the amount of acetic anhydride and filtrate were varied. The temperature was constant, at 35°C.

If three milliliters of filtrate and six milliliters of acetic anhydride are used and shaken for the times indicated before the addition of 0.5 grams of hexamine dinitrate the amount of R.D.X. produced within 30 minutes after the addition of the hexamine dinitrate is shown in Figure 33, Curve I. These data show that the amount of R.D.X. rises steeply to a maximum when the filtrate has been treated for from 15 to 30 minutes. For convenience this effect has been called the "activation" of the

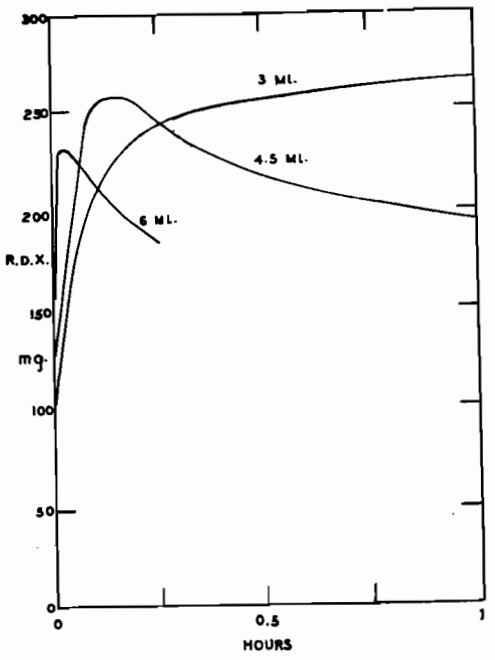


FIGURE 33 -Activation of the filtrate as a function of the amount of filtrate used.

filtrate. Increasing the amount of filtrate to 4.5 milliliters and decreasing the length of time for which the reaction is allowed to proceed after the addition of the hexamine dinitrate to 15 minutes gave the results shown in Curve II. Increasing the amount of filtrate to six milliliters and reducing the time of reaction after the hexamine dinitrate was added to 10 minutes the results shown in Curve III were obtained.

The fact that different times were used after the addition of the hexamine dinitrate makes the quantitative results difficult to interpret since the rate of the reaction between hexamine dinitrate and the filtrate factor enters into the picture and this rate is affected very greatly. Qualitatively it can be seen that the rate of activation increases as the amount of filtrate used is increased, as also is the rate of destruction after the maximum is passed.

It would not be expected that the amount of hexamine dinitrate added would affect the activation

of the filtrate. This is true although the rate of conversion of hexamine dinitrate to R.D.X. after the addition of the dinitrate is so altered that different amounts of R.D.X. are produced. Figure 34 shows the results obtained using 0.25, 0.5 and 1.0 grams of hexamine dinitrate added at the times indicated and the R.D.X. determined after 60, 30 and 30 minutes respectively at 35°C, using three milliliters of filtrate and six milliliters of acetic anhydride in every case. Ignoring the numerical values it is evident that the rate of activation is the same, but that the rate of reaction after the addition of the dinitrate must be altered to account for the anomalous decrease in the amount of R.D.X. produced under otherwise identical conditions when higher amounts of hexamine dinitrate are used.

Figure 35 shows the effect of variations in the amount of acetic anhydride added. In all cases three milliliters of filtrate and 0.5 grams of hexamine dinitrate were used, the hexamine dinitrate being added at the times indicated. The results show the effect of six, 4.5, three and two milliliters of

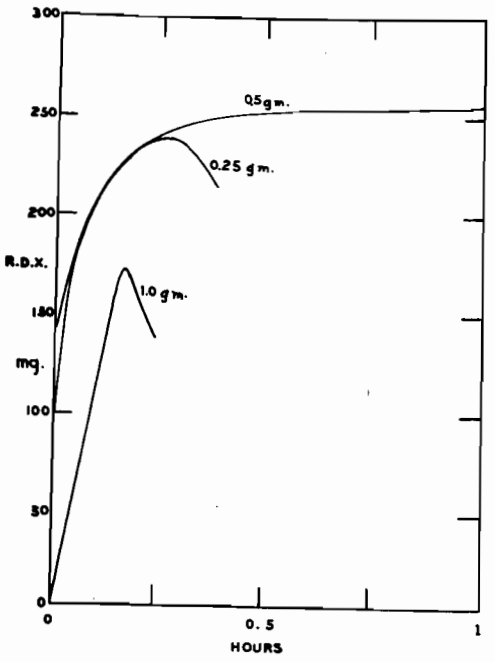


FIGURE 34 - Effect of the amount of Hexamine Dinitrate on the Form of the Activation Curve for the Filtrate.

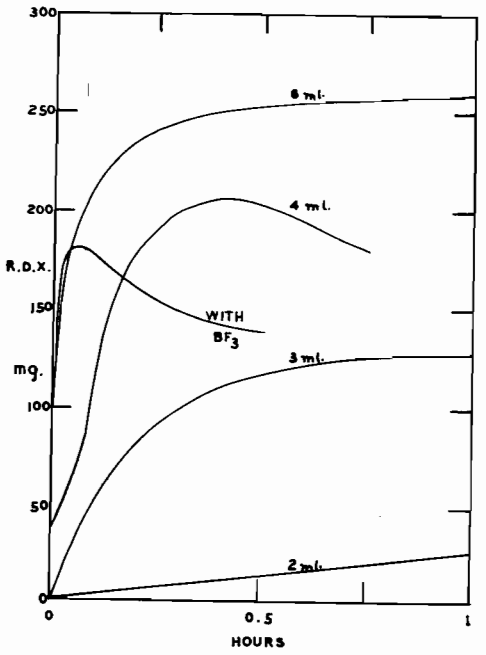


FIGURE 35 - Effect of the Amount of Acetic Anhydride on the Activation of the Filtrate.

acetic anhydride on three milliliters of filtrate during the times indicated when the R.D.X. is determined 30, 45, 60 and 60 minutes respectively after the addition of the 0.5 grams of hexamine dinitrate. Together these curves indicate that the amount of acetic anhydride affects the activation very markedly. There is a virtual disappearance of the effect when but two milliliters of the anhydride are used. The curve marked "with BF_3" is based on the observation that boron trifluoride catalizes the hydrolysis of anhydrides (46). The data for this curve were obtained in every way identical to that used to obtain the data in the curve marked "3 ml" except that the acetic acid was replaced by an acetic acid solution of boron trifluoride, probably about 100 grams of boron trifluoride per liter. This shows that the activation with acetic anhydride is very slight under these conditions and that the boron trifluoride causes practically complete activation before the acetic anhydride is added, or else that the activation occurrs so rapidly in the presence of hexamine dinitrate that the rates with which hexamine dinitrate reacts with the filtrate factor before and

after activation are the same. Boron trifluoride may act to overcome the deleterious effect of hexamine dinitrate on the rate of the reaction involved in the activation of the filtrate, or may promote the reaction in the same way that the activation does normally. It must be remembered that the rôle of boron trifluoride in nitration reactions is suspected to be that of a dehydrating agent (47).

It would seem very probable that the forms of the curves in Figures 33, 34 and 35 are caused by variations in the rate of the reaction between the activated filtrate and unactivated filtrate present in varying proportions. This is shown to be probable when the rates of conversion of hexamine dinitrate to R.D.X. using activated and unactivated filtrates are measured.

Figure 36 shows the influence of variations in the amount of filtrate used. In all cases the amount of anhydride added was six milliliters and the amount of hexamine dinitrate 0.5 grams. The rate determined using the activated filtrate was obtained using the filtrate activated to its

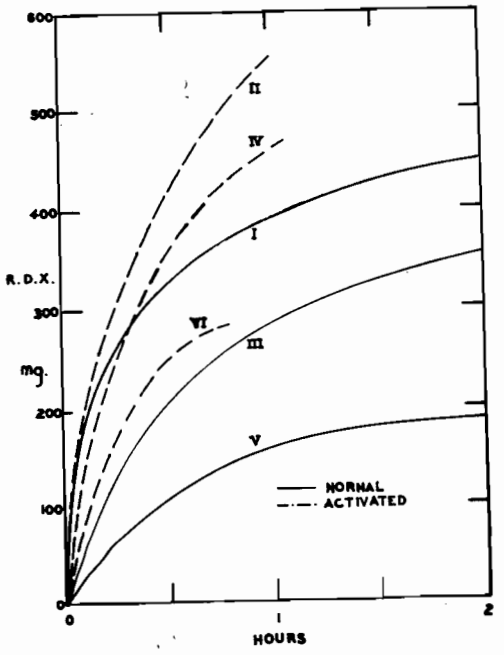


FIGURE 36 - Rates of Conversion of Hexamine Dinitrate to R.D.X. using Activated and Normal Filtrates

I and II - Six milliliters of Filtrate

III and IV - 4.5 milliliters of Filtrate

V and VI - Three milliliters of Filtrate

maximal activity as shown from Figure 33. Curve I is the shows the rate of conversion using six milliliters of normal filtrate, and Curve II the same after activation of the filtrate. The increased rate and yield is evident in Curve II. Curve III similarly was obtained using 4.5 milliliters of filtrate unactivated while Curve IV was obtained using the same volume of activated filtrate. In Curves V and VI the amount of filtrate was reduced to three milliliters.

Figure 37 shows a similar series of curves when the amount of filtrate is kept constant at three milliliters and tha amount of hexamine dinitrate varied. In all cases six milliliters of acetic anhydride was used. Curve I shows the course of the reaction when one gram of hexamine dinitrate is used and the filtrate is unactivated, while Curve II shows similar data when the activated filtrate is used. Curves III and IV were obtained when the amount of hexamine dinitrate was reduced to 0.5 grams, and Curves V and VI when the amount of dinitrate was reduced again to 0.25 grams. These show the very great depressing effect of large

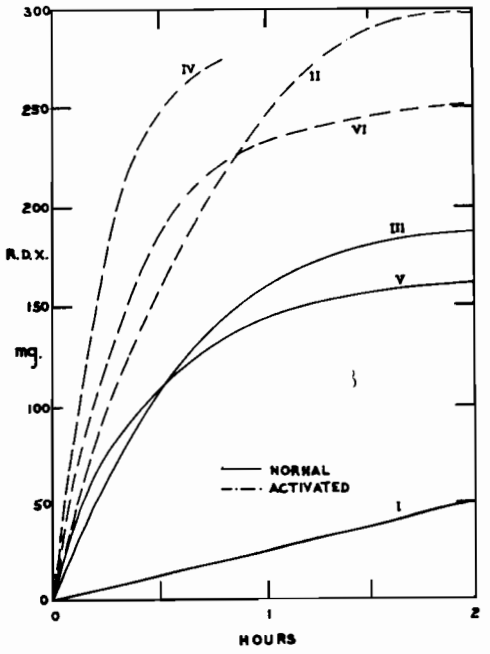


FIGURE 37 - Rates of Conversion of Hexamine Dinitrate to R.D.X. using Activated and Normal Filtrates with variable Amounts of Hexamine Dinitrate.

I and II - 1.0 grams of Hexamine Dinitrate

III and IV - 0.5 grams of Hexamine Dinitrate

V and VI - 0.25 grams of Hexamine Dinitrate

amounts of hexamine dinitrate, an effect not entirely eliminated by activation of the filtrate. This does show however that part of the depressing effect of hexamine dinitrate is on the process which is involved in the activation of the filtrate. It should be noted that both the rate of conversion and the yield are improved by activation of the filtrate, but it has been observed generally that the two effects usually occur together.

Figure 38 shows the effect of using various amounts of acetic anhydride with a constant amount of filtrate, three milliliters, and 0.5 grams of hexamine dinitrate. Curve I shows the results using normal filtrate and six milliliters of acetic anhydride, and Curve II similarly using activated filtrate. Curves III and IV were obtained using four milliliters of acetic anhydride, while for Curves V and VI the amount of anhydride was reduced to three milliliters. Reduction of the acetic anhydride to two milliliters gave the results shown in Curves VII and VIII. It is evident that the reaction using normal filtrates is very markedly affected by the decrease in the amount of

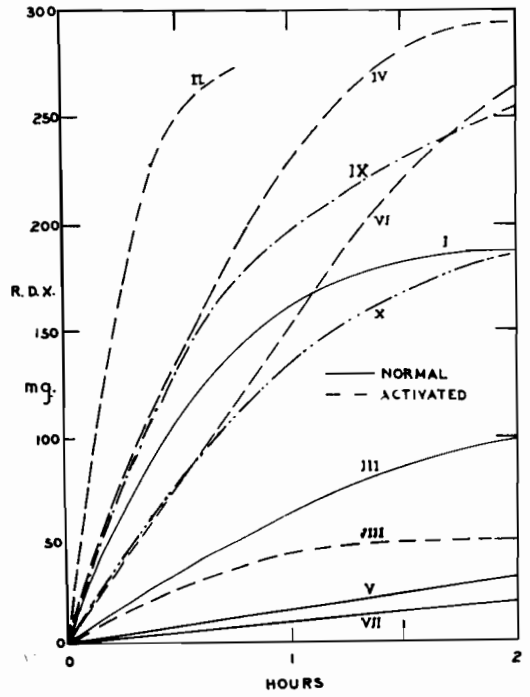


FIGURE 38 - Rates of Conversion of Hexamine Dinitrate to R.D.X. using Activated and Normal Filtrates and various Amounts of Acetic Anhydride.

I and II - Six Milliliters of Anhydride

III and IV - Four Milliliters of Anhydride

V and VI - Three Milliliters of Anhydride

VII and VIII - Two Milliliters of Anhydride

anhydride, and that the effect of activation is very great. The rapid decrease in the effectiveness between three and two milliliters of anhydride has made possible a criterion for the identification of beneficial dehydrating agents which will be discussed in the next section. Even after activation of the filtrate the amount of acetic anhydride has a marked effect on the rate of conversion of hexamine dinitrate to R.D.X. and the resultant yield of R.D.X.

Defining the amount of R.D.X. produced during the first 15 minutes of the reaction as a rough estimate of the initial rate of the reaction and the maximum yield indicated as the probable end-point of the reaction the results tabulated below are obtained. In Table 36 the relation of rate of conversion and yield to the amount of filtrate used is shown.

TABLE 36

EFFECT OF AMOUNT OF FILTRATE ON THE RATE OF CONVERSION AND YIELD

Amount of Filtrate	Before Activation		After Activation	
	Rate	Yield	Rate	Yield
6 ml	260	430	276	650
4.5	150	352	230	500
3	58	195	164	350

It can be seen that after activation both the rate of conversion to R.D.X. and the yield become more nearly proportional to the amount of filtrate used.

Similarly Table 37 shows the relation to the amount of hexamine dinitrate used.

TABLE 37

EFFECT OF AMOUNT OF HEXAMINE DINITRATE ON THE RATE OF CONVERSION AND YIELD OF R.D.X.

Amount of Hexamine Dinitrate	Before Activation		After Activation	
	Rate	Yield	Rate	Yield
1.0 gm	10	50	90	300
0.5	58	195	164	350
0.25	66	160	121	250

There is no indication of proportionality in this series, but only that both the rate and yield are much improved relative to the amount of hexamine dinitrate used as the amount of hexamine dinitrate is reduced. The smallest amount of hexamine dinitrate was converted at the greatest relative rate and with the greatest relative yield.

Table 38 shows the effect of variations in the amount of acetic anhydride on the rate of conversion to R.D.X. and the yield of R.D.X.

TABLE 38

EFFECT OF AMOUNT OF ACETIC ANHYDRIDE ON THE RATE OF CONVERSION AND YIELD OF R.D.X.

Amount of Anhydride	Before Activation		After Activation	
	Rate	Yield	Rate	Yield
6 ml	58	195	164	350
4	18	96	82	294
3	6	30	47	254
2	2	26	12	51

There does not seem to be any proportionality shown in this series. There is the sharp cut-off in rate of conversion and yield between two and three milliliters of acetic anhydride when activated filtrate is used, and a less marked one between six and four milliliters when the normal or unactivated filtrate is used.

Curve IX of Figure 38 shows the data obtained in a manner exactly as in Curve VI except that boron trifluoride was added as catalyst. It can be seen that boron trifluoride has a less marked effect at this stage of the reaction than on the process of activation. This suggested that the process which boron trifluoride catalized, probably hydrolysis or acetylation, is not the rate determining factor in this case but may be in the activation process.

Curve X of Figure 38 is intended to show that the intermediate as prepared in acetic acid medium from paraformaldehyde and ammonium nitrate can be replaced by hexamine dinitrate prepared from

hexamine. All of the data recorded in this section and preceding sections, unless otherwise stated, were obtained using the intermediate prepared in acetic acid. When hexamine dinitrate prepared from hexamine replaces this intermediate under identical conditions used in obtaining Curve VI, Curve X results. The smaller yield and rate of conversion are not considered sufficiently different to be inexplicable on the basis of different samples of filtrate and hexamine dinitrate. These data were used as evidence in favour of the identification of the intermediate as hexamine dinitrate.

It had been reported that propionic anhydride (34) could replace acetic anhydride but the quality of the propionic anhydride and the limited amount available did not permit a thorough investigation. Thus the problem was reinvestigated.

In Figure 39 are shown the results obtained when propionic anhydride replaces acetic anhydride. These curves were obtained using six milliliters of the anhydride with six milliliters of filtrate and 0.5 grams of hexamine dinitrate. Curve 1 shows the rate of production of R.D.X. using normal filtrate,

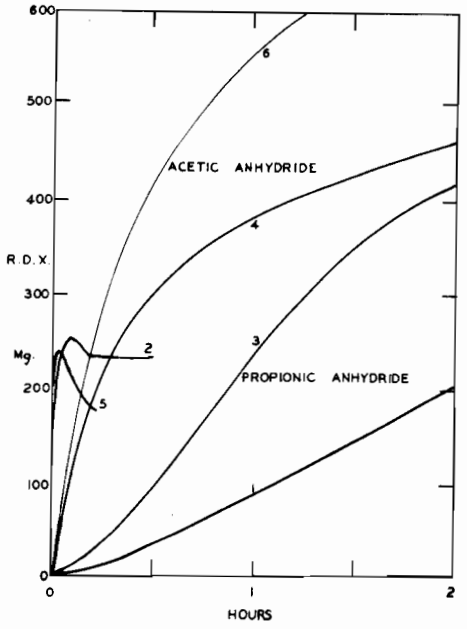


FIGURE 39 - Comparison of Propionic and Acetic Anhydrides, six milliliters of Anhydride with six milliliters of Filtrate.

1 and 4 - Normal Filtrates

2 and 5 - Activation Curves

3 and 6 - Activated Filtrates

while Curve 2 shows the rate of activation of the filtrate, both with propionic anhydride. Curve 3 shows the rate after the filtrate has been activated. Curves 4, 5 and 6 are comparable curves using acetic anhydride.

These data show that while the rate and yield when propionic anhydride is used are lower than when acetic anhydride is used, they are of the same order of magnitude and do not differ by a factor of 225 such as do the rates of hydrolysis of the two anhydrides at 25°C (48). Later it will be shown that these effects can be explained on the basis of solvent effect.

Thus there appears to be two phases to the reaction to produce R.D.X. after the addition of the anhydride. One involves the hydrolysis of the anhydride. This is inhibited by the presence of hexamine dinitrate probably as a result of its basic character in acetic acid medium, and is promoted by boron trifluoride. The second phase,

the production of R.D.X., proceeds at its optimal rate and to optimal yield on the completion of the first phase, but inefficiently otherwise. The rates of conversion of the hexamine dinitrate and the yield resulting seem to be independent of the rates of hydrolysis of the anhydrides but seem to be related to the absolute amount of the anhydrides present. The first phase would seem to be the drying of the filtrate by the anhydride; this is supported by the findings of the next section.

USE OF OTHER DEHYDRATING AGENTS

Since acetic and propionic anhydrides are the only two dehydrating agents which the previous investigations had shown to be effective, it was of interest to determine in which phase of the process they were indispensable and to replace them if possible. Later Bachmann reported (49) that butyric anhydride could be used also.

It was assumed that acetic anhydride could have three rôles, (a) dehydration of the medium since it was noted visibly that water was liberated when the intermediate was formed in heptane or nitromethane and could be presumed to do so also in acetic acid, (b) a solvent effect by which it favoured the nitration of hexamine dinitrate, and (c) the specific effect if any on the reaction between hexamine dinitrate and the filtrate factor.

All of the studies on the effect of other dehydrating agents upon the filtrate indicated that the removal of water was one of the important rôles

of the anhydride. The criterion used to determine the effectiveness of a reagent was that it should lower the amount of acetic anhydride required to produce R.D.X. with three milliliters of activated filtrate and 0.5 grams of hexamine dinitrate in a total volume of 12 milliliters, the residual volume being acetic acid. Three milliliters of acetic anhydride was considered to be the normal lower limit; if three milliliters was insufficient then the added reagent was deleterious while if less than three milliliters sufficed then the reagent was considered to be acting in the same way as acetic anhydride, and with benefit to the process.

Drying the filtrate with Drierite or Activated Alumina resulted in a filtrate which gave no R.D.X. even with the three milliliters of acetic anhydride. Treating the filtrate with acetyl chloride, sulphuryl chloride or phosphoric oxide and leaving the reagents in the filtrate also resulted in no yield of R.D.X. with three milliliters of acetic anhydride. All of the above reagents were deleterious.

In the chance that the solvent effect might be at fault, some heptane and carbon tetrachloride was added to the filtrate dried by phosphorus pentoxide, but the results were negative. However if the filtrate were decanted from the residual reagent then the results whoen in Table 39 were obtained.

TABLE 39

EFFECT OF PHOSPHORUS PENTOXIDE ON THE AMOUNT OF ACETIC ANHYDRIDE REQUIRED

Anhydride Added	Treated Filtrate	Untreated Filtrate
3 ml	233 mg	254 mg
2	182	30

This shows the beneficial effect of phosphorus pentoxide and indicates that this material was removing part of the water which normally had to be removed by acetic anhydride. The addition of boron trifluoride to the above mixture was deleterious, lowering the yields to 136 and 97 milligrams respectively with three and two milliliters of acetic anhydride.

It was of interest to study other acid anhydrides and dibasic ones were readily available. Unfortunately their rates of hydrolysis are very slow. Succinic anhydride failed to replace acetic anhydride even to the slightest extent, but if boron trifluoride catalyst was added first and the filtrate allowed to stand with the catalyst and succinic anhydride for 18 hours, then under the experimental conditions laid down above, two milliliters of acetic anhydride was sufficient to produce 93 milligrams of R.D.X. While the beneficial effect is not great and there is no control experiment to show the effect, if any, which the boron trifluoride might have over that time period, it may be inferred that succinic anhydride was slightly effective. Under the same conditions maleic anhydride failed to give any R.D.X.

Azeotropic distillation using benzene seemed a possible means of dehydrating the medium. Some of the filtrate was overlayered by benzane and the mixture distilled in vacuo at 35°C until the benzene was removed. The filtrate was restored to its original volume. The results obtained are shown in Table 40.

TABLE 40

EFFECT OF AZEOTROPIC DISTILLATION WITH BENZENE ON THE AMOUNT OF ACETIC ANHYDRIDE REQUIRED

Anhydride Added	Treated Filtrate	Untreated Filtrate
3 ml	251 mg	254 mg
2 ml	156 mg	30 mg

This shows that the distillation enabled R.D.X. to be produced with a lower concentration of acetic anhydride. Following this further, the intermediate was prepared in heptane and the water removed by azeotropic distillation. Then hexamine dinitrate was added and the distillation continued. No R.D.X. was formed.

The information accumulated seems to favour the idea that one of the rôles of acetic anhydride is to remove water liberated in the condensation of formaldehyde and ammonium nitrate to give hexamine dinitrate. In as much as this difficulty is overcome by the use of hexamine or hexamine dinitrate in the Bachmann Process, no further investigations were made along this line. If necessary either a chemical

means, phosphorus pentoxide, or a physical means, azeotropic distillation with benzene could be used to dry the filtrate, that is to activate it, and so reduce the amount of anhydride required for the process.

EFFECT OF SOLVENT ON THE RATE OF NITROLYSIS OF HEXAMINE DINITRATE

Ingold and co-workers (50) studied the effect of solvent on the nitration of benzene. They divided the solvents into fast, intermediate and slow. The fast solvent was sulphuric acid but no attempt to use that solvent for the nitration of hexamine dinitrate was made since R.D.X. is decomposed by concentrated sulphuric acid. Intermediate solvents were nitromethane and acetic anhydride, and the slow solvents were acetic acid, acetonitrile and dioxane. In the present investigations, propionic anhydride, propionic acid, benzene and nitrobenzene were also used. Attempts to use heptane resulted in the formation of two phases.

The technique was as follows: To three milliliters of the filtrate from which the hexamine dinitrate had been removed was added six milliliters of the solvent under investigation followed by three milliliters of acetic anhydride. The filtrate was

activated for 30 minutes and 0.5 grams of hexamine dinitrate added. The amount of R.D.X. was determined at various times thereafter in the normal manner. The results are shown in Figure 40.

From these data it is evident that the solvents may be arranged in the order of decreasing effectiveness in promoting nitrolysis of hexamine dinitrate: acetic anhydride, propionic anhydride, nitromethane, nitrobenzene, acetic acid, acetonitrile, benzene, propionic acid, and entirely ineffective, dioxane. The best substitutes for the solvent effect of acetic anhydride would be nitromethane, nitrobenzene and acetic acid in that order, omitting propionic anhydride as a possible substitute.

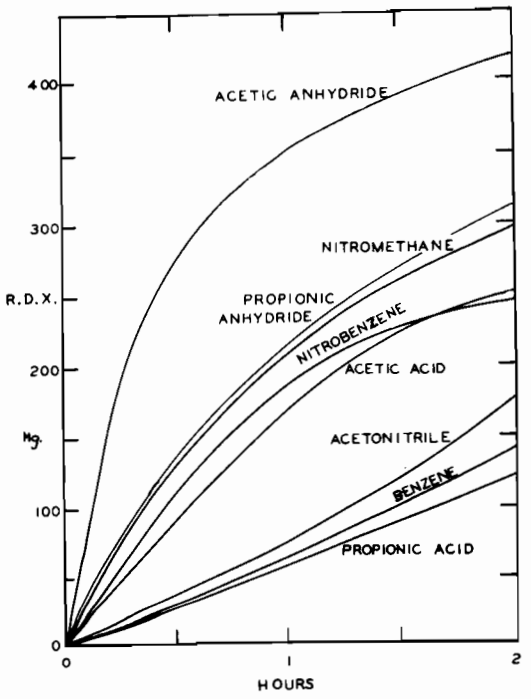


FIGURE 40 - Effect of Solvent on the Rate of Nitrolysis of Hexamine Dinitrate at 35°C.

FORMATION OF HEXAMINE DINITRATE FROM HEXAMINE IN ACETIC ACID MEDIUM

The amount of nitric acid required to convert hexamine to hexamine dinitrate in acetic acid medium (10 milliliters) is shown from Figure 41. From this it can be seen that the amount of hexamine dinitrate recovered by filtering the solution rises to a maximum with a comparatively small amount of nitric acid, and then falls off slowly. The amount of nitric acid required for maximal recovery is about 0.01 moles for about 0.004 moles of hexamine, that is, slightly more than enought to convert the hexamine to the dinitrate.

The lower curve of the same figure shows the recovery of hexamine dinitrate when 0.5 grams of that material are shaken in 10 milliliters of acetic acid solution of the various nitric acid contents. It shows that as the nitric acid increases the amount of hexamine dinitrate added is less and less completely recovered.

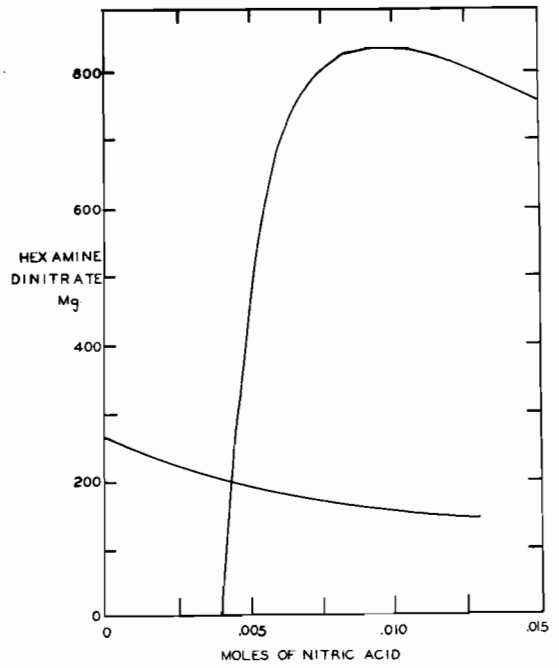


FIGURE 41 - Formation of Hexamine Dinitrate from Hexamine (Upper) and solubility of Hexamine Dinitrate (Lower), in Acetic Acid Solution of various Acid Concentrations.

The rôle of nitric acid in governing the appearance and recovery of hexamine dinitrate may explain why under certain conditions no hexamine dinitrate forms in the McGill Process at 35°C.

There seems to be no correlation between the amounts of sulphuric acid or ammonium nitrate added and the appearance of the precipitate of hexamine dinitrate. Six milliliters of acetic acid and six milliliters of a mixture of one volume of 70 percent nitric acid and 11 volumes of acetic acid were mixed and 0.5 grams of hexamine added as well as the indicated amounts of sulphuric acid and ammonium nitrate. The hexamine dinitrate was filtered off after one hour at 35°C, dried with acetone and weighed. As shown from Table 41, in all cases the yield was over 90 percent (theoretical yield 0.95 grams) with some indication that the sulphuric acid increased the yield to over 100 percent which may be due to the formation of mixed salts of higher acid content.

TABLE 41

EFFECT OF AMMONIUM NITRATE AND SULPHURIC ACID ON THE FORMATION OF HEXAMINE DINITRATE

Ammonium Nitrate	Sulphuric Acid	Yield of Hexamine Dinitrate
0.0 gm		.94 gm
0.05		.90
0.10		.91
0.25		.89
0.40		.85
0.60		.90
0.25	0.00 ml	.92
0.25	0.05	.95
0.25	0.10	.92
0.25	0.15	1.00
0.25	0.20	1.00
0.25	0.25	1.03

BACHMANN PROCESS

OPTIMAL NITRIC ACID AND AMMONIUM NITRATE CONCENTRATIONS FOR THE NITROLYSIS OF HEXAMINE AND HEXAMINE DINITRATE IN ACETIC AND PROPIONIC ANHYDRIDES.

The study of the Ross Reaction showed that hexamine dinitrate or hexamine was an intermediate in that process and hence that the final conversion of intermediate to R.D.X. was essentially the same as in the Bachmann Process. In the latter process the first rôle of acetic anhydride, that of removing the water formed at the same time as the intermediate in the McGill Process, is eliminated by the use of prepared intermediate and absolute nitric acid. The second rôle, that of solvent is common to both processes and presumably the same considerations and conclusions apply. However the third rôle which was postulated, the specific effect, if any, which the anhydride may play in the final conversion of intermediate to R.D.X. is much more easily studied in what is essentially the Bachmann Process, by which the filtrate of uncertain composition is replaced by nitric acid, ammonium nitrate and acetic acid. This

section is concerned entirely with determining the effect of variations of these three components, as well as comparing acetic and propionic anhydrides.

A solution of acetyl nitrate was prepared by mixing one volume of 70 percent nitric acid with 12 volumes of acetic anhydride. A second solution of equal volumes of acetic acid and acetic anhydride was saturated with ammonium nitrate. Various proportions of these two solutions were mixed and the R.D.X. yield obtained after two hours at 35°C for 10 milliliters of the solution and 0.5 grams of hexamine dinitrate. R.D.X. was obtained only when the first solution was present in about 40 percent of the total volume, and even then the yields were poor.

Using the first solution as 40 percent of the total volume, various amounts of ammonium nitrate were added. The yield of R.D.X. after two hours at 35°C rose from a very small value to an appreciable value when 250 milligrams of ammonium nitrate were present. The yield failed to increase with further addition of ammonium nitrate, and even when 250 milli-

grams of the nitrate were used some excess remained on the bottom of the flask. The data are summarized in Table 42.

TABLE 42

EFFECT OF AMMONIUM NITRATE ON THE YIELD OF R.D.X.

Ammonium Nitrate	Yield R.D.X.
0.0 gm	0.035 gm
0.25	0.215
0.50	0.230
0.75	0.230
1.00	0.215
1.50	0.230

These data seemed to indicate that the maximal amount of ammonium nitrate required was about 0.25 grams (0.003 moles) in the 10 milliliter volume and this amount was used in most of the remaining investigations of this section.

With the amount of ammonium nitrate determined it was possible to determine the optimal nitric acid concentration. The solution of nitric acid in the appropriate acid-anhydride mixture was obtained by mixing various proportions of two solutions. The first one in each case was made by

mixing 70 percent nitric acid with enough of the anhydride to give the medium when the water was taken up a composition of about 50 percent anhydride and 50 percent the corresponding acid. The second solution was an equal volume mixture of the anhydride and the corresponding acid. Thus the mixtures were always 50 percent anhydride when the reaction was started. The R.D.X. was determined after a fixed time at 35°C.

The results are shown in Figure 42. Curve i shows that the optimal nitric acid content in the 10 milliliter volume is about 0.009 moles for the conversion of 0.002 moles of hexamine dinitrate to R.D.X. in the propionic anhydride - propionic acid medium, while the optimal amount is but 0.003 moles in acetic anhydride - acetic acid medium, Curve 2. This shows that much higher amounts of acid (nitric) are required when propionic anhydride is used. When hexamine replaces hexamine dinitrate the amounts of nitric acid for optimal yields are respectively 0.014 moles (Curve 3) and 0.008 moles ¢Curve 4). The increased amount of nitric acid is approximately

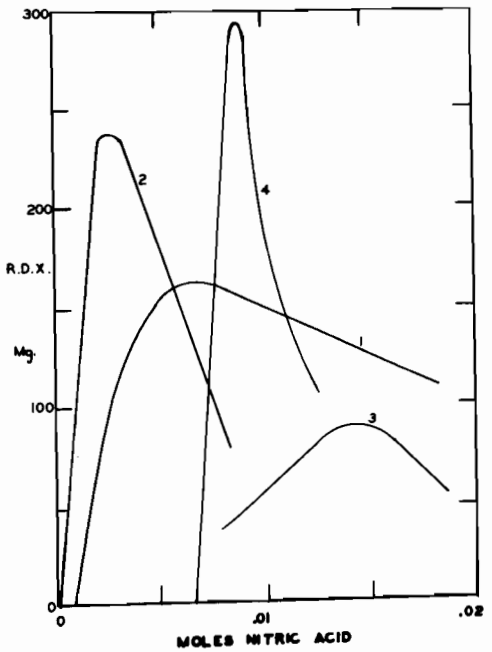


FIGURE 42 - Effect of Nitric Acid Concentration on the Yield of R.D.X. in Acid-Anhydride Mixtures.

1 - Propionic Anhydride and Hexamine Dinitrate

2 - Acetic Anhydride and Hexamine Dinitrate

3 - Propionic Anhydride and Hexamine

4 - Acetic Anhydride and Hexamine

that amount required to convert the 0.002 moles of hexamine to the dinitrate.

The differences in the heights of the peaks are due partly to differences in the length of time chosen before the R.D.X. was determined, which time differed from curve to curve but was constant for a given curve, and partly due to the solvent effect. Thus referring to Figure 40 it can be seen that the rate and yield for the conversion to R.D.X. are going to be much less in a propionic anhydride - propionic acid medium.

These data are of considerable interest in connection with the work reported in the previous sections on the study of the McGill Process. There, in most cases, 0.02 moles of formaldehyde were used in an excess of ammonium nitrate. If all of the formaldehyde went to form hexamine dinitrate then there would be 0.003 moles of hexamine dinitrate and 0.006 moles of nitric acid formed. These values lie very close to the optimal values determined above. Thus it is evident that if hexamine or hexamine dinitrate is

the intermediate in the McGill Process, ample nitric acid would be liberated to convert the hexamine to R.D.X. either directly or through the dinitrate stage.

The rates of conversion of hexamine dinitrate and hexamine to R.D.X. in the acetic acid- acetic anhydride medium and propionic acid - propionic anhydride medium are shown in Figure 43. Curve 1 and Curve 3 are the results when hexamine dinitrate (0.5 grams) and ammonium nitrate (0.25 grams) are used is propionic acid - propionic anhydride and acetic acid - acetic anhydride media respectively with the optimal amounts of nitric acid as shown from Figure 42. Curves 2 and 4 represent similar data when hexamine (0.265 grams) is used instead of the dinitrate. All determinations were made at 35°C.

The rate is decreased by replacing acetic acid and acetic anhydride by propionic acid and propionic anhydride as would be expected from the solvent effect, Figure 40. The inversion of the effect of the two anhydrides on hexamine and hexamine dinitrate is interesting. When acetic anhydride is

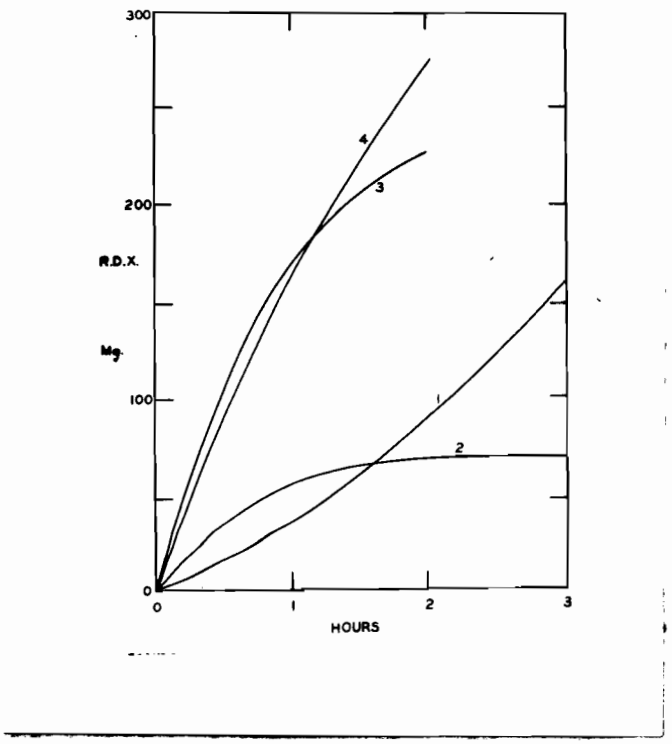


FIGURE 43 - Rates of Formation of R.D.X. in Acid-Anhydride Mixtures at 35°C.

1 - Propionic Anhydride and Hexamine Dinitrate

2 - Propionic Anhydride and Hexamine

3 - Acetic Anhydride and Hexamine Dinitrate

4 - Acetic Anhydride and Hexamine

used the rate is higher and yield lower when hexamine dinitrate is converted to R.D.X., but when propionic anhydride is used the same is true of the conversion of hexamine. The fact that the rates of conversion of hexamine and the dinitrate lie so close together for a given solvent suggests that the same reaction is involved in each case, or else that the conversion of the one to the other is so rapid that no induction period is observed.

The results given above were obtained in media which were 50 percent anhydride to start with. Later investigations involved the use of copper nitrate trihydrate with acetic anhydride. In these the amount of acetic or propionic acid formed by hydrolysis of the water of crystallization varied as the amount of the trihydrate varied. Hence to compare the data obtained when copper nitrate was used with comparable data using nitric acid it was necessary to repeat the work outlined in the immediately foregoing section using different experimental conditions. It was observed that 70 percent nitric acid could be considered to be

$$(HNO_3)_2 \cdot 3\ H_2O.$$

Thus an appropriate mixture of 70 percent nitric acid and the anhydride under test was mixed in variable amounts with pure anhydride to give a total volume of 10 milliliters. Thus as the amount of nitric acid increased, the amount of acid formed by the hydrolysis of the anhydride by the "water of crystallization" also increased. This is acknowledged to complicate the system but would seem to have the virtue of allowing one to compare the effect of the substituted nitric acid with the nitric acid itself.

The data for the optimal amounts of nitric acid required for this system are shown in Figure 44. In all cases 0.25 grams of ammonium nitrate were included. When 0.002 moles of hexamine dinitrate are used the optimal amount of nitric acid is 0.004 moles (Curve 1) and when an equivalent amount of hexamine was used the optimal amount was 0.007 moles, Curve 2, a somewhat smaller increase than is necessary for complete conversion of the hexamine to the dinitrate. When propionic anhydride is used the optima are respectively 0.008 moles, Curve 3, and 0.011 moles, Curve 4. Again less additional nitric acid must be added than is required to convert the

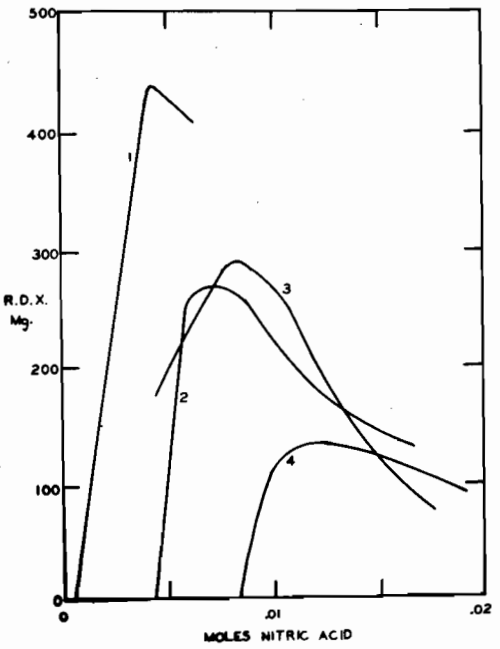


FIGURE 44 - Effect of Nitric Acid Concentration on The Production of R.D.X. in Anhydride at 35°C.

1 - Acetic Anhydride and Hexamine Dinitrate

2 - Acetic Anhydride and Hexamine

3 - Propionic Anhydride and Hexamine Dinitrate

4 - Propionic Anhydride and Hexamine

hexamine to the dinitrate, and this together with the lower yield in contrast with the results shown in Figure 42 suggest that when the acetic acid is omitted from the medium the conversion of hexamine to hexamine dinitrate is not taking place so readily or completely as it is when the medium is 50 percent acetic or propionic acid to start with.

Using the optimal concentrations of nitric acid as indicated from Figure 44, the rates of conversion of hexamine and hexamine dinitrate to R.D.X. in acetic and propionic anhydrides were measured at 35°C. These are shown in Figure 45. Curves 1 and 2 show the results obtained using hexamine dinitrate and hexamine respectively with acetic anhydride, and Curves 3 and 4 are for hexamine dinitrate and hexamine respectively with propionic anhydride. In all cases 0.002 moles of reactant were used, and 0.250 grams of ammonium nitrate. These data show the slowing down of the rate due to the propionic anhydride replacing acetic anhydride, and it is evident that hexamine is no longer being converted to R.D.X. at a rate comparable

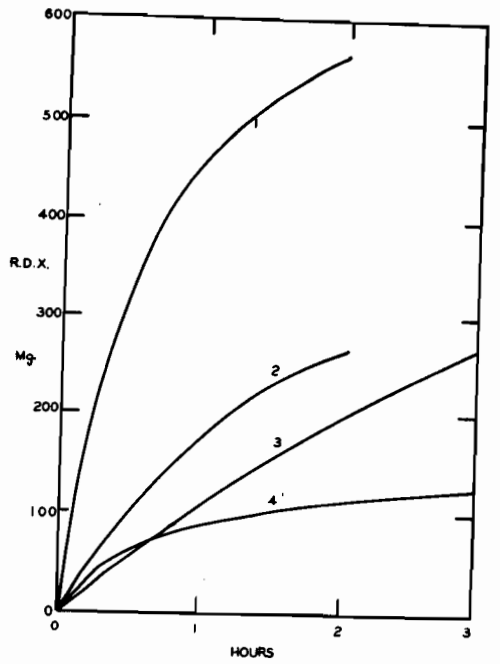


FIGURE 45 - Rates of Formation of R.D.X. in Anhydride Medium at 35°C.

1 - Acetic Anhydride and Hexamine Dinitrate

2 - Acetic Anhydride and Hexamine

3 - Propionic Anhydride and Hexamine Dinitrate

4 - Propionic Anhydride and Hexamine

with hexamine dinitrate in contrast with the results in Figure 43. The lowering of the acetic acid content has resulted in a slower and less complete conversion of hexamine to R.D.X.

When it was observed in later investigations that 0.250 grams of ammonium nitrate were insufficient for optimal yield under certain conditions, and that the amount of ammonium nitrate was of great importance in the reaction, the effect of the amount of ammonium nitrate on the yield was determined for the experimental conditions used above. The results are shown in Figure 46. There the yield of R.D.X. using 0.002 moles of hexamine dinitrate or hexamine and the optimal concentrations of nitric acid in a 10 milliliter volume of the anhydride as indicated from Figure 44 are plotted against the amount of ammonium nitrate added. They show that rather than 0.250 grams of ammonium nitrate, the amount should be of the order of 0.5 grams or about 0.01 moles. However this affects the absolute magnitude of the values in the preceding work and not the relative values, so that this does not invalidate the conclusions drawn.

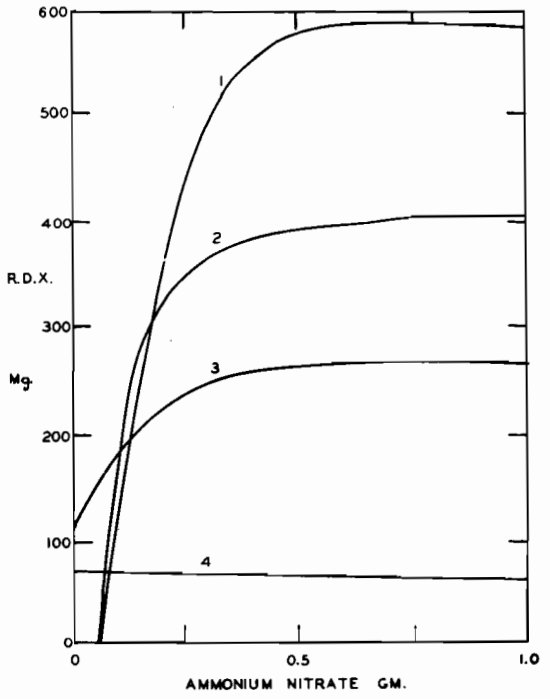


FIGURE 46 - Effect of Ammonium Nitrate on the Yield of R.D.X. in Anhydride Medium at 35°C.

1 - Hexamine Dinitrate in Acetic Anhydride

2 - Hexamine in Acetic Anhydride

3 - Hexamine Dinitrate in Propionic Anhydride

4 - Hexamine in Propionic Anhydride

The differences between the series using 70 percent nitric acid and anhydride mixtures and the earlier series in which there was added acetic or propionic acid might be accentuated by using absolute nitric acid instead of the 70 percent nitric acid. In this way less anhydride is used up in removing the water and very little acetic or propionic acid is present. The technique was in every way the same as previously.

The optimal nitric acid concentrations in 10 milliliter volumes of anhydride with 0.250 grams of ammonium nitrate present may be found from Figure 47, where the effect of nitric acid added on the yield is recorded. Curve 1 shows that the optimal amount of nitric acid for the conversion of hexamine dinitrate (0.002 moles) to R.D.X. in acetic anhydride is 0.004 moles while when hexamine is used (0.002 moles also) the optimum is raised to 0.007 moles, Curve 2, an increase less than that required to convert the hexamine to the dinitrate. Curves 3 and 4 are similar data when propionic anhydride is used, and the optima are respectively 0.011 and 0.015 moles.

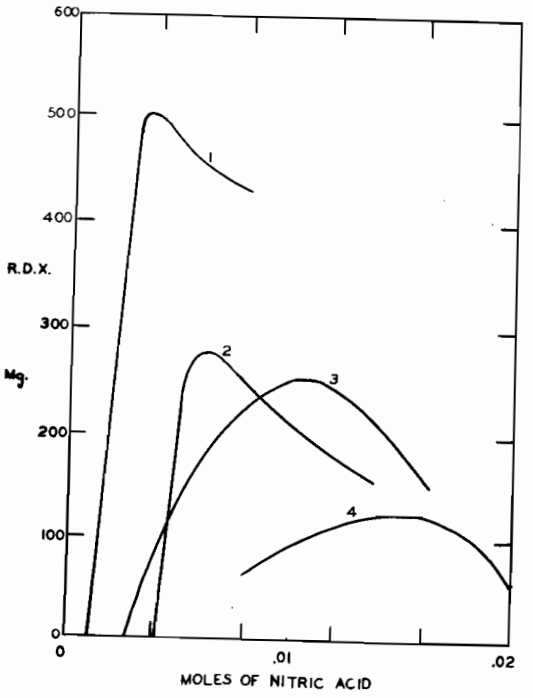


FIGURE 47 - Effect of Nitric Acid (Absolute) Concentration on the Yield of R.D.X. in Anhydride Medium at 35°C.

1 - Hexamine Dinitrate in Acetic Anhydride

2 - Hexamine in Acetic Anhydride

3 - Hexamine Dinitrate in Propionic Anhydride

4 - Hexamine in Propionic Anhydride

The increase in the amount of acid in this case is the same as that required to convert the hexamine to the dinitrate, but the very great decrease in the yield when hexamine is used suggests that the hexamine is not being so converted.

The rates of conversion of hexamine dinitrate and hexamine to R.D.X. under the above conditions are shown in Figure 48. Curve 1 shows the rate at which hexamine dinitrate (0.002 moles) is converted to R.D.X. using the optimal amount of nitric acid as given by Figure 47, in a 10 milliliter volume with 0.250 grams of ammonium nitrate present. Similar results when hexamine is used are shown in Curve 2, while the results when propionic anhydride is used are shown in Curves 3 and 4 respectively for hexamine dinitrate and hexamine.

The results in the preceding two figures were obtained with only 0.250 grams of ammonium nitrate present. The effect of ammonium nitrate on this system is indicated in Figure 49. Curves 1 and 2 are the results obtained when hexamine di-

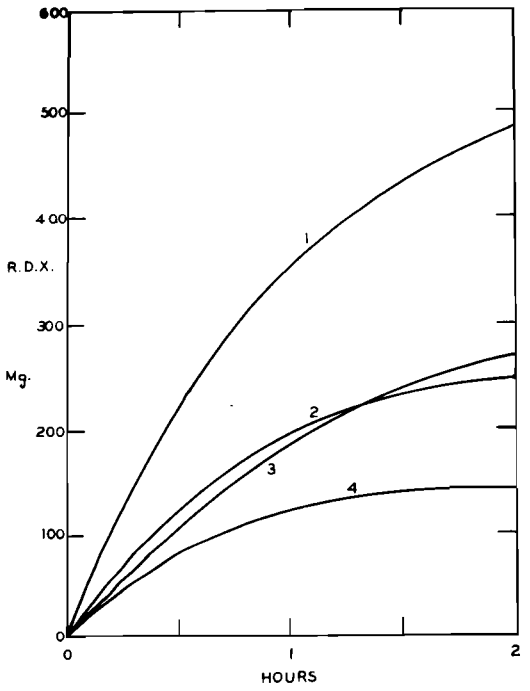


FIGURE 48 - Rates of Production of R.D.X. in Anhydride Medium at 35°C, Absolute Nitric Acid.

1 - Hexamine Dinitrate in Acetic Anhydride

2 - Hexamine in Acetic Anhydride

3 - Hexamine Dinitrate in Propionic Anhydride

4 - Hexamine in Propionic Anhydride

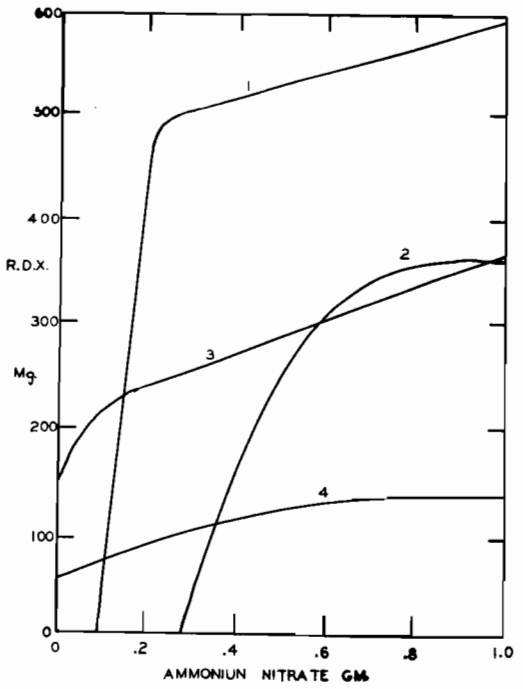


FIGURE 49 - Effect of Ammonium Nitrate on the Yield of R.D.X. in Anhydride Medium at 35°C, Absolute Nitric Acid.

1 - Hexamine Dinitrate in Acetic Anhydride

2 - Hexamine in Acetic Anhydride

3 - Hexamine Dinitrate in Propionic Anhydride

4 - Hexamine in Propionic Anhydride

nitrate (0.002 moles) and hexamine (0.002 moles) are used respectively in acetic anhydride with optimal amounts of nitric acid as shown from Figure 47 present in the 10 milliliter volume of anhydride. Curves 3 and 4 are similar data when propionic anhydride is used. Again it can be seen that amounts less than 0.5 grams of ammonium nitrate are not sufficient for optimal yield.

Only a few experiments were conducted using nitrogen pentoxide instead of nitric acid, a solution of acetyl nitrate being made by dissolving nitrogen pentoxide in acetic anhydride and diluting this as required with acetic anhydride. The few determinations indicated that the optimal concentrations of nitrogen pentoxide calculated on the basis of potential nitric acid were 0.006 and 0.007 moles respectively for hexamine dinitrate and hexamine in 10 milliliters of acetic anhydride, 0.002 moles of hexamine dinitrate or hexamine and 0.250 grams of ammonium nitrate being used. That the rates of conversion and yields are quite similar to those obtained when absolute nitric acid is used is shown in Table 43.

TABLE 43

RELATIVE RATES AND YIELDS WHEN NITRIC ACID AND NITROGEN PENTOXIDE ARE USED IN ACETIC ANHYDRIDE

	Nitric Acid		Nitrogen Pentoxide	
	Rate	Yield	Rate	Yield
Hexamine Dinitrate	130	500	115	450
Hexamine	60	225	50	250

The effect of ammonium nitrate is also the same as shown from Figure 50. The upper curve shows the effect on the yield of R.D.X. from hexamine dinitrate (0.002 moles), the lower the effect on the yield from hexamine. The yields are those obtained using optimal amounts of nitrogen pentoxide and the indicated amounts of ammonium nitrate in a 10 milliliter volume of acetic anhydride, and as in the previous experiments, after two hours at 35°C.

Thus there are four series of experiments in which nitric acid or nitrogen pentoxide was used, a medium 50 percent anhydride, a medium with about 75 percent anhydride, a medium practically pure

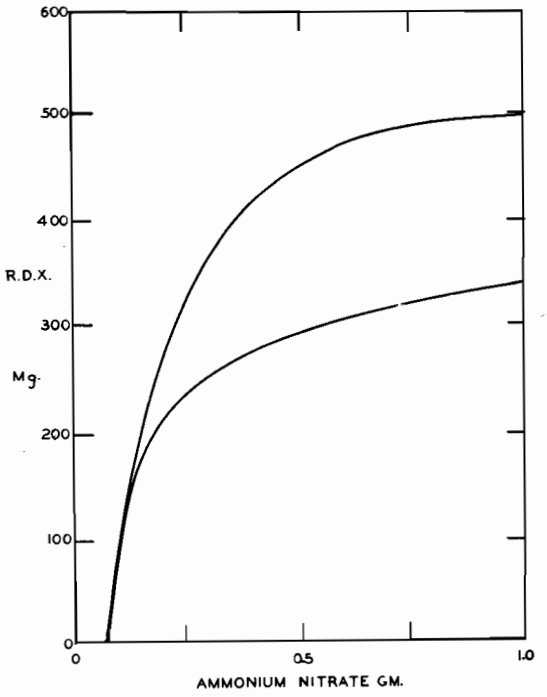


FIGURE 50 - Effect of Ammonium Nitrate on the Yield of R.D.X. in Anhydride Medium at 35°C, Nitrogen Pentoxide.

Upper - Hexamine Dinitrate in Acetic Anhydride

Lower - Hexamine in Acetic Anhydride

anhydride and then one composed of acetyl nitrate in acetic anhydride medium. Comparison of these shows some interesting facts.

From Table 44 it can be seen that as the amount of acetic or propionic acid present or formed by hydrolysis of the anhydride is reduced the rate of production of R.D.X. and the yield are increased when hexamine dinitrate is used while this is not true when hexamine is used. While the results are rather irregular there is some indication that the complete disappearance of acetic acid may lower the rate of production of R.D.X. and yield. This may be related to the effect of acetic acid in lowering the induction period in the Ross Reaction (34), or to the solubility of ammonium nitrate in the medium. The results do not permit an estimate of the optimal amount of acetic acid which should be present. The results using propionic anhydride differ in that there is no indication of an optimal concentration of propionic acid.

TABLE 44

EFFECT OF ACETIC OR PROPIONIC ACID ON RATE OF PRODUCTION AND YIELD OF R.D.X. FROM HEXAMINE AND THE DINITRATE

	50 percent anhydride	Nitric Acid 70%	Nitric Acid Absolute	Nitrogen Pentoxide
Acetic Anhydride				
Hexamine Dinitrate				
Rate	60	160	130	115
Yield	250	575	500	450
Hexamine				
Rate	55	50	60	50
Yield	300	300	225	250
Propionic Anhydride				
Hexamine Dinitrate				
Rate	10	30	80	
Yield	160	275	270	
Hexamine				
Rate	20	25	50	
Yield	70	125	140	

A second point of interest is that as the form in which the nitric acid is introduced is varied, the optimal concentration remains very nearly constant. The results are shown in Table 45.

TABLE 45

OPTIMAL NITRIC ACID CONCENTRATIONS

	50 Percent Anhydride	Nitric Acid 70%	Nitric Acid Absolute	Nitrogen Pentoxide
Acetic Anhydride				
Hexamine Dinitrate	0.003	0.004	0.004	0.006
Hexamine	0.008	0.007	0.007	0.007
Propionic Anhydride				
Hexamine Dinitrate	0.009	0.008	0.011	
Hexamine	0.014	0.012	0.015	

If one concedes that one of the rôles of ammonium nitrate is to take part in what might be called a Ross Reaction with the formaldehyde liberated from the hexamine dinitrate, then one would expect the amount of ammonium nitrate required for optimal yield would be related to the yield as the yield increases. This is generally true but no extensive investigation has been made of this point. The data are summarized in Table 46. The correlation is not sufficiently close to make any estimate of the amount of ammonium nitrate which enters into the reaction, and in addition it will be shown later that the effect

of the ammonium nitrate upon the rate is much greater than its effect upon the yield, and that indeed the latter may be altered by the change in rate of conversion of hexamine or hexamine dinitrate to R.D.X. rather than independently.

TABLE 46

EFFECT OF YIELD ON THE MINIMAL AMOUNT OF AMMONIUM NITRATE NECESSARY FOR OPTIMAL YIELD

Medium	Hexamine Dinitrate		Hexamine	
	Yield	Ammonium Nitrate	Yield	Ammonium Nitrate
50 Percent Anhydride	.250	.250		
70 Percent Nitric Acid				
Acetic Anhydride	.620	.5	.400	.3
Propionic Anhydride	.275	.25	.075	.0
Absolute Nitric Acid				
Acetic Anhydride	.620	.75	.375	.5
Propionic Anhydride	.350	.5	.130	.3
Nitrogen Pentoxide				
Acetic Anhydride	.475	.5	.325	.5

All of the foregoing tables show that propionic anhydride is generally less effective than acetic anhydride, and that it follows the same trends in it action in most cases.

NITROLYSIS OF HEXAMINE AND HEXAMINE DINITRATE USING COPPER NITRATE AND ACETIC OR PROPIONIC ANHYDRIDE

The use of copper nitrate or other heavy metal nitrates with acetic anhydride is a well known method of nitrating. A preliminary experiment showed that mixtures of copper nitrate trihydrate and either acetic or propionic anhydride would produce R.D.X. with hexamine dinitrate and ammonium nitrate. Ammonium nitrate alone under the same circumstances would not do so. Thus it was evident that the active nitrating agent was produced by the action of acetic anhydride or propionic anhydridee upon copper nitrate trihydrate as well as upon nitric acid as shown in the previous section.

The optimal amounts of copper nitrate were determined exactly as previously when nitric acid was used, and in Figure 51 the results are recorded and expressed in terms of their nitric acid equivalent. The indicated amounts of copper nitrate trihydrate were treated with 10 milliliters of the anhydride for 30 minutes at 35°C and 0.002 moles of hexamine dinitrate

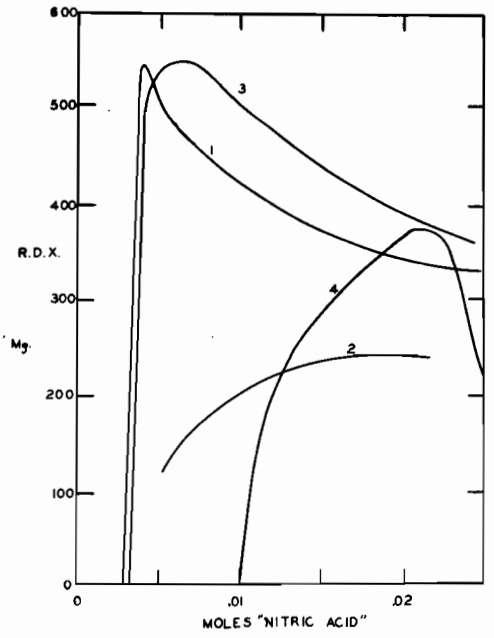


FIGURE 51 - Effect of Amount of Copper Nitrate Trihydrate on the Yield of R.D.X. in Anhydride Medium at 35°C.

1 - Hexamine Dinitrate in Acetic Anhydride

2 - Hexamine in Acetic Anhydride

3 - Hexamine Dinitrate in Propionic Anhydride

4 - Hexamine in Propionic Anhydride

or hexamine and 0.250 grams of ammonium nitrate added and the R.D.X. determined after two hours at 35°C. From Curve 1 it can be seen that the optimal amount of copper nitrate trihydrate for the conversion of hexamine dinitrate to R.D.X. in acetic anhydride is equivalent to 0.004 moles of nitric acid. Similarly the optimal amount for the conversion of hexamine is 0.016 moles, Curve 2. The respective values when propionic anhydride is used are 0.006 moles, Curve 3, and 0.022 moles, Curve 4. It is evident immediately that the conversion of hexamine dinitrate is favoured by this nitrating combination, but not so the conversion of hexamine. The very much higher optimal amounts of copper nitrate trihydrate required suggest that hexamine under these conditions is no longer being converted to the dinitrate before nitrolysis, and that the omission of this step slows the reaction down, and lowers the yield.

A comparison of the optimal amounts of nitric acid and of copper nitrate trihydrate calculated on the basis of nitric acid equivalents is shown in Table 47.

TABLE 47

OPTIMAL NITRIC ACID CONCENTRATION IN MOLES

	Hexamine Dinitrate		Hexamine	
	Copper Nitrate	Nitric Acid	Copper Nitrate	Nitric Acid
Acetic Anhydride	0.004	0.004	0.016	0.007
Propionic Anhydride	0.006	0.009	0.020	0.012

The rates of conversion at 35°C of hexamine dinitrate (0.002 moles) and hexamine (0.002 moles) to R.D.X. using the optimal amounts of copper nitrate trihydrate are shown in Figure 52. These data were obtained using 10 milliliters of anhydride and 0.250 grams of ammonium nitrate. Curve 1 shows the rate of conversion of hexamine dinitrate in acetic anhydride, and Curve 2 similarly for hexamine. Curves 3 and 4 are the same respectively when propionic anhydride is used. These show that the rates of conversion and yield are quite comparable to those obtained when nitric acid is used. This is shown more clearly in Table 48 where the results obtained in the previous section using 70 percent nitric acid are compared with those obtained using copper nitrate trihydrate.

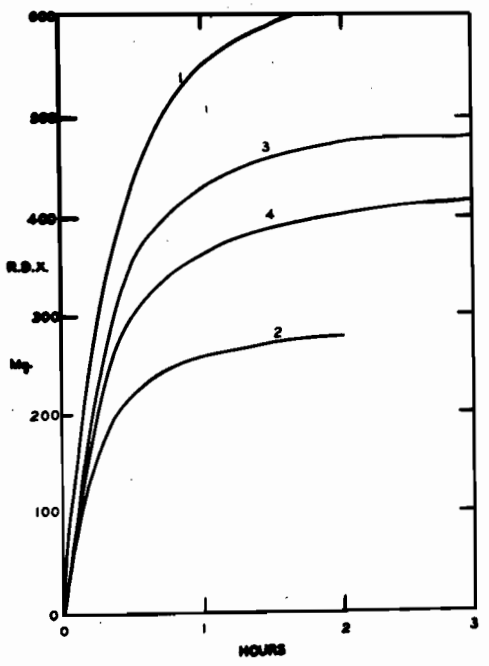


FIGURE 52 - Rates of Production of R.D.X. in Anhydride Medium at 35°C, Copper Nitrate Trihydrate.

1 - Hexamine Dinitrate in Acetic Anhydride

2 - Hexamine in Acetic Anhydride

3 - Hexamine Dinitrate in Propionic Anhydride

4 - Hexamine in Propionic Anhydride

TABLE 48

EFFECT OF NITRIC ACID AND COPPER NITRATE ON THE RATE OF CONVERSION AND YIELD OF R.D.X. FROM HEXAMINE AND HEXAMINE DINITRATE IN ACETIC AND PROPIONIC ANHYDRIDES

	Initial Rate		Yield	
	Copper Nitrate	Nitric Acid	Copper Nitrate	Nitric Acid
Acetic Anhydride				
Hexamine Dinitrate	230	160	600	575
Hexamine	160	50	300	300
Propionic Anhydride				
Hexamine Dinitrate	275	30	475	275
Hexamine	200	25	425	125

These data indeed show that copper nitrate may be more effective than nitric acid under their respective optimal conditions.

The effect of ammonium nitrate on the yield is shown in Figure 53. The data are similar to those recorded previously when nitric acid is used except that the amount required for optimal yield when hexamine is used with either acetic or propionic anhydrides seems to be reduced to zero. Curve 1

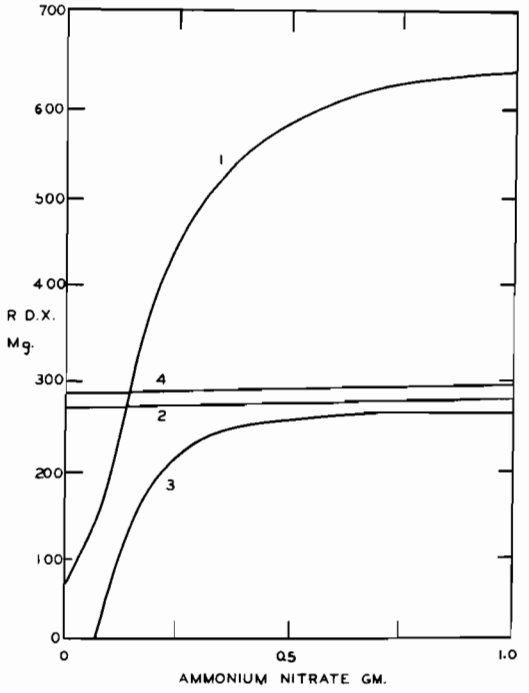


FIGURE 53 - Effect of Ammonium Nitrate on the Yield of R.D.X. in Anhydride Medium, Copper Nitrate Trihydrate.

1 - Hexamine Dinitrate in Acetic Anhydride

2 - Hexamine in Acetic Anhydride

3 - Hexamine Dinitrate in Propionic Anhydride

4 - Hexamine in Propionic Anhydride

shows the effect of ammonium nitrate on the yield of R.D.X. from hexamine dinitrate (0.002 moles) in acetic anhydride, and Curve 2 similar data using 0.002 moles of hexamine. Curves 3 and 4 are respectively the same in propionic anhydride. In all cases the optimal amounts of copper nitrate trihydrate given by Figure 51 were used in a volume of 10 milliliters of anhydride.

The fact that ammonium nitrate has so little effect upon the yield when copper nitrate trihydrate is used with hexamine suggests that one of the rôles of ammonium nitrate is to furnish nitrate or ammonium ion which in this case may be replaced by copper nitrate. The introduction of nitric acid either as such or as hexamine dinitrate then requires a minimal amount of ammonium nitrate before the conversion to R.D.X. proceeds at a measurable rate.

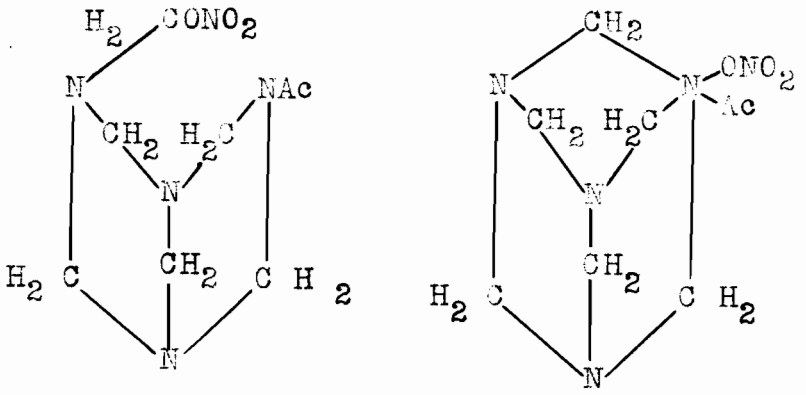
Drying of copper nitrate trihydrate drives off nitric acid as well as water and leaves a solid which is no longer deliquescent and represents only about 50 percent of the original material by weight.

Completely dried samples failed to give any R.D.X. with acetic anhydride, ammonium nitrate and hexamine dinitrate, while semi-dry samples did. Thus it seemed possible that the acetic or propionic acid formed by the hydrolysis of the anhydride by the water of crystallization might be essential. However, addition of acetic acid when the completely dry samples of copper nitrate were used was ineffective, as also was the addition of more ammonium nitrate, of sulphuric acid or of ammonium acetate. Prolonged extraction of the dried copper nitrate with acetic anhydride did give a solution which produced a small amount of R.D.X. from hexamine dinitrate and ammonium nitrate suggesting that the basic nitrate formed on drying either reacted very slowly with the anhydride, or else slowed down the nitrolysis of hexamine dinitrate to R.D.X. Mixtures of trihydrate and oven-dried material yielded less and less R.D.X. with hexamine dinitrate, acetic anhydride and ammonium nitrate as the amount of dried material was increased.

It would be of interest to extend these investigations by using anhydrous copper nitrate prepared by crystallization from fuming nitric acid.

NITROLYSIS OF H2

The conversion of hexamine or hexamine dinitrate to R.D.X. must involve the rupture of many bonds in the molecule. The work of Linstead (45) indicated that the compound H2 which he isolated and identified might be the first step in such a process, although the formulae which were favoured did not have a nitramine group. The formulae are:



Obviously if these tentative formulae are correct there must still be three bonds broken and three nitramine groups formed, but if for any reason these formulae are wrong, then there might be a nitramine group so situated that only two further ruptures would be required and H2 could then be an intermediate in the formation of R.D.X.

H2 was prepared according to directions of Linstead (45). Attempts to find an optimal concentration of nitric acid for the conversion of this material to R.D.X. with ammonium nitrate (0.5 grams) and acetic anhydride (10 milliliters) showed that the yield was much lower than could be expected from an equivalent amount (0.002 moles) of hexamine or hexamine dinitrate, as shown in Table 49. The theoretical yield is 0.83 grams of R.D.X.

TABLE 49

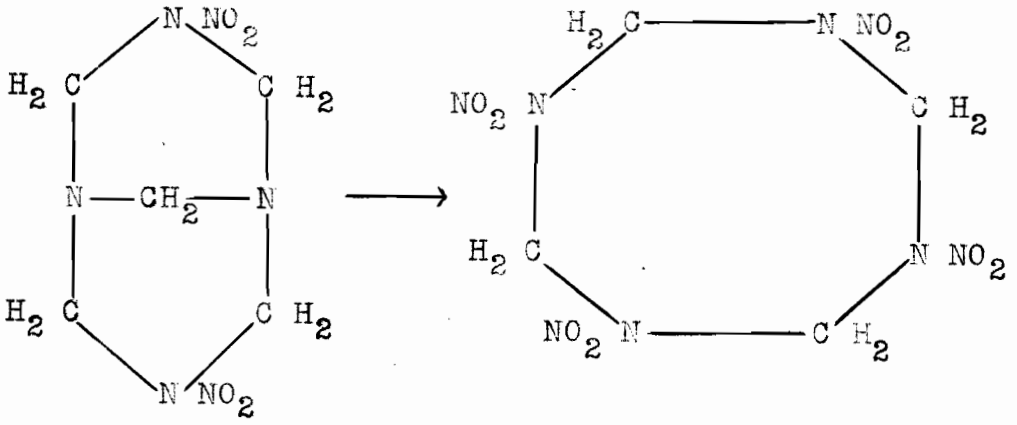
CONVERSION OF H2 TO R.D.X.

Moles of Nitric Acid	Yield R.D.X.
0.0038	0.150 gm
0.0050	0.125
0.0063	0.156
0.0076	0.092
0.0089	0.091
0.0102	0.050

These data are interpreted to mean that in the process as carried out at 35°C, H2 is not an intermediate since the small yields shown above could be interpreted as due to impurities or to the very slow conversion of H2, not of the same magnitude as the normal process.

OPTIMAL NITRIC ACID CONCENTRATION FOR THE CONVERSION OF D.P.T. TO H.M.X. AND OF HEXAMINE, HEXAMINE MONONITRATE AND HEXAMINE DINITRATE TO R.D.X. IN ACETIC ANHYDRIDE

The conversion of D.P.T., dinitropentamethylene tetramine, to H.M.X.



involves the rupture of only two bonds. Comparing this with the series involving the production of R.D.X. from hexamine, hexamine mononitrate and hexamine dinitrate should show some correlation between the bonds to be broken and the activation energies involved. The conversion of hexamine to R.D.X. must involve the breaking of at least three C-N bonds and the formation of three nitramine groups concurrently. Hexamine mononitrate requires a similar number of bonds to be broken but there exists

one N-nitrate group which can be rearranged to nitramine by acetic anhydride alone, and this fact is accentuated in hexamine dinitrate which possesses two N-nitrate groups. These may be summarized:

Hexamine + 3 acetyl nitrate

Hexamine mononitrate + 2 acetyl nitrate +1 acetic anhydride

Hexamine dinitrate + 1 acetyl nitrate + 2 acetic anhydride

to produce R.D.X.

The optimal nitric acid concentrations were determined at 35°C in acetic anhydride with 0.5 grams of ammonium nitrate present and 0.002 moles of the appropriate solid in 10 milliliter volumes. The results are shown in Figure 54. Curve 1 shows that the optimal nitric acid concentration is 0.005 moles for the conversion of D.P.T. to H.M.X., while Curve 2 shows that the optimal amount is 0.007 moles for the conversion of hexamine to R.D.X. Curves 3 and 4 show that the amounts are 0.005 moles and 0.004 moles for the conversion of hexamine mononitrate and hexamine dinitrate respectively.

These data indicate that the amount of nitric

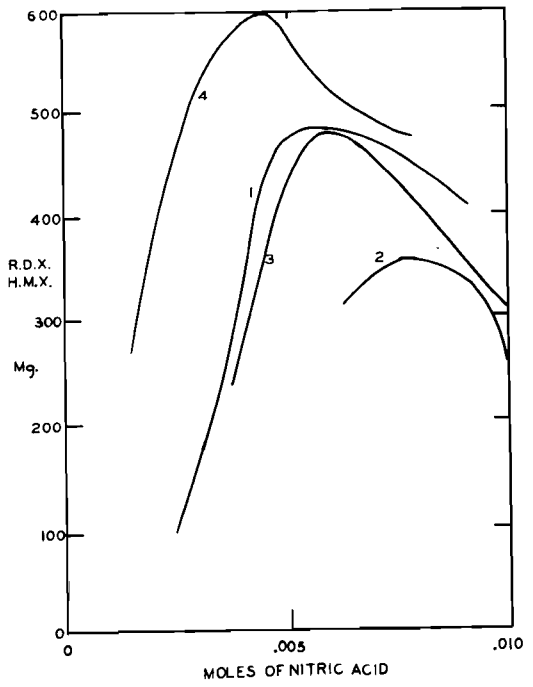


FIGURE 54 - Effect of Nitric Acid on the Production of H.M.X. and R.D.X.

1 - H.M.X. from D.P.T.

2 - R.D.X. from Hexamine

3 - R.D.X. from Hexamine Mononitrate

4 - R.D.X. from Hexamine Dinitrate

acid required for the conversion of the mononitrate is intermediate between that for hexamine and hexamine dinitrate, as is also the resultant yield. The amount of nitric acid required and yield for the conversion of D.P.T. to H.M.X. is very similar to that for the conversion of the mononitrate to R.D.X.

EFFECT OF AMMONIUM NITRATE ON THE RATE OF CONVERSION OF D.P.T. TO H.M.X. AND OF HEXAMINE, HEXAMINE MONO-NITRATE AND HEXAMINE DINITRATE TO R.D.X. IN ACETIC ANHYDRIDE

In an effort to obtain a measure of the activation energies of these various conversions the rates were measured at several temperatures. The very great irregularity of the results and the failure of the rates to vary in a normal manner with temperature suggested that the ammonium nitrate in some way had a marked effect. Larger amounts of ammonium nitrate were used, therefore, and this was ground to a moderately small particle size. The rates of conversion to H.M.X. or R.D.X. and the yield of either were affected greatly as shown by Figures 55, 56, 57 and 58.

Figure 55 shows the effect of ammonium nitrate on the rate of conversion of D.P.T. to H.M.X. at 30°C, 35°C and 40°C. The upper curve for each temperature was obtained with 0.85 grams of ammonium nitrate present, the lower with 0.5 grams present.

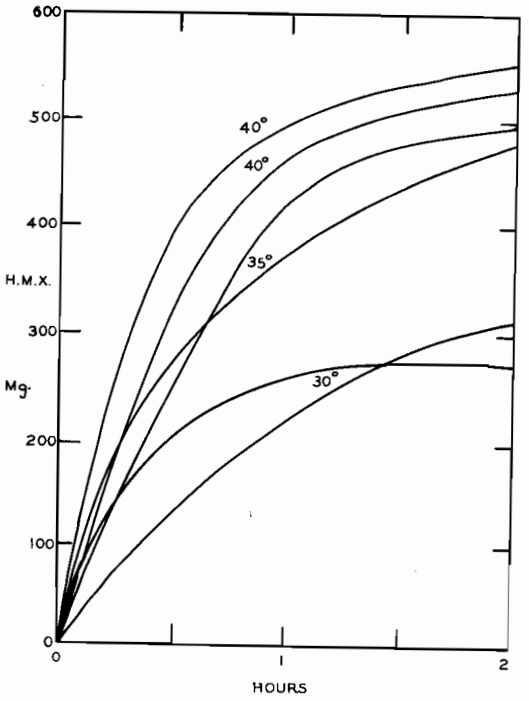


FIGURE 55 - Effect of Ammonium Nitrate on the Rate of Production of H.M.X. from D.P.T.

Upper Each Pair - 0.85 grams Ammonium Nitrate

Lower Each Pair - 0.50 grams of Ammonium Nitrate

Otherwise the determinations were identical, 10 milliliters of acetic anhydride and optimal nitric acid concentration as shown from Figure 54. The increase in the rate is much more marked than the increase in the yield. The theoretical yield is 0.55 grams of H.M.X.

Similarly the data shown in Figure 56 were obtained using 0.002 moles of hexamine in 10 milliliters of acetic anhydride with the optimal nitric acid concentration as shown in Figure 54. The upper curve of each pair was obtained when 0.85 grams of ammonium nitrate was used, while the lower was obtained when but 0.5 grams were used. At 35°C a third curve still lower was obtained with 0.25 grams of ammonium nitrate present. The theoretical yield is 0.83 grams of R.D.X.

Figure 57 shows the data obtained when 0.002 moles of hexamine mononitrate in 10 milliliters of acetic anhydride is used with the optimal concentration of nitric acid as shown from Figure 54. The upper of each pair was obtained using 0.85 grams of ammonium nitrate, the lower with 0.50 grams of

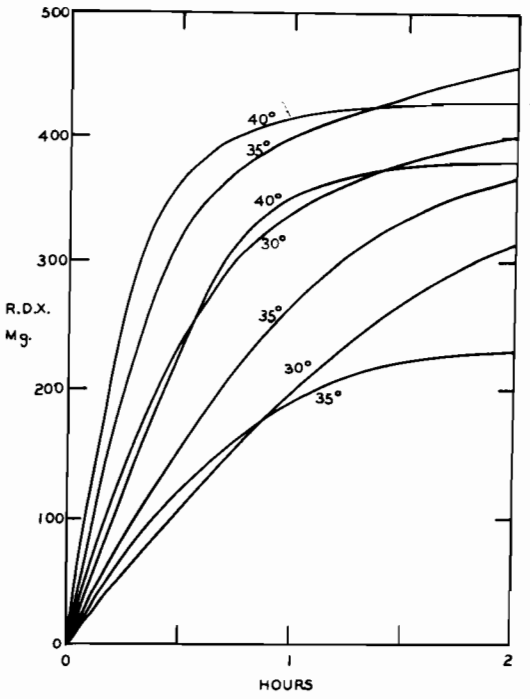


FIGURE 56 - Effect of Ammonium Nitrate on the Rate of production of R.D.X. from Hexamine.

Upper of Each Pair - 0.85 grams of Ammonium Nitrate

Lower of Each Pair - 0.50 grams of Ammonium Nitrate

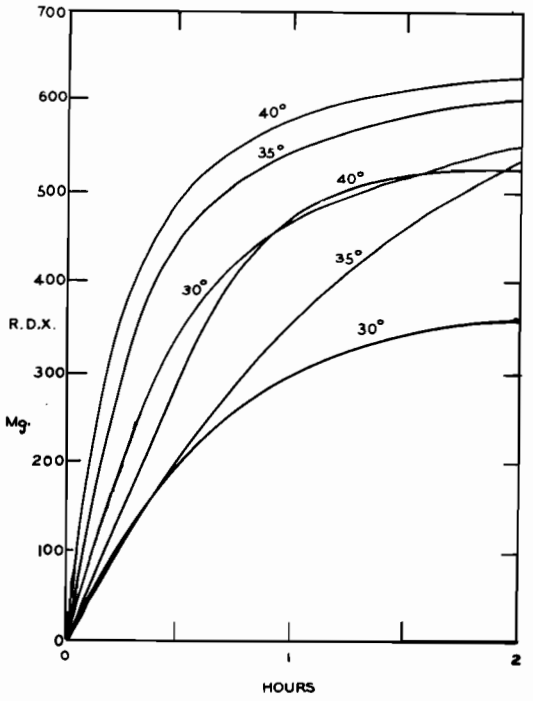


FIGURE 57 - Effect of Ammonium Nitrate on the Rates of Formation of R.D.X. from Hexamine Mononitrate in Acetic Anhydride.

Upper of Each Pair - 0.85 grams of Ammonium Nitrate

Lower of Each Pair - 0.50 grams of Ammonium Nitrate

ammonium nitrate. The theoretical yield is 0.83 grams of R.D.X.

Figure 58 shows the data obtained when 0.002 moles of hexamine dinitrate are used in 10 milliliters of acetic anhydride and with the optimal concentration of nitric acid as shown in Figure 54. The upper of each pair was obtained using 0.85 grams of ammonium nitrate, and the lower with 0.50 grams of ammonium nitrate. The third and lowermost curve obtained at 35°C was the result of using but 0.25 grams of ammonium nitrate. The theoretical yield was 0.83 grams of ammonium nitrate.

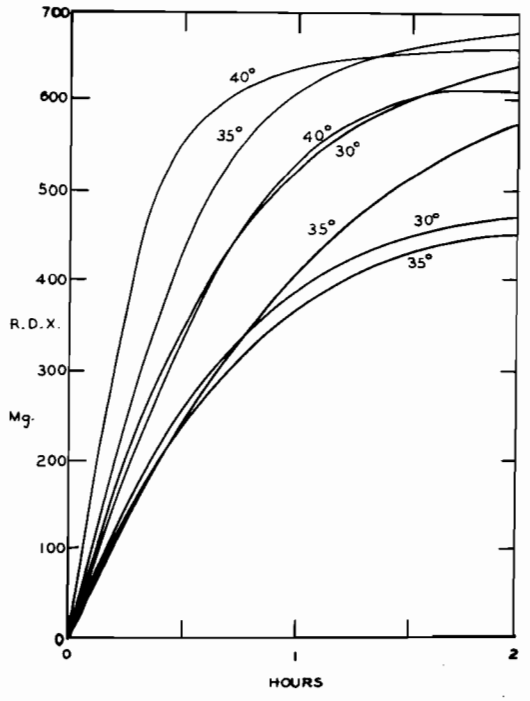


FIGURE 58 - Effect of Ammonium Nitrate on the Rate of Production of R.D.X. from Hexamine Dinitrate in Acetic Anhydride.

Upper of Each Pair - 0.85 grams of Ammonium Nitrate

Lower of Each Pair - 0.50 grams of Ammonium Nitrate

EFFECT OF TEMPERATURE ON THE RATES OF CONVERSION OF D.P.T. TO H.M.X. AND OF HEXAMINE, HEXAMINE MONONITRATE AND HEXAMINE DINITRATE TO R.D.X. IN ACETIC ANHYDRIDE

These data are only such as to give an estimate of the activation energies involved but do indicate that more must be known about the reaction before precise values can be obtained.

In all cases 0.002 moles of the reactant was used with 0.85 grams of ammonium nitrate in 10 milliliters of acetic anhydride and the optimal nitric acid concentration as shown in Figure 54. The results are self-explanatory and are shown in Figures 59, 60, 61 and 62.

Figure 59 shows the effect of temperature on the conversion of D.P.T. to H.M.X. A large scale plot of these data indicate that the activation energy is about 12 kilocalories per mole. Similarly the data obtained for hexamine, Figure 60, indicates an activation energy of about 11 kilocalories per mole for the conversion to R.D.X. Unlike the

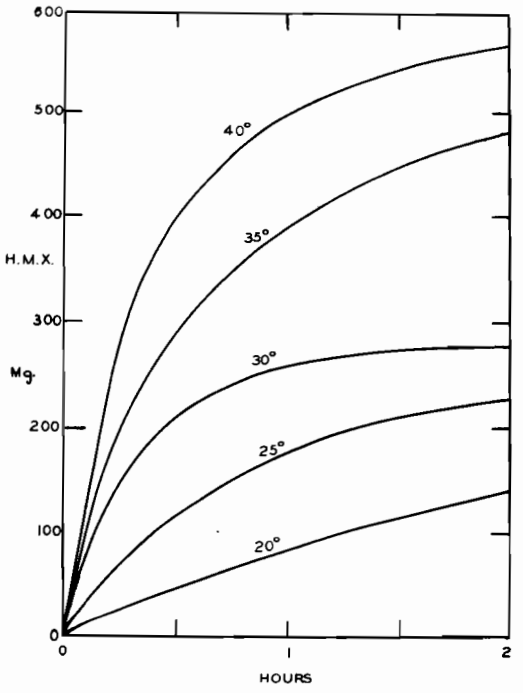


FIGURE 59 - Effect of Temperature on the Rate of Production of H.M.X. from D.P.T., in Acetic Anhydride

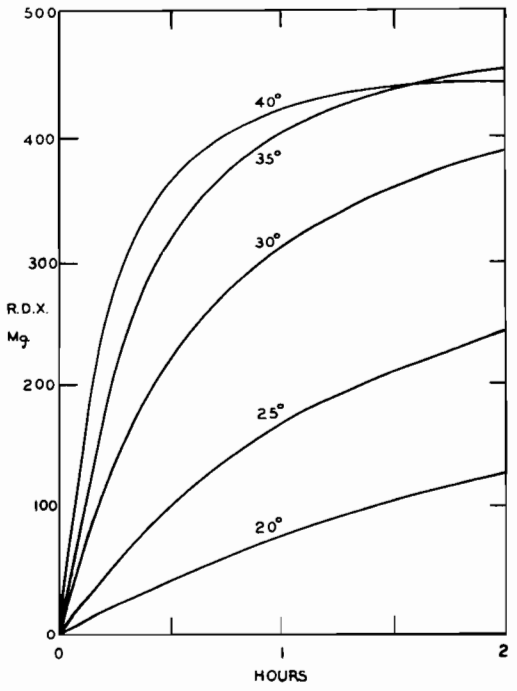


FIGURE 60 - Effect of Temperature on the Rate of Production of R.D.X. from Hexamine in Acetic Anhydride

conversion of D.P.T. to H.M.X. in which the amount of formaldehyde liberated per mole of D.P.T. is only one mole, the number liberated, potentially at least, per mole of hexamine is three in the conversion to R.D.X. Thus the effect of the second process or Ross Reaction both in affecting the rate and yield would likely be greater in the conversion of hexamine to R.D.X. than in the conversion of D.P.T. to H.M.X. Since initial rates were used in the calculation of the activation energies, this consideration does not alter the values of the activation energies.

Similarly the data in Figure 61 for the effect of temperature on the conversion of hexamine mononitrate to R.D.X. gave an activation energy of between 12 and 13 kilocalories per mole, while the data shown in Figure 62, obtained when hexamine dinitrate is used, gave an activation energy for the conversion to R.D.X. of between 16 and 17 kilocalories.

While the activation energies for the first three conversions may not be significantly different,

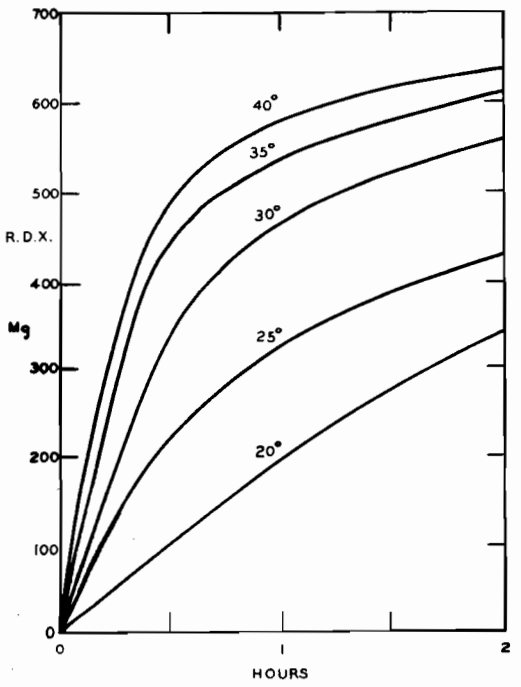


FIGURE 61 - Effect of Temperature on the Rate of Production of R.D.X. from Hexamine Mononitrate in Acetic Anhydride.

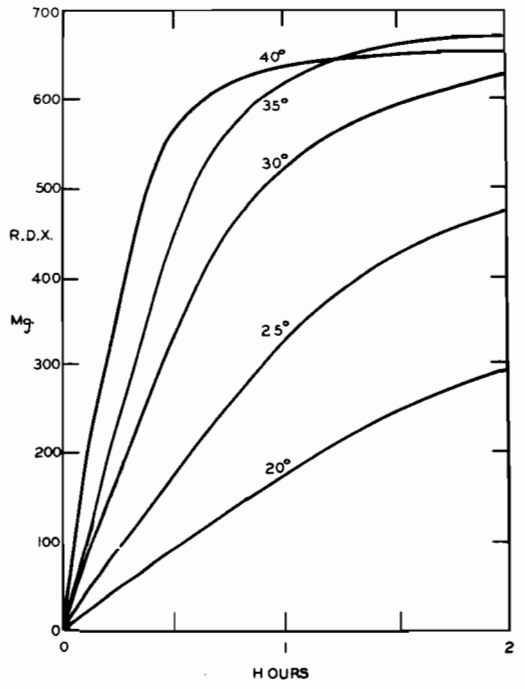


FIGURE 62 - Effect of Temperature on the Rate of Production of R.D.X. from Hexamine Dinitrate in Acetic Anhydride.

that for the conversion of hexamine dinitrate to R.D.X. is significantly higher, with some indication that, like the rates of conversion at a given temperature and the yield, the value of the activation energy for the conversion of hexamine mononitrate to R.D.X. is intermediate between the values for hexamine and hexamine dinitrate.

These values may be compared with those determined on the unisolated intermediate in the Ross Reaction (34). These were between 17 and 20 kilocalories for the conversion of the intermediate prepared in acetic anhydride, and between 19 and 20 kilocalories for the conversion of the intermediate prepared in acetic acid.

DISCUSSION

It would seem hardly appropriate to attempt a discussion of reactions about which so little is known. However, certain facts of interest have been observed which shed new light on these reactions.

In the Ross Reaction or McGill Process it would appear that the paraformaldehyde is depolymerized and condenses with the ammonium nitrate to give hexamine dinitrate, nitric acid and water. This reaction is of great academic interest but loses much as an urgent problem under existing conditions for three reasons. The first is that hexamine may be produced quite cheaply from ammonium salts or ammonia and formaldehyde in very good yield while it is uncertain just what yield is obtained in the Ross Reaction. The second fact following on this is the ease with which hexamine may be converted to hexamine dinitrate with practically complete yield and with little loss of nitric acid. Thirdly the water produced in the Ross

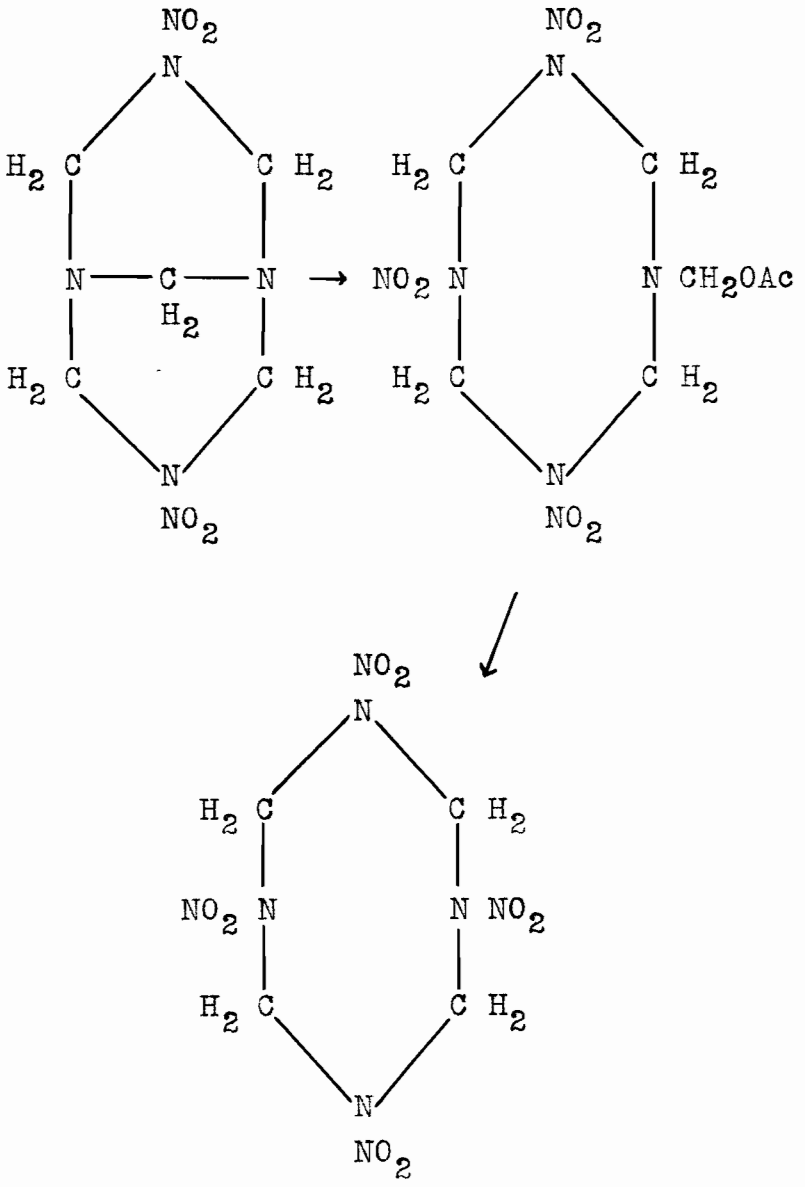
Reaction must be removed and this is done by the acetic anhydride. On a theoretical basis twice as much anhydride is required for the Ross Reaction as for the Bachmann in which the intermediate, hexamine, is already prepared. Thus if acetic anhydride is the controlling reagent this is an important factor. The "activation" of the filtrate by which the intermediate is removed from the filtrate and returned to it after the acetic anhydride has been added does increase the yield, but such a procedure is then essentially a Bachmann run with the over all yield of a Ross Reaction.

When the Bachmann Process is studied using different starting materials, dinitropentamethylene tetramine, hexamine, hexamine mononitrate and hexamine dinitrate, it is evident immediately that there are differences in the paths by which these are converted to H.M.X. or R.D.X., otherwise the differences in the rates of conversion, the yields, and above all in the activation energies cannot be explained, and yet the paths must be so similar that none of these differences can be very great in order to agree with fact.

The nitrating reagent is rather uncertain but it would appear that it must be acetyl nitrate. This reagent forms under the experimental conditions used in these invesigations (51), and is stable over the time period used in most instances. However, there is the additional reagent, acetic or propionic anhydride, with which all of the reaction mixtures were swamped, and these anhydrides most certainly will react with the N-nitrate groups to produce nitramine groups. The velocity of this reaction may be quite rapid since the optimal yield of D.P.T. from hexamine dinitrate is reached in about seven hours at room temperature. A precise analytical method for D.P.T. would enable a study of this important reaction.

On the basis of the fact that the conversions of D.P.T. to H.M.X. and hexamine, hexamine mononitrate and hexamine dinitrate to R.D.X. appear to be first order and to proceed at comparable rates but with different rates, yields and paths at a given temperature, and with comparable but slightly different activation energies, the following mechanism is proposed:

If the formulae for D.P.T. and H.M.X. are correct, there are only two bonds which must break to convert D.P.T. to H.M.X., according to the scheme:



Since the yield from this conversion is very good and mostly H.M.X., breaks in the outer ring must be difficult relative to a break leading to removal of the bridge. Thus the presence of the nitramine groups stabilizes the ring structure and favours the formation of H.M.X. over R.D.X.

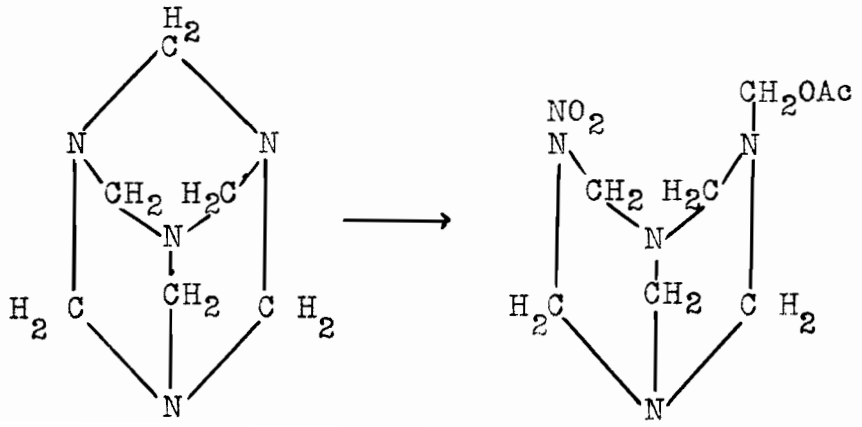
Since the formation of H.M.X. appears to be a first order reaction with no induction period evident, then one of the two steps in the conversion of D.P.T. to H.M.X. must occur very much more rapidly than the other, something of the order of one hundred times. There is much indirect evidence to indicate that the first step is rate-determining.

For the second step to be rate-determining, removal of the side chain must be slow, but must be very fast relative to any rupture of the ring. Therefore the breaking of the bridge in the first step must occur at an exceedingly greater rate than the breaking of the ring, that is that this particular bond in the ring structure must be most weak relative to all the others. This seems inconsistant, one would expect rather that the breaking of the bridge would

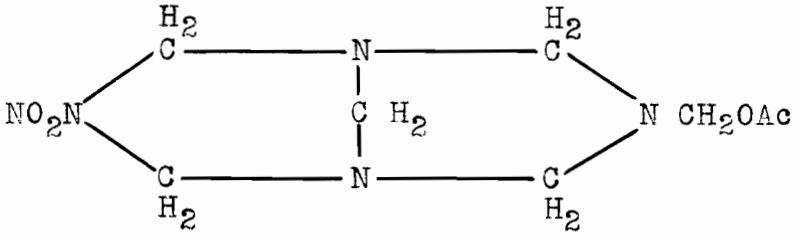
approach breaking of the ring as far as difficulty goes. A second piece of evidence is the comparative ease of formation of D.P.T., and the fairly good yields obtained. This would favour the view that the next step in the degradation processes is slow.

However, the conversion of hexamine to R.D.X. proceeds at very nearly the same rate as the conversion of D.P.T. to H.M.X., and the reaction is also first order with about the same activation energy. One would expect that one or both of the breaks which appear in the conversion of D.P.T. to H.M.X. would also appear in the conversion of hexamine to R.D.X.

If three body and higher order collisions are excluded, then the first break in the hexamine ring must be:



that is, a break quite analogous to the first step in the conversion of D.P.T. to H.M.X. Rewriting the product of this first step in the conversion of hexamine to R.D.X., it is evident that it must be analogous to D.P.T.



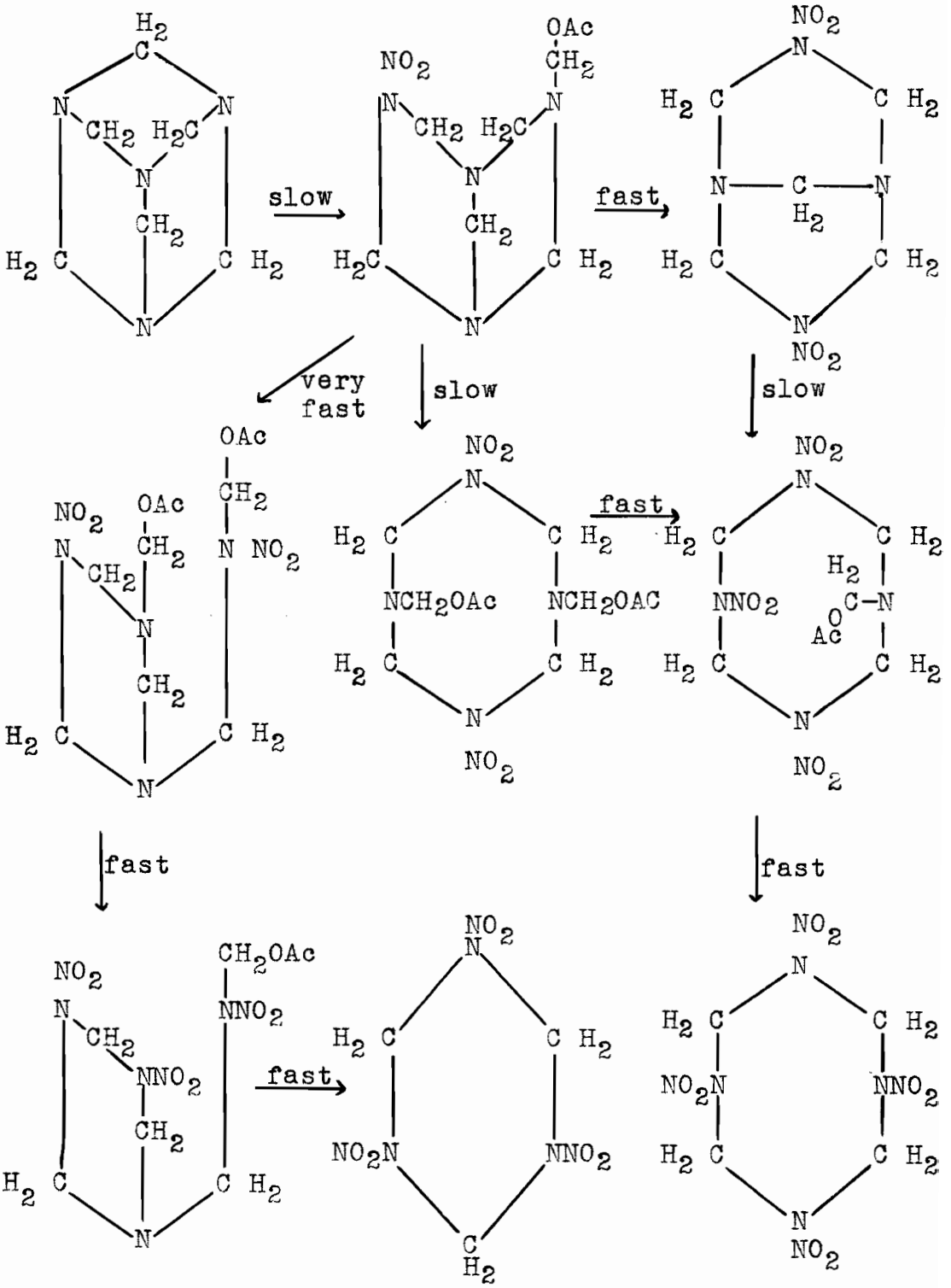
As in the case of D.P.T. the nitramine group stabilizes the left hand ring. However, the presence of the side chain must weaken the right hand ring to a very considerable extent, for breaking of this ring is a requisite for the formation of R.D.X. and this must predominate. Thus breaking of the right hand ring must be easier than breaking of the bridge, or removal of the side chain, either of which will lead to the formation of H.M.X. eventually. Thus there are two possible paths which might be followed in the conversion of the above compound to R.D.X., as will be shown.

Again, largely by inference the first

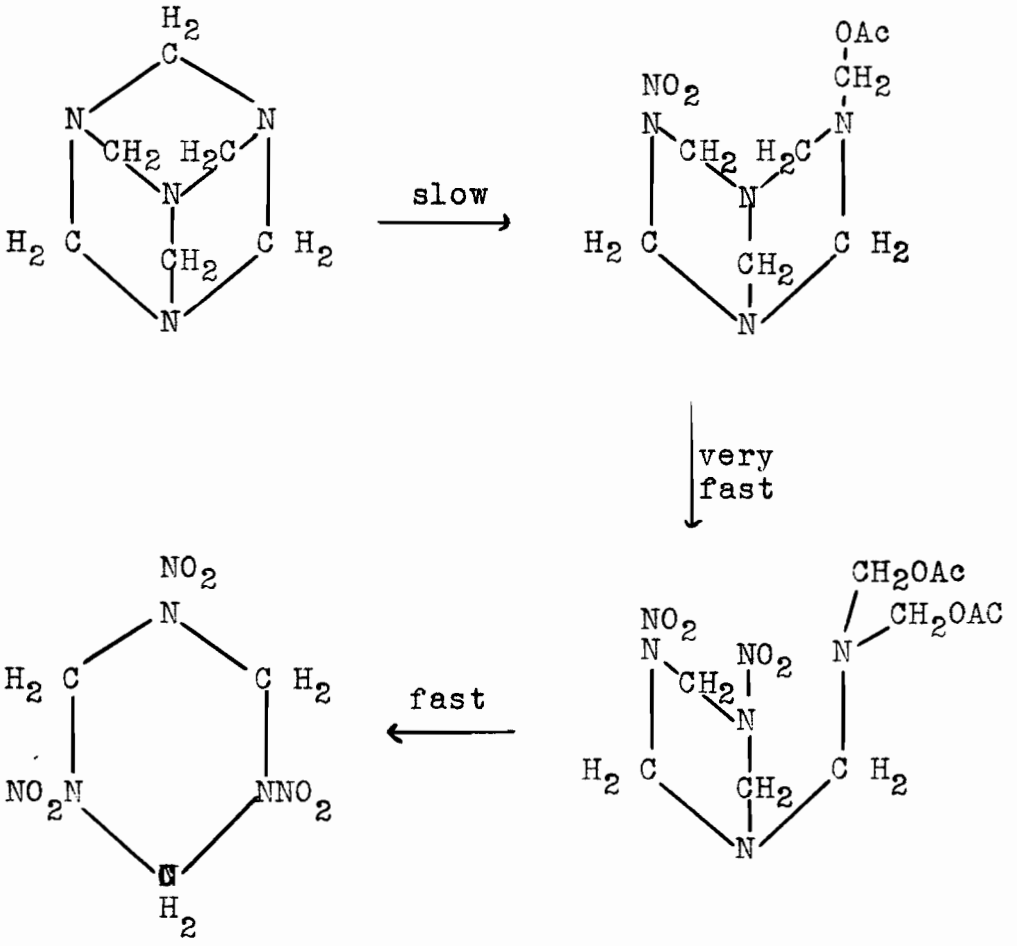
break in the hexamine ring must be the rate-determining step. The fact that no intermediates between hexamine, or hexamine dinitrate, and R.D.X. have been isolated would indicate that after the initial break all further breaks were very rapid. Secondly since the reaction is first order with no induction period the rate-determining step must be at least 100 times slower than the others. Since the reaction may be complete in about one hour that would mean that hexamine dinitrate must disappear from the reaction mixture exceedingly rapidly if any step after the first is rate-determining. In fact, hexamine dinitrate persists for very much longer times, indicating that its disappearance must be associated with the rate-determining step, that is the first initial break of the hexamine ring.

Based on the assumptions that the rate-determining step in the formation of R.D.X. from hexamine, or of H.M.X. from D.P.T., is the rupture of a stable ring, followed in the former case by the crumbling of a weakened ring and the removal of side chain(s) and in the latter case by the removal of a side chain, two possible mechanisms are suggested:

The first mechanism is :



The second mechanism is:



In this scheme those reactions which lead to H.M.X. are identical with those in the previous scheme. The only difference between the two schemes lies in the choice of which bond in the weakened ring breaks.

There is little definite evidence upon which to choose between these two schemes if indeed a choice

is necessary. Each agrees with the fact that the conversion of D.P.T. to H.M.X. and of hexamine to R.D.X. occurrs with about the same rate, and with about the same activation energy since the rate determining step in each conversion is the breaking of a stable ring structure. In addition the low yield of H.M.X. in the Bachmann Process is explained by the fact that the formation of D.P.T. is slower than the crumbling of the weakened ring structure to lead to R.D.X. Each has its disadvantages, lying in the fate of the side-chains and the path by which they are removed. Thus in the first mechanism the effect of the nitramine groups in stabilizing rings might be carried over and so stabilize the bond holding the side chain to the ring and so make the last break in the chain to produce R.D.X. slow. But in the second mechanism if the side chain comes off intact it must be broken down before it can be recycled to give R.D.X. Thus one might expect it to break down at least partially before it is removed. Then too if the $-CH_2OAc$ side chain weakens the ring in the compound produced after the first break in the hexamine ring, it is not irrational to assume that it would have the greatest effect on the bond nearest the substituent group, and hence lead to the

first mechanism. Until further data is available, in particular intermediate compounds, there does not seem to be a more certain method of differentiating between these two mechanisms.

The mechanisms of Connor (52) favour recycling of broken rings in the formation of D.P.T. The mechanism proposed here eliminates that assumption.

The mechanism of Davey (52) favours breaking of the ring followed by closure by ammonium nitrate. From the data presented here it is evident that ammonium nitrate is not necessary for the formation of R.D.X. from hexamine if copper nitrate is used with acetic or propionic anhydrides.

It would appear that the rôle of nitric acid, nitrogen pentoxide or copper nitrate in the reaction is to produce acetyl nitrate with acetic anhydride or propionyl nitrate with propionic anhydride, but the rôles of acetic acid and of ammonium nitrate are less clear and of very great importance.

The rôle of acetic acid seems to be related to the conversion of hexamine to hexamine dinitrate. If the medium is 50 percent or over acetic acid there does not appear to be any difference between the rates of conversion of hexamine and the dinitrate to R.D.X., that is that the hexamine is converted to the dinitrate under these conditions and so is then converted to R.D.X. with the same rate and to the same extent as the latter. However, as the acetic acid content decreases this is no longer so, as can be seen by the falling off of the rate and yield. This is suggested to be due to a shifting of the equilibrium, or completeness of the reaction, between acetic anhydride, nitric acid and acetic acid in such a way as to use up the nitric acid which would normally convert the hexamine to the dinitrate.

However, it is also possible that the decreased rate and yield of R.D.X. from hexamine relative to that obtained from hexamine dinitrate may be explained on the higher nitric acid concentration required for optimal yield. To have sufficient nitric acid present for the conversion

of the hexamine to R.D.X. may raise the concentration of acetyl nitrate to such an extent that the rates of bond splitting are reduced just as in the case of excess acid present in the conversion of hexamine dinitrate to R.D.X. Thus for optimal yield of R.D.X. from hexamine, rate of conversion may have been sacrificed under those experimental conditions in which all of the nitric acid was added at one time.

Also the increased rate of conversion and yield from hexamine dinitrate may be explained on a purely collision basis. The dinitrate requires only acetic anhydride for the conversion of two N-nitrate groups to nitramine, and the reaction is swamped in acetic anhydride. Thus the effective concentration of acetyl nitrate is greatly increased and side reactions are less likely to occur, that is nitration of the solvent or formaldehyde. The higher activation energy of the conversion of the dinitrate to R.D.X. over that for the conversion of hexamine may be related to the higher effective concentration of acetyl nitrate which must be formed in situ. Thus there might be a contribution of this latter reaction to the velocity of the overall reaction as far as temperature coefficient is concerned.

The rôle of ammonium nitrate is of very great interest. Not only must it be concerned with the using up of the split-out formaldehyde, but it affects the rate of conversion of the ring structures to R.D.X. and H.M.X. Dr. Connor states (52) that it is concerned with the splitting out of $-CH_2OAc$ groups but this is hardly true if the mechanism proposed here is true for the formation of D.P.T. Rather the rôle of ammonium nitrate is believed to be related to the rates of acetylation. It is well known that the rate of acetylation is very greatly affected by pH and it is not inconsistant to carry this over to the nitric acid system in which one is no longer concerned with acetic anhydride and water but acetyl nitrate and C-N bonds. From the data presented it is shown that as the amount of ammonium nitrate increases for a given amount of nitric acid the yield of R.D.X. and the rate of conversion to R.D.X. increase until the solution appears to be saturated with ammonium nitrate after which the rate appears to remain constant. Thus there must be a relationship between the amount of ammonium nitrate and the amount of nitric acid, and a relationship between the ratio of the amounts of the two and the rate of conversion

of hexamine or its nitrates to R.D.X. and the conversion of D.P.T. to H.M.X. Also it appears that ammonium nitrate may be replaced by copper nitrate when hexamine is used, but not when hexamine dinitrate is used, and the latter differe only in that nitric acid is added in effect with the hexamine. Just what ion or group is affected by the ratio of ammonium nitrate to nitric acid (acetyl nitrate) is difficult to predict.

The fate of the "central core" removed from these rings is of interest since this portion of the molecule represents one half of the potential R.D.X. Unfortunately little is known about how these materials are split out. The yield obtained in the Bachmann Process suggests that the recycling of these carbon atoms is much more efficient than a Ross Reaction. In the foregoing mechanisms it is suggested that these are split out possibly as methylene diacetate, diacetate of dimethylolamine or triacetate of trimethylolamine. The first one could easily form hexamine with ammonium nitrate, and the second could lead to R.D.X. by combination with ammonium nitrate. The third must be decomposed before it can lead to either hexamine or R.D.X. The

amount converted to R.D.X. is far in excess of the amount which would be converted by the equivalent amount of paraformaldehyde under the same conditions, which would suggest not only that the time of depolymerization had been saved but probably that partial condensation to hexamine or R.D.X. had been accomplished, even though this condensation does take place very rapidly normally.

SUMMARY

Part A

NICKEL IMPREGNATED RESPIRATOR CHARCOAL

Unimpregnated respirator charcoal adsorbs nickel carbonyl without decomposition in the absence of air. The presence of oxygen leads to rapid oxidation of the carbonyl producing carbon monoxide, carbon dioxide and probably an amorphous nickel oxide - nickel carbonate mixture. The nickel carbonyl may be decomposed thermally to give metallic nickel and carbon monoxide, the metallic nickel giving a resolved x-ray diffraction pattern in contrast with the deposit left on the charcoal after oxidation of the nickel carbonyl. Thus charcoals catalize the oxidation of nickel carbonyl but not the decomposition.

From studies of the adsorption of nickel carbonyl it is suggested that the adsorption is in the form of a monomolecular layer and differs in no way essentially from the adsorption of water or carbon tetrachloride.

Part B

AN X-RAY INVESTIGATION OF H.M.X. CRYSTALS

H.M.X. crystallizes in monoclinic crystals whose unit cell dimensions are a_o equal to 7.35 Angstroms, b_o equal to 11.27 Angstroms and c_o equal to 6.50 Angstroms. The beta angle is 103 degrees, and the density 1.90, so that there must be two molecules per unit cell. The molecular weight must be 296.

Part C

KINETICS OF THE REACTIONS TO PRODUCE R.D.X.

An investigation of the Ross Reaction or McGill Process to produce R.D.X. showed that the principal intermediate in the process at 35°C was hexamine dinitrate, and that this probably true also at 70°C. The hexamine dinitrate was identified analytically and by x-ray diffraction photographs.

One of the rôles of acetic anhydride is to remove the water formed in the Ross Reaction by the condensation of ammonium nitrate and formaldehyde

to produce hexamine dinitrate. This is shown by the "activation" of the filtrate by which the filtrate from which the hexamine dinitrate has been removed in the preparation of the intermediate is treated with acetic anhydride before the intermediate is returned to the filtrate. There is an increased yield of R.D.X. under these conditions, and this increase can be accomplished also by drying the filtrate chemically or by azeotropic distillation with benzene.

The second rôle of acetic anhydride is to form a rapid nitrating medium for the nitrolysis of hexamine or its nitrates to R.D.X. Next to acetic anhydride in effectiveness are propionic anhydride, nitromethane, nitrobenzene and acetic acid.

The conversion of hexamine to hexamine dinitrate takes place readily in acetic acid medium with amounts of nitric acid comparable with those liberated by the condensation of formaldehyde and ammonium nitrate to give hexamine and nitric acid. Enough additional nitric acid remains to convert the

hexamine dinitrate to R.D.X. when acetic anhydride is added.

The optimal amounts of nitric acid for the conversion of hexamine dinitrate and hexamine to R.D.X. in acetic and propionic anhydrides were determined using 70 percent nitric acid, absolute nitric acid, nitrogen pentoxide and copper nitrate trihydrate as sources of the active nitrating agent with the anhydride. Comparison of the results within this series shows that, in general, the purer the nitric acid the greater is the yield and the rate of conversion to R.D.X., and that substitution of copper nitrate for the nitric acid improves the rate of conversion and the yield of R.D.X. The optimal concentrations are relatively independent of the means of introduction, and the rates of conversion using propionic anhydride are less than under corresponding conditions using acetic anhydride. It is strongly indicated that the active nitrating agent is acetyl or propionyl nitrate. There may be an optimal acetic acid concentration.

Minimal amounts of ammonium nitrate appear to be necessary except possibly when copper nitrate trihydrate is used as the source of the nitrating agent for the conversion of hexamine to R.D.X. The yield, but in particular the rate of conversion of hexamine, hexamine mononitrate and hexamine dinitrate to R.D.X., and of D.P.T. to H.M.X. is affected very greatly by the amount of ammonium nitrate present.

From a study of the conversion of H2 to R.D.X. it is indicated that this material cannot be an important intermediate in the Bachmann process.

The optimal nitric acid concentration for the conversion of hexamine mononitrate to R.D.X. lies between the values for hexamine and hexamine dinitrate, as does also the rate of conversion and the yield at a given temperature.

From a study of the effect of temperature on the rates of conversion of D.P.T. to H.M.X. and of hexamine, hexamine mononitrate and hexamine

dinitrate to R.D.X. it is estimated that the activation energies of these conversions are respectively 12, 11, 12-13 and 16-17 kilocalories per mole. The reactions seem to be first order, and the rates are of comparable order of magnitude at a given temperature.

A mechanism of the reactions involved is presented which is in agreement with these data.

CLAIMS TO ORIGINALITY

Part A

NICKEL IMPREGNATED RESPIRATOR CHARCOALS

The adsorption of nickel carbonyl on unimpregnated respirator charcoal has been studied and shown to be non-specific. The oxidation of the adsorbed nickel carbonyl is catalized but not the thermal decomposition. The probable products of oxidation have been determined.

Part B

AN X-RAY INVESTIGATION OF H.M.X. CRYSTALS

X-ray diffraction studies of H.M.X. crystals led to the determination of the size of the unit cell. The density of H.M.X. was determined and the number of molecules per unit cell calculated.

Part C

THE KINETICS OF THE REACTIONS TO PRODUCE R.D.X.

Hexamine dinitrate was isolated as the intermediate in the Ross Reaction or McGill Process to produce R.D.X.

Acetic anhydride has three rôles, the removal of water formed in the Ross Reaction as the intermediate is formed, and in both the Ross and Bachmann Processes it forms a rapid nitrating medium and unites with the nitric acid to form acetyl nitrate, the active nitrating agent in the reactions.

The condensation of ammonium nitrate and formaldehyde in the Ross Reaction to form hexamine liberates enough nitric acid to convert the hexamine to the dinitrate, and in addition to convert the dinitrate to R.D.X. on the addition of acetic anhydride.

The optimal nitric acid concentrations for the conversion of hexamine or hexamine dinitrate to R.D.X. were determined in acetic and propionic anhydrides using various sources of nitrate ion.

H2 is not an important intermediate in the processes.

Ammonium nitrate plays an important rôle

in the rates of formation of R.D.X. and H.M.X. as well as in the determination of the yield.

From a study of the effect of temperature on the rate of conversion of D.P.T. to H.M.X. and of hexamine, hexamine mononitrate, and hexamine dinitrate to R.D.X., approximate activation energies for the conversions were calculated. The reactions are first order.

A mechanism of the reactions has been postulated.

APPENDIX

A - AZEOTROPIC DISTILLATION OF BACHMANN MIXTURES

An 18 inch Steadman column operated under reduced pressure was used to remove water from the system using benzene to form the azeotrope. Acetic acid, nitromethane or nitrobenzene were used as solvents, and hexamine dinitrate and ammonium nitrate were added in solid form. The optimal amount of 70 percent nitric acid as determined from data obtained at 35°C with acetic anhydride was used. Distillation was continued until no further water was being removed, then hexamine dinitrate was added and distillation continued. No R.D.X. was formed although the distillation was continued for as much as seven hours at 70°C.

The mixtures so dried yielded R.D.X. with very small amounts of acetic anhydride as shown from the fact that water insoluble material was obtained from a medium but four percent acetic anhydride and definite quantities of R.D.X. were obtained when the medium was but eight percent acetic anhydride, the rest being nitromethane. However there would appear to be

some specific effect of acetic anhydride in the reaction which azeotropic distillation cannot duplicate. This is assumed to be the formation of acetyl nitrate.

REFERENCES

1. Adam Hilger Limited, Publication Number 138/3, London, 1939.

2. Barnes, W. H. and Hampton, W. F., Can. J. Research, A, 13, 73 - 81, 1935.

3. Matthews, F. W., Ph.D. Thesis, McGill University, April, 1941.

4. Bernal, J. D., J. Sci. Instrument. 4, 273, 5, 241, 1928, 6, 314, 343, 1929.

5. Taylor, L. W., College Manual of Optics, Ginn and Company, 1924.

6. Davis, J., Report to Advisory Comm. Indust. Chemists, C.E.51, Nov. 25, 1940.

7. McIntosh, R. and Mungen, R., ibid, C.E.51, Jan. 2, 1941.

8. Pierce, W. C., N.D.R.C. Report, Contract B-50, April 2, 1941.

9. Hodgins, J. W., Personal Communication to Dr. W. H. Barnes, June 13, 1941.

10. Emmett, P. H., N.D.R.C. Report, Contract B-74, April 14, 1941.

11. Ellis, C., Hydrogenation of Organic Substances, D. Van Nostrand, New York, 1930.

12. Berthelot, M., Compt. Rend. 113, 679, 1891.

13. Lehrer, V. and Loos, H. A., J.A.C.S. 22, 114, 1900.

14. Hatschek, E. and Thorne, P. C. L., Kolloid. Zeit. 33, 1, 1923; Proc. Roy. Soc. 103A, 276, 1923.

15. Thorne, P. C. L., J. Chem. Soc. 125, 1967, 1924.

16. Hatschek, E. and Thorne, P. C. L., Kolloid. Zeit. 36, 12, 1925.

17. Mond, L., Langer, C. and Quincke, F., J. Chem. Soc. 57, 749, 1890.

18. Dewar, J. and Jones, H. O., Proc. Roy. Soc. 71A, 427, 1903.

19. Garratt, A. P. and Thompson, H. W., J. Chem. Soc. 1934, page 1822.

20. Bawn, C. E. H., Trans. Faraday Soc. 31, 440, 1935.

21. Mittasch, A., Z. Physik. Chem. 40, 1, 1902.

22. Kelley, K. K. and Anderson, C. T., Bur. Mines Bull. 384, 1935.

23. Srebrow, B., Kolloid Z. 71, 293, 1935.

24. Kolthoff, I. M. and Sandell, E. B., Textbook of Quantitative Analysis, Macmillan, New York, 1937.

25. Emmett, P. H., N.D.R.C. Report B6B74, December 12, 1941.

26. Johnstone, H. F. and Clark, C. L., N.D.R.C. Report Contract B-59, March 25, 1941.

27. Noyes, W. A., Jr., Personal Comm. to Dr. O. Maass, October 28, 1941.

28. Davis, J., Ph.D. Thesis, McGill University, April, 1941.

29. Danby, Davoud, Everett, Hinshelwood and Lodge. Some Aspects of the Physical Chemistry of the Respirators.

30. Johnstone, H. F., Communication of August 12, 1941.

31. Coffin, C. C., Advis. Comm. Indust. Chem. C.E.41, March 1941.

32. Henning, German Patent 104280, June 14, 1899.

33. Linstead, R. P., Chemistry of R.D.X., B.C.S.O. Washington, Oct. 1, 1941.

34. Gillies, A., Ph.D. Thesis, McGill University, April 1941.

35. Cox, E. G., D.S.R. Extramural F 72/63, June 25, 1941.

36. Springall, H. D., Brit. Res. Report No. 9, June 24, 1940.

37. Terpstra, P., Z. Krist. 64, 150, 1926.

38. Hultgren, R., J. Chem. Physics, 4, 84, 1936.

39. Cox, E. G., R. D. Exp. Rep. 6/42, January 30, 1942.

40. Wyckoff, R. W. G., Structure of Crystals, Chemical Catalogue Co. Inc., New York, 1931.

41. Conant, J. B. and Hall, N. F., J.A.C.S. 49, 3062, 1927.

42. Hall, N. F. and Spengeman, W. F., J. A. C. S., 62, 2487, 1940.

43. Cohen, J. B., Organic Chemistry, Edward Arnold, London.

44. Russell, J. and Cameron, A. E., J. A. C. S., 60, 1345, 1938.

45. Linstead, R. P., B.C.S.O. Report, August 4, 1942.

46. Smith, D., Bryant, W. M. D., Mitchel, J., Jr., J. A. C. S., 62, 608, 1940.

47. Thomas, R. J., Anzilotti, W. F. and Hennion, G. F., Ind. Eng. Chem. 32, 408, 1940.

48. Barr, E. S. and Phyler, E. K., J. Chem. Physics, 4, 90, 1936.

49. Bachmann, W. E., Progress Report 15-A10(B2A)13 Sept. 15, 1942.

50. Benford, G. A. and Ingold, C. K., J. Chem. Soc. 1938, page 929.

51. Pictet, A. and Khotinsky, E., Comp. Rend. 144, 210; Ber. 40, 1163, 1907.

52. Minutes, R.D.X. Comm., Toronto, Can. Dec. 19 - 20, 1942.