

# The Thermal Decomposition of 1,3,5 Trinitro Hexahydro 1,3,5 Triazine (RDX)—Part I: The Products and Physical Parameters

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The thermal decomposition of RDX has been investigated in a static system below its melting point at 195°C. The initial decomposition of RDX takes place in the vapor phase. Hydroxymethyl formamide and polymeric materials formed from hydroxymethyl formamide have been shown to be major products. These comparatively low molecular weight materials are highly hydrogen bonded liquids of low volatility which subsequently act as a solvent for RDX. Nitrogen, due to its effect on the rate of diffusion of RDX vapor away from the crystal surface, is shown to have an inhibiting effect.

## Introduction

The thermal decomposition of RDX has been investigated by following the pressure in a closed system below and above its melting point (204°C) by Robertson [1], who concluded that below the melting point a slow solid state decomposition occurred. A product of the solid phase decomposition was assumed to lower the melting point of RDX, and the liquified RDX then decomposed more rapidly than the original solid state decomposition. Bawn [2] has given a similar interpretation, based on the results of Adams [3]; the ratio of the rate of decomposition in the liquid and solid phases was assumed to be approximately 10:1.

In an earlier paper [4] we presented evidence which showed that in the initial stages the decomposition takes place in the vapor phase with the formation of a liquid product, hydroxymethyl formamide, i.e., in our system, RDX does not decompose to any significant extent in the solid state. Maksimov [5] has also observed that the initial decomposition of RDX was slower when

the volume of reaction vessel was filled than when it was empty. More recently, Rauch and Fanelli [6] who quantitatively measured the residual RDX and gaseous products have concluded that in a vacuum system, the thermal decomposition above the melting points occurs both in the gaseous phase and in the liquid phase. Nitrogen dioxide was identified as a product in the early stages of the decomposition, its concentration, although low, being approximately proportional to the volume of the reaction vessel, i.e., nitrogen dioxide was formed in the gaseous phase decomposition. The small concentration of nitrogen dioxide reached a maximum after a few minutes and then disappeared. Unspecified secondary reactions were proposed to account for the phenomenon.

In a series of papers, Batten et al. [7-10] have suggested that where the reaction is carried out in the presence of nitrogen and followed by pressure measurements in a closed system, the influence of the gaseous decomposition products on the undecomposed RDX in the condensed phase is of primary importance. Batten has further suggested that formaldehyde and nitrogen dioxide catalyse the decomposition positively and negatively, respectively.

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The present paper describes in detail the results reported in our previous note and examines the physical processes which occur in the decomposition of RDX below its melting point.

### Experimental

Two samples of RDX were used. One was recrystallised from cyclohexanone at 203.5°C and the other was material sublimed at 100°C and had a mp of 204°C. No significant differences were observed between the results obtained with either material. Hydroxymethyl formamide was prepared by heating 1:1 ratios of formamide and paraformaldehyde to 140°C in sealed tubes, or by reacting 36% formalin with formamide in the presence of Amberlite IRA 400 at 60°C and distilling off the water and excess formamide under vacuum [11]. Methylene diformamide was prepared by heating a 2:1 mixture of formamide with formaldehyde at 160°C. Nitrogen was obtained from oxygen-free nitrogen in a cylinder. Formaldehyde was introduced into reaction vessels in the form of dry paraformaldehyde.

The apparatus and procedure were modifications of a previously described system [12]. Experiments were carried out in Pyrex reaction vessels. In the majority of experiments, they consisted of spherical reaction bulbs and an entry tube, 15 cm long, comprising a B10 cone on the end of a 70-mm stem of a B14 cone. In some experiments, the reaction vessels were cylindrical, approximately 200 mm long and having a volume of 868 ml. Solid reactants were introduced into the weighed reaction vessel of known volume by means of a long scoop to prevent the solids from adhering to the side of the inlet tube. After weighing, the tubing between the glass joints was drawn down to a coarse capillary, the reaction vessel connected to a vacuum line by the B10 joint, evacuated, and sealed. In experiments where nitrogen was added, a known pressure of the gas was admitted prior to sealing. Filled reaction vessels were placed for a known time in a well-stirred polypropylene glycol bath, the temperature being maintained at 195°C to within  $\pm 0.1^\circ\text{C}$ . The temperature distribution within the bath was less than  $0.1^\circ\text{C}$ . To minimize evaporation, the surface of the bath liquid was covered with pearshaped glass globes.

At the end of an experiment, the reaction vessels were removed from the bath, allowed to stand for 24 hours and then opened on a vacuum line. The purpose of the delay in opening the flask was to allow any formaldehyde and hydrogen cyanide present to polymerise. The total gas evolved was estimated by expansion of the gases into a known volume.

### Analysis

The products of decomposition which were isolated and identified were nitrogen, nitric oxide, nitrous oxide, carbon dioxide, carbon monoxide, water, methylol formamide and similar compounds, formaldehyde, hydrogen cyanide, a nitrate, and a nitrite.

Gaseous products were estimated on a mass spectrometer. In early experiments, when the reaction flasks were opened soon after reaction, peaks attributable to hydrogen cyanide and formaldehyde were observed. The former was present in approximately 1% concentration in the gas phase. Water was estimated in only a limited number of experiments by evaporation into a weighed cold trap, or occasionally by the Karl Fischer method. Approximately one molecule of water was formed from every molecule of RDX decomposed.

In preliminary experiments, repeated decomposition of small (0.2 g) RDX samples *in vacuo* produced sufficient liquid product to permit its analysis by elemental methods and acid-alkali hydrolysis. The infra-red spectrum of this liquid, observed initially as droplets on the walls of the reaction flask, was then shown to be similar to the spectrum of hydroxymethyl formamide containing 10% of nitric acid. In subsequent experiments the following analysis scheme was adopted.

After removing the gaseous products, the reaction vessel was filled with nitrogen and removed from the vacuum line. Residual RDX was separated from the products by refluxing with 10 ml water, followed by decantation of the cooled solution, and final washing of the crystals with water. The RDX was then estimated either by weighing the dried crystals or by aqueous titration [13]. Both methods gave the same result. To check the determination, duplicate experiments

were performed, and the RDX estimated by titration without prior separation of the other non-gaseous products. No significant differences in the RDX values were observed.

The major aliquot of the aqueous extract was transferred to a semi-micro steam distillation apparatus for hydrolysis, and the rest was used for colorimetric nitrite, nitrate determination:

(a) *Formic acid, formaldehyde, ammonia determination*

The aqueous solution was transferred to the reaction flask of the distillation apparatus, acidified with sulphuric acid, and the mixture distilled. The distillate was analysed for formic acid by direct titration with N/40 sodium hydroxide solution. Bisulphite was then added and the formaldehyde estimated by titration against N/40 hydrochloric acid. The residue was allowed to cool and made alkaline with 40% sodium hydroxide solution. The ammonia released was distilled into 4% boric acid solution and estimated by titration against N/40 hydrochloric acid.

(b) *Nitrite and Nitrate determination*

Nitrite and nitrate were determined by the

method of Morris and Riley [14]. RDX is soluble in water to the extent of approximately 50 mg/liter and accounts for 10-20% of the reported nitrate value.

It is probable that the nitrate and nitrite were present as an amine salt, but we were unable to identify the constitution of the amine.

## Results and Discussion

The results are given in Tables 1 to 3.

### The Course of the Decomposition

A series of experiments were carried out with 0.2 g RDX in 150-ml reaction flask at 195°C for various reaction times. The results are summarized in Table 1.

The course of the decomposition exhibits the well known S-shaped curve. In our previous communication, this has been shown to be due to both gaseous phase and solution phase decompositions, and this thesis will be further substantiated in the present paper.

The results in Table 1 show that most of the nitrogen available from the decomposed RDX has been recovered as products. Some of the unre-

TABLE I  
The Course of the Decomposition<sup>a</sup>

| Time<br>min                        | RDX Reacted<br>mM | Products       |                  |       |                 |       |                   |       |                 |                              |                              | $\Sigma N^b$<br>N | $\Sigma C^c$<br>C |
|------------------------------------|-------------------|----------------|------------------|-------|-----------------|-------|-------------------|-------|-----------------|------------------------------|------------------------------|-------------------|-------------------|
|                                    |                   | N <sub>2</sub> | N <sub>2</sub> O | NO    | CO <sub>2</sub> | CO    | CH <sub>2</sub> O | HCOOH | NH <sub>3</sub> | NO <sub>3</sub> <sup>-</sup> | NO <sub>2</sub> <sup>-</sup> |                   |                   |
|                                    |                   | mM             |                  |       |                 |       |                   |       |                 |                              |                              |                   |                   |
| 31                                 | 0.042             | 0.035          | 0.058            | 0.036 | 0.021           | 0.008 | 0.048             | 0.039 | 0.035           |                              |                              | 1.01              | 0.92              |
| 60                                 | 0.105             | 0.100          | 0.120            | 0.069 | 0.056           | 0.046 | 0.110             | 0.101 | 0.071           | 0.019                        | 0.004                        | 0.96              | 1.00              |
| 64                                 | 0.120             | 0.111          | 0.135            | 0.079 | 0.058           | 0.049 | 0.126             | 0.107 | 0.081           |                              |                              | .91               | .97               |
| 90                                 | 0.252             | 0.256          | 0.244            | 0.139 | 0.108           | 0.100 | 0.191             | 0.132 | 0.114           | 0.037                        | 0.008                        | .92               | .69               |
| 120                                | 0.361             | 0.414          | 0.394            | 0.221 | 0.183           | 0.170 | 0.292             | 0.164 | 0.156           |                              |                              | .95               | .75               |
| 150                                | 0.570             | 0.661          | 0.626            | 0.342 | 0.345           | 0.232 | 0.630             | 0.270 | 0.240           | 0.050                        | 0.012                        | .94               | .86               |
| 180                                | 0.705             | 0.859          | 0.775            | 0.396 | 0.443           | 0.278 | 0.650             | 0.282 | 0.252           |                              |                              | .95               | .82               |
| 210                                | 0.825             | 1.040          | 0.888            | 0.420 | 0.576           | 0.296 | 0.854             | 0.303 | 0.282           | 0.078                        | 0.019                        | .94               | .81               |
| Volume of reaction vessel 868 mls. |                   |                |                  |       |                 |       |                   |       |                 |                              |                              |                   |                   |
| 15                                 | 0.083             | 0.054          | 0.076            | 0.108 | 0.025           | 0.013 | 0.096             | 0.050 | 0.057           | 0.024                        |                              | .90               | .74               |

<sup>a</sup>Initial RDX = 0.900 mM. T = 195°C. Volume of reaction flasks ~ 150 ml.

<sup>b</sup> $\Sigma N$  = total nitrogen in products.

<sup>c</sup> $\Sigma C$  = total carbon in products.

<sup>d</sup>N = nitrogen from reacted RDX.

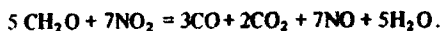
<sup>e</sup>C = carbon from reacted RDX.

covered nitrogen was in the form of polymerised hydrogen cyanide and some as a water insoluble polymer of the type  $[\text{CH}_2\text{N}-\text{CHO}]_n$ . The amount of carbon recovered in the initial stages of the decomposition is nearly 100%, but in the later stages, approximately 20% has not been identified and estimated in the products.

Throughout the course of the decomposition, nitrous oxide and formaldehyde are in a 1:1 ratio with the amount of RDX decomposed. The nitrogen formed is initially close to a 1:1 ratio, but as the decomposition proceeds, the ratio becomes greater than 1:1. Nitric oxide is formed in greater proportions in the initial stages than in the later stages of the reaction. Similarly, the yields of carbon monoxide, formic acid, and ammonia show the same tendency, while yields of carbon dioxide exhibit the opposite effect of increasing in proportion with the RDX decomposed in the later stages of the reaction.

Although nitrogen dioxide was not isolated, the presence of nitrate and nitrite ions among the products suggests that the gas is formed. The nitrate ion is formed in a constant, but low ratio, with RDX decomposed. Nitrite ions are present in a much smaller concentration than might be expected from the reaction of nitrogen dioxide with water, i.e., where the nitrate ion concentration would be equal to the nitrite ion concentration. Probably the nitrite has reacted further with other products. If it is assumed that the nitrate ion is formed from nitrogen dioxide, then this gas would have been present in substantial quantities. The concentration of nitrogen dioxide would certainly be much greater than that indicated by

the nitrate ion concentration, since formaldehyde reacts vigorously with nitrogen dioxide at this temperature [15] according to the equation



While the formaldehyde, formic acid, and ammonia yields are expressed separately in the tables, the formic acid and ammonia and the equivalent amount of formaldehyde are present in combined form as hydroxymethyl formamide, its condensation dimer, and polymeric materials of this type. Extensive investigation of hydroxymethyl formamide has shown that its synthesis by published methods [16] yields mainly the *N* methylol derivation of methylene diformamide together with  $\text{NN}^1$  formyl amino-methyl ether and other high molecular weight materials.

#### Variation of Initial Charge of RDX

The initial charge weight of RDX was varied from 0.094 mM to 0.925 mM in a series of experiments at 195°C and a reaction time of 60 min., the volume of the reaction flasks being kept approximately constant at 150 mls. The results are listed in Table 2.

For a ten-fold variation in the charge weight of RDX, the rate of decomposition remained almost constant, even though the extent of reaction varied from 96.7% for the smallest charge weight to 11.9% for the largest charge weight. These results clearly show that the volume of the reaction vessel is the most important factor in these experiments. If RDX exerted its equilibrium vapor pressure [17] in the initial stages of these experiments,

TABLE 2  
Variation of Initial RDX<sup>a</sup>

| RDX<br>Initial<br>mM | RDX<br>Reacted | Products       |                  |       |                 |       |                   |       |                 |                 |                 | $\Sigma$ N<br>N | $\Sigma$ C<br>C |
|----------------------|----------------|----------------|------------------|-------|-----------------|-------|-------------------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                      |                | N <sub>2</sub> | N <sub>2</sub> O | NO    | CO <sub>2</sub> | CO    | CH <sub>2</sub> O | HCOOH | NH <sub>3</sub> | NO <sub>3</sub> | NO <sub>2</sub> |                 |                 |
|                      |                | mM             |                  |       |                 |       |                   |       |                 |                 |                 |                 |                 |
| 0.090                | 0.087          | 0.070          | 0.094            | 0.097 | 0.041           | 0.035 | 0.090             | 0.070 | 0.060           | 0.025           |                 | 0.97            | 0.87            |
| 0.324                | 0.103          | 0.102          | 0.100            | 0.102 | 0.062           | 0.028 | 0.100             | 0.083 | 0.083           | 0.024           |                 | 0.99            | 0.88            |
| 0.461                | 0.096          | 0.100          | 0.090            | 0.079 | 0.057           | 0.037 | 0.100             | 0.087 | 0.087           | 0.033           |                 | 1.00            | 0.97            |
| 0.885                | 0.105          | 0.100          | 0.120            | 0.069 | 0.056           | 0.046 | 0.110             | 0.101 | 0.071           | 0.019           | 0.004           | 0.96            | 1.00            |

<sup>a</sup>Temperature = 195°C. Volume of reaction flask ~ 150 mls. Time of reaction 60 min.

then in the experiment in which the charge weight was 0.090 mM, 2.5% would be present in the gas phase.

#### Variation of the Volume of the Reaction Vessels

Table I lists the results of a series of experiments in which the volume of the reaction vessel was varied from 11 mls to 150 mls using RDX charges of 0.900 mM and a reaction time of 60 min. Using a larger reaction vessel of 868 mls capacity and an initial charge of 0.900 mM RDX, a 9.2% decomposition was obtained in 15 min, reaction time. On cooling this reaction vessel, RDX was observed condensing on the walls making them opaque. These experiments show that the rate of decomposition of RDX was directly proportional to the volume of the reaction vessel.

#### The Effect of Nitrogen

The effect of nitrogen on the rate of decomposition of RDX was studied in experiments where reaction flasks containing 0.9000 mM of RDX were filled to initial pressure of 96, 314, and 625 mms with nitrogen, and heated at 195°C for 60 min. and 150 min. Attempts were made to analyse the gaseous products, but the presence of large quantities of nitrogen swamped the mass spectrum and made the analysis imprecise.

The results of the other analysis are given in Table 3. They show that the rate of decomposi-

tion of RDX is retarded by the presence of the inert gas nitrogen<sup>1</sup> an effect being observed even at 625 mm. The yield of hydroxymethyl formamide, as measured by the formic acid and ammonia yields, remained approximately constant at 0.5 mM for each mole of RDX decomposed which, in conjunction with the yields in the absence of nitrogen, suggests that there are two different mechanisms operating in the present system.

#### The Physical Processes

The results presented in this paper show conclusively that under these experimental conditions the gas phase decomposition of RDX is of primary importance in the initial stages. It will be shown in Part II that both formaldehyde and hydroxymethyl formamide catalyse the decomposition, the latter because it acts as a solvent for the RDX.

Two opposing factors control the rate of decomposition. One is concerned with processes which effect the vaporisation of RDX, and the other with the processes which effect the hydroxymethyl formamide coming into contact with RDX crystals thus affecting the solution phase decomposition. Both will be diffusion controlled and this will be effected by the sample geometry as suggested by Batten and Murdie [7], by the presence of an inert gas and by other constraints, such as the use of sample tubes. We are of the opinion that the results quoted by Batten and Murdie [7] are not at variance with our thesis.

In all but one of their experiments at 196.5°C, 100 mm Hg of nitrogen was added initially to reduce sublimation of the RDX. We have shown that this is not sufficient to prevent a vapor phase decomposition. When the RDX was spread on the bottom of the reaction vessel, the rate of decomposition was significantly faster than when the RDX was confined in sample tubes (see Fig. 4 and Table 2 of Ref. 7). When 0.2 g RDX was held in either 1, 5, or 10 sample tubes, the induction rates as measured by the slope of the initial reaction in

TABLE 3  
The Effect of Nitrogen<sup>a</sup>

| Time<br>min. | N <sub>2</sub> <sup>b</sup><br>mm | RDX<br>Reacted<br>mM | Products          |                     |                 |
|--------------|-----------------------------------|----------------------|-------------------|---------------------|-----------------|
|              |                                   |                      | CH <sub>2</sub> O | H <sub>2</sub> COOH | NH <sub>3</sub> |
|              |                                   |                      | mM                |                     |                 |
| 60           | 0                                 | 0.105                | 0.110             | 0.101               | 0.071           |
|              | 96                                | 0.102                | 0.107             | 0.054               | 0.056           |
|              | 314                               | 0.058                | 0.062             | 0.034               | 0.040           |
|              | 625                               | 0.050                | 0.055             | 0.036               | 0.041           |
| 150          | 0                                 | 0.570                | 0.630             | 0.270               | 0.240           |
|              | 96                                | 0.465                | 0.416             | 0.216               | 0.214           |
|              | 314                               | 0.268                | 0.314             | 0.121               | 0.126           |
|              | 625                               | 0.218                | 0.247             | 0.091               | 0.115           |

<sup>a</sup>Temperature 195°C. Initial RDX 0.900 mM. Volume of reaction flask ~ 150 ml.

<sup>b</sup>N<sub>2</sub> pressure at 0°C.

<sup>1</sup>In our previous communication [4], the caption to the points are wrongly listed as 58 mm and 119 mm nitrogen. They should read 314 mm and 625 mm, respectively.

the three separate experiments were in the ratio of 1.5:10 (Fig. 4 of Ref. 7). This is what would be expected if the initial decomposition occurred in the gaseous phase.

Batten and Murdie also performed experiments in which the sample tube was almost sealed and in which two 0.2 g charges of RDX were placed in a sample tube and separated by a sinter, 100 mm Hg of nitrogen being present. They rightly suggest that this would be expected to impede the movement of RDX vapor out of the tube. However, the vapor phase reaction would be expected to be localised in the vicinity of the crystals and, moreover, the constraints would have the effect of localising the migration of the product hydroxymethyl formamide which in any case has a low vapor pressure, i.e., hydroxymethyl formamide would condense on the crystals rather than on the sides of the reaction vessel. Thus, the relatively long induction period, during which time the gaseous phase decomposition is mainly taking place, would be expected to be shorter, after which the solution phase decomposition would be of primary importance. Consequently, the rate of decomposition of 0.4 g of RDX in one sample tube separated by the sinter would be expected to be faster than that of 0.2 g RDX in one sample tube. This is clearly shown to be the case in Fig. 6 of Ref. 7.

The same argument may be used to explain the slightly faster rate of reaction obtained when the

pressure of nitrogen was increased to 600 mm Hg (see runs number 9 and 19 of Table 2 Ref. 7).

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