

The Thermal Decomposition of 1,3,5 Trinitro Hexahydro 1,3,5 Triazine (RDX)—Part II: The Effects of the Products

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The effect of products and 1,3,5 trinitrobenzene on the thermal decomposition of RDX in a static system at 195°C has been studied. Formaldehyde, hydroxymethyl formamide, methylene diformamide, and 1,3,5, trinitrobenzene are all shown to enhance the reaction rate. Different initial steps in the mechanisms are indicated for the gaseous and solution phase decompositions.

Introduction

In Part I [1], the products of the thermal decomposition of RDX in a static system at 195°C were quantitatively measured and the course of the decomposition followed. The initial step was shown to take place in the vapor phase. In the present paper, the effects of the products nitrogen, nitrous oxide, nitric oxide, carbon dioxide, carbon monoxide, water, formaldehyde, hydroxymethyl formamide, and methylene diformamide on the decomposition are studied. The effect of a small quantity of 1,3,5 trinitrobenzene has also been included, since an extensive investigation of the decomposition of RDX in 1,3,5 trinitrobenzene [2] has shown that 1,3,5 trinitrobenzene is relatively inert as a solvent.

Experimental

The experimental procedures have been described previously [1]. Analytical grade 1,3,5 trinitrobenzene (mpt 122°C) was melted, solidified, and the mass broken down into granular form.

Hydroxymethyl formamide was introduced into the reaction flask by means of a hypodermic needle. Crystalline materials were mixed with the RDX prior to charge of the reaction vessel.

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Results and Discussion

The results are given in Tables 1 and 2.

The Effect of Product Gases

The effect of the product gases nitrogen, nitrous oxide, nitric oxide, carbon dioxide, carbon monoxide, and water is given in Table 1, which shows that the addition of 314 mm of all the product gases, with the exception of nitric oxide, exhibited the same inhibiting effect as nitrogen. This has been discussed previously and attributed to retardation of the vaporization of RDX. Nitric oxide, while retarding the rate of decomposition enhances the rate of decomposition over that of an inert gas. The effect is, however, small and probably due to minor secondary oxidation reactions of the combustible products.

Formaldehyde is shown in Table 2 to enhance the rate of decomposition. This has also been observed by Batten [3]. In the early stages, the effect is relatively small but it must be remembered that, as a gas, it necessarily retards the vaporization of the RDX; formaldehyde has a greater effect on the later stages of the decomposition. The rate of decomposition is proportional to a function of the concentration of formaldehyde. Formaldehyde is clearly shown to have reacted in those experiments with high initial concentration of formaldehyde, that recovered being less than

TABLE I
The Effect of Product Gases

Temperature 195°C. Initial RDX 0.900 mM. Volume of Reaction Flask 150 ml.
Reaction time 150 mins. Pressure of added gas 314 mm.

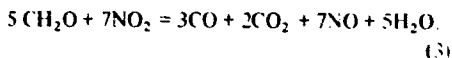
Added Gas	N ₂	N ₂ O	NO	CO ₂	CO	H ₂ O
RDX reacted mM	0.268	0.270	0.310	0.266	0.268	0.270

that initially added. Comparison of experiments with and without added formaldehyde (see also Table I of Part I) show that the yields of nitric oxide, carbon dioxide, and carbon monoxide for a given RDX decomposition are enhanced by the presence of formaldehyde, while the yields of nitrogen and nitrous oxide are unaffected.

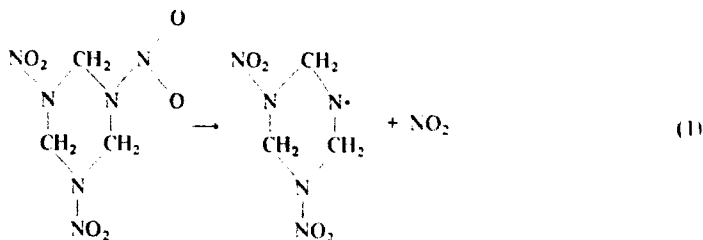
The Mechanism of the Gas Phase Decomposition

The above observations are consistent with the thesis given in Part I [1] and that of Rauch and Fanelli [4] that the first step in the decomposition of RDX in the gaseous phase is the elimination of nitrogen dioxide.

It is suggested that the $\cdot\text{CHOH}\cdot\text{NH}\cdot\text{CHO}$ radicle would be stabilized by delocalisation of electrons and hydrogen bonding. Subsequent reaction with a proton would lead to hydroxymethyl formamide or alternatively the radicle could dimerise. Nitrogen dioxide and formaldehyde react rapidly at 195°C, the reaction being first order with respect to each reactant [5], the overall reaction is represented by the equation:



The reaction scheme leads to the correct ratios of the products in the early stages of the decomposition.



The radicle then breaks down possibly according to the scheme given below

tion with the exception of carbon dioxide and hydroxymethyl formamide. However, hydroxy-

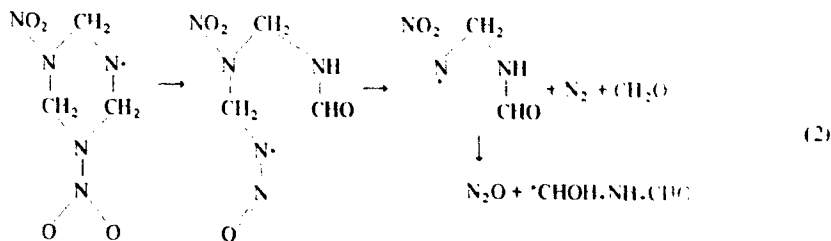
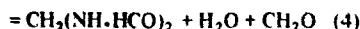


TABLE 2
The Effect of (a) Formaldehyde, (b) Hydroxymethyl formamide, (c) Methylene Di-formamide
and (d) 1,3,5 Trinitrobenzene.^a

Time mins	Additions mM	RDX reacted mM	Products								
			N ₂	N ₂ O	NO	CO ₂	CO	CH ₂ O	HCOOH	NH ₃	NO ₂
			mM								
31		0.042	0.035	0.053	0.036	0.021	0.008	0.048	0.039	0.035	0.010
60		0.105	0.100	0.100	0.069	0.056	0.046	0.110	0.101	0.071	0.019
(a) Formaldehyde											
20	0.076	0.032	0.032	0.029	0.037	0.020	0.025	0.092	0.041	0.036	
40	0.080	0.083	0.062	0.095	0.079	0.050	0.065	0.128	0.056	0.058	
60	0.070	0.153	0.154	0.165	0.123	0.095	0.111	0.174	0.092	0.093	
20	0.370	0.036						0.301	0.039	0.025	0.012
40	0.360	0.101	0.081	0.103	0.087	0.063	0.087	0.337	0.069	0.063	
60	0.380	0.180	0.157	0.210	0.138	0.115	0.131	0.417	0.096	0.094	0.032
(b) Hydroxymethyl formamide											
21	0.180	0.110	0.115	0.139	0.065	0.068	0.037	0.284	0.185	0.200	0.018
30	0.145	0.140	0.158	0.169	0.081	0.078	0.041	0.253	0.162	0.149	
40	0.168	0.204	0.210	0.262	0.109	0.101	0.095	0.358	0.226	0.224	0.025
(c) Methylene di-formamide											
20½	0.115	0.172						0.262	0.242	0.281	0.027
30½	0.114	0.231	0.239	0.307	0.126	0.119	0.091	0.332	0.250	0.316	
40	0.115	0.363	0.400	0.500	0.135	0.202	0.156	0.430	0.325	0.320	0.038
(d) 1,3,5 Trinitrobenzene											
30	0.050	0.140	0.135	0.154	0.100	0.058	0.045	0.088	0.052	0.057	

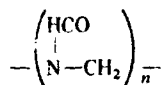
^aTemperature 195°C. Initial RDX 0.900 mM. Volume at reaction flask 150 ml.

methyl formamide decomposes slowly at the reaction temperature to give methylene di-formamide, carbon dioxide, formaldehyde, trimethylamine, and water according to the equations



It is probable that the amine nitrate observed in the decomposition of RDX [1] is trimethylamine nitrate. The pyrolysis of hydroxymethyl formamide is retarded by the presence of nitric acid. Under acid conditions, there is a greater tendency for the formation of a liquid product which is

believed to be a polymer of hydroxymethyl formamide, e.g.,



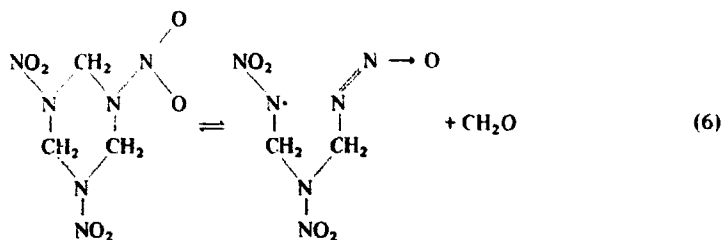
The Effect of 1,3,5 Trinitrobenzene, Hydroxymethyl Formamide, and Methylene Di-formamide

In a study of the decomposition of RDX in 1,3,5 trinitrobenzene [2] it was shown that the initial step was a reversible reaction involving the elimination of formaldehyde. The addition of a small amount of 1,3,5 trinitrobenzene in the present work shows that its presence as a solvent results in a much accelerated rate of decomposition.

Additions of hydroxymethyl formamide and

methylene diformamide also lead to a much accelerated rate of decomposition, even in the early stages of decomposition, (in contrast to the effect of formaldehyde). The greater effect of methy-

ever, that the initial step in the solution phase decomposition is that originally proposed by Robertson [6] and shown to be reversible [2], namely the elimination of formaldehyde



lene diformamide over hydroxymethyl formamide may be due to better mixing of the addition with the RDX. Mass balances show that over 90% of the nitrogen has been recovered, but that not all the carbon containing species have been recovered. Comparison of experiments with and without additions show that the yields of nitrous oxide are enhanced in those experiments with additions, while the yields of hydroxymethyl formamide, as measured by the formic acid and ammonia values, are considerably reduced. The yield of formaldehyde, however, still shows an approximate 1:1 dependence with the RDX decomposed.

The Mechanism of the Solution Phase Decomposition

The experiments with additions, which act as solvents, show clearly that the mechanism of RDX decomposition in the solution phase is different to that in the vapor phase. The absence of an inert gas in these experiments, has meant that the results refer to a combination of solution and gaseous phase decompositions. It is suggested, how-

Subsequent breakdown of the radicle almost certainly involves the formation of two molecules of nitrous oxide. The detailed mechanism of the breakdown, however, must await further experimentation in which the gas phase decomposition is considerably reduced or eliminated.

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*Received May 8, 1973; revised
August 20, 1973*