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TECHNICAL REPORT BRL-TR-2659

CRITICAL ANALYSIS OF NITRAMINE DECOMPOSITION DATA: PRODUCT DISTRIBUTIONS FROM HMX AND RDX DECOMPOSITION

Michael A. Schroeder

June 1985

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A summary of a critical interpretative literature review on product distributions from HMX and RDX decomposition is presented. Principal products formed include N_2O, N_2, H_2CO, CO, CO_2, and NO; these and a number of other products such as HCN, HCOOH, NO_2^-, NO_3^-, hydroxymethyl formamide, H_2, and H_2O are tabulated. NO_2 appears to be formed, but is so reactive that many failures to report it may well be due to the fact that it disappears too rapidly due to further reaction. Relative amounts of HCN and NO_2 may increase at high temperature, while H_2CO, etc., decreases.

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20. Abstract (Cont'd):

A discussion of the first step of the decomposition is presented; at present the nature of this step is still uncertain, although available evidence seems most consistent with N-NO_2 cleavage under at least some conditions, especially in the liquid phase. In the gas phase, possibly a combination of N-NO_2 cleavage and HONO elimination is operating. A possible solution to this problem is offered by isotope-scrambling studies, including both singly labeled and mixtures of un- and fully-^{15}N labeled HMX and RDX; studies of this type now in progress should be continued, and more such studies are needed, under as many types of conditions as possible.

A discussion of some possible unimolecular and bimolecular follow-up steps is also presented; among other things the N_2/N_2O ratio and some possible mechanisms for formation of molecular nitrogen (N_2) are discussed; these pathways are analogous to those often written for formation of N_2O via $H_2C=NNO_2$, except that they involve nitrosoamines, possibly formed via homolytic interchange of NO and NO_2; or via free-radical deoxygenation of HMX or RDX, leading to nitrosoamines, then $H_2C=NNO$, which then breaks down yielding N_2 and formaldehyde. It is suggested that further isotope-labeling studies of the type mentioned above would also contribute to our understanding of the follow-up processes in HMX and RDX decomposition.

In conclusion, it is pointed out that possibly the most useful aspect of thermal decompostion studies at low temperatures and pressures is not to provide product distributions and kinetic parameters that can be applied directly to combustion conditions, but rather to elucidate the types of chemical decomposition processes involved, including minor (at low temperatures and pressures) pathways, in addition to the principal ones. Informed extension of this body of knowledge to combustion conditions could then provide the basis for improved understanding and control of combustion processes and operational properties such as stability, sensitivity, and burning rate behavior.

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I. INTRODUCTION

The voluminous literature on thermal decomposition of nitramines is being reviewed; the compounds of greatest interest are HMX (I) and RDX (II). The emphasis of the present work is on thermal decomposition behavior from the point of view of an organic chemist; the resulting review will thus be complementary to that of McCarty,[1] which emphasizes combustion behavior from the point of view of a physical chemist or combustion engineer. We will spend considerable effort on understanding the thermal decomposition behavior of these compounds at temperatures from 200-300° C and pressures <1 atmosphere. However, the ultimate objective is to use this information to contribute to the understanding of the thermal decomposition processes occurring under combustion and explosion conditions, as well as their relationship to combustion and explosion behavior. A brief discussion[2] of some possible chemical mechanisms has already been prepared; as well as a report[3] summarizing activation energies, frequency factors and other features of HMX and RDX decomposition kinetics.

There are a number of reviews and summaries[1,4-6] of the literature on HMX and RDX Thermal Decomposition, but there is still a need for a critical,

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[1] K.P. McCarty, "HMX Propellant Combustion Studies," AFRPL-TR-76-59 (AD-B017 527L).

[2] M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Results: Some Comments on Chemical Mechanisms," Proceedings of 16th JANNAF Combustion Meeting, CPIA Publication No. 308, Volume II, p. 17, September 1979.

[3] (a) M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Results: Activation Energies and Frequency Factors," BRL report being typed; (b) A short summary of this work is given in the Proceedings of 17th JANNAF Combustion Meeting, CPIA Publication No. 329, Vol. II, p. 493, September 1980; (c) A short summary on the material covered in the present report is given in the Proceedings of 18th JANNAF Combustion Meeting, CPIA Publication No. 347, Volume II, p. 395, October 1981.

[4] F.C. Rauch and R.B. Wainwright, "Studies on Composition B," Final Report, Contract No. DAAA21-68-C-0334, American Cyanamid Company, AD-850 928, February 1969.

[5] (a) K.K. Andreyev, "Thermal Decomposition and Combustion of Explosives," FTD-HT-23-1329-68, AD-693 600, pp. 87-92 and 129-30; (b) F.I. Dubovitskii and B.L. Korsundkii, "Kinetics of the Thermal Decomposition of N-Nitro Compounds," Russian Chemical Reviews, Vol. 50, p. 1828, 1981.

[6] M. BenReuven and L.H. Caveny, "Nitramine Monopropellant Deflagration and General Nonsteady Reacting Rocket Chambers," Princeton University Department of Mechanical and Aerospace Engineering, MAE Report No. 1455, Chapter II. January 1980.

interpretative review of this subject, written from the point of view of a mechanistically oriented physical organic chemist. The present report describes such a review.

The present report is a continuation of the earlier[2,3] pattern of reviewing selected topics in nitramine, HMX and RDX decomposition, chemistry; it consists of a critical analysis of product distributions from HMX and RDX decomposition, together with a discussion of the implications, to the chemical mechanisms of HMX and RDX decomposition, of the results summarized. The studies of product distribution are divided into three headings: (a) Studies of slow thermal decomposition; (b) High temperature, high pressure and high heating rate studies; and (c) Mass spectrometric studies of HMX and RDX decomposition products.

II. SUMMARY OF AVAILABLE LITERATURE DATA ON PRODUCT DISTRIBUTIONS FROM THERMAL DECOMPOSITION OF HMX AND RDX

We now present brief summaries of each of the studies of product distributions from HMX and RDX thermal decomposition of which we are aware. In the preparation of this part of the report, the literature was searched carefully and an attempt was made to include every known study in the above area up to the summer of 1980. If any reader of this report knows of any work that has inadvertently been omitted, the author would very much appreciate being informed of this, so that the omission can be corrected in a later edition or update of the present report.

Tables 1, 2 and 3 show observed product distributions for thermal decomposition of pure RDX, pure HMX, and RDX in solution respectively. Only those studies in which product distributions were given in absolute terms are included in these tables; a considerably larger number of other studies in which products were only identified qualitatively, or were normalized to 100 percent are summarized in the text (part II of the present report). Note also that the product distributions in Tables 1-3 are representative; many of the References cited actually gave more data at different temperatures, etc., much of which has for the sake of brevity been omitted from these tables.

It should be remembered that, as a result of changes in relative rates of the various chemical reactions with temperature, pressure and heating rates, the product distributions of the various low-temperature and low-pressure decompositions summarized here most likely do not reflect the actual product distributions under combustion and explosive conditions; their greatest usefulness will probably arise from the resulting understanding of the basic chemical decomposition processes involved. Together with this understanding, they could then be used as a basis for more realistic estimation of product distributions under actual combustion and explosion conditions.

A. Product Distributions: Slow Decomposition at Relatively Low Temperatures

In general, the products of HMX and RDX thermal decomposition include large amounts of the gases, H_2CO, N_2O, N_2, CO, CO_2, and NO. NO_2 and HCN are sometimes reported and sometimes not, but are so reactive (see below) that failure to detect them does not necessarily have any significance unless special pains were taken to detect them. Minor products sometimes mentioned

Table 1. Product Distributions (Moles/Mole RDX Decomposed) from Thermal Decomposition of Pure RDX

Temperature, °C	195	195	195	206	212	212	225	267	300	600	800	
	°K	468	468	468	479	485	485	498	540	573	873	1073
Reference	21[a]	21[b]	21[c]	9[d]	17[e]	17[f]	7	7	33	33	33	
N_2		0.83	0.65	1.261	1.00	1.08	0.99	1.16	1.03	0.66	0.66	0.60
N_2O		1.4	0.92	1.08	0.95	1.22	1.36	0.98	0.76	0.72	0.60	0.57
NO		0.86	1.30	0.509	0.98	0.23	0.45	0.54	0.75	2.22	2.70	
H_2CO		1.1	1.2	1.04	Present	Present	0.97	Present	Present	0.33		
CO	0.2	0.16	0.359	0.76		0.41	0.52	0.40	0.29	0.18	0.93	0.90
CO_2		0.50	0.30	0.698	0.89	0.54	0.61	0.48	0.44	0.12	0.18	0.15
HCN		Present	Present		Present	0.23	0.03			0.18	1.32	1.38
NO_2						Present						
NH_3		0.83	0.69	0.342								
HCOOH		0.93	0.60	0.367								
NO_3^-			0.29	0.095								
NO_2^-				0.023								
H_2O		Present	Present	Present	Present	Present	0.97	Present	Present			
H_2							0.09	0.06				

a - 4.7% reaction, 150 ml reaction flask; b - 6.0% reaction, 868 ml reaction flask; c - 92% reaction, 150 ml reaction flask; d - average of two runs summarized in Table 3 of Reference of 9; e - 19% of RDX decomposed; f - 93% of RDX decomposed.

Table 2. Product Distributions (Moles/Mole HMX Decomposed) from Thermal Decomposition of Pure HMX

Temperature, °C	226	226	258	280	285	300	600	800	
	°K	499	499	531	553	558	573	873	1073
Reference	29[a]	29[b],55[b]	29[b],55[b]	7	55[b,c]	33	33	33	
N_2		0.19	0.47	0.47	0.16	0.93	0.80	1.00	0.88
N_2O		1.56	2.52	2.57	1.51	1.60	1.72	1.00	0.68
NO		0.24	0.42	0.55	0.95	1.20	2.40	2.80	
H_2CO		2.71	1.26	0.47	Present	0.86	1.44	0.16	
CO		0.19	0.40	0.47	0.57	0.42	0.24	1.44	1.28
CO_2		0.30	0.56	0.54	0.64	0.30	0.16	0.24	0.20
HCN		0.02	0.02	0.07		0.52	0.48	1.60	1.84
NO_2						d	d	d	
NH_3							0.12		
H_2O					Present				
H_2		Present	Present	Present					
$(CN)_2$		Present	Present	Present					

a - "Gas Removal" run; b - "Gas Accumulation" run; c - Decomposing as liquid?; d - Any present included in NO

Table 3. Product Distributions (Moles/Mole RDX Decomposed) from Thermal Decomposition of RDX in the Indicated Solvent

Temperature, °C	184	184	220	225		264	
	°K	457	457	493	498		532
Solvent/Mole fraction RDX	TNB[a]/0.13	TNB[a]/0.13	TNT[d]/0.05	Ester[e]/0.05		TNT[d]/0.05	
Reference	28[b]	28[c]	7	7		7	
N_2		1.88	2.042	1.65	0.89	1.33	
N_2O		0.493	0.558	0.63	1.13	0.47	
NO		1.00	0.558	0.70	0.15	1.02	
H_2CO		0.754	0.815				
CO		0.569	0.603	0.57	0.16	0.32	
CO_2		0.659	0.768	0.83	0.35	0.85	
HCN		0.261	0.12				
NO_2							
NH_3		0.36	0.205				
HCOOH		0.156	0.14				
H_2		Present	Present	0.20	0.05	0.30	
$C_{12}H_5(NO_2)_5$[f]		0.095	0.088				
H_2O		Present	Present				

a - 1,3,5-trinitrobenzene; b - 31% Reaction; c - 81% Reaction; d - 2,4,6-Trinitrotoluene; e - Dicylohexylphthalate; f - 2,4,6,3',5' Pentanitrodiphenyl.

formamide. Small amounts of the liquid product N-hydroxymethylformamide have also been reported. In addition, there is a solid residue which generally accounts for ca 5 percent of the starting material; its composition is uncertain but is quite possibly related to formaldehyde and HCN polymer, or to hydroxymethyl formamide.

In an early and still-important paper,[7] Robertson reports kinetic and product studies on the decomposition of neat liquid HMX and RDX, and of RDX in solution in dicyclohexyl phthalate and in TNT. The apparatus and analytical methods used in Reference 7 are those described in an earlier study.[8] The reaction was followed manometrically, using two types of apparatus: (a) An apparatus in which the sample was dropped suddenly into a hot glass bulb about 2 cm in diameter; and (b) An oven apparatus, in which the sample was suddenly enclosed between two parallel copper surfaces maintained at the required temperature. The pressure rise on decomposition was followed with an oil manometer (slow reactions) or a membrane manometer with photographic recording (fast reactions). Varying pressures (up to atmospheric) of added air, N_2 or H_2 were added to retard vaporization; the rates were first-order and independent of these additions (in vacuo, the material sublimed without decomposing). The products were analyzed chemically, by methods described in Reference 8. The products found included N_2O, N_2, NO, CO, CO_2, and H_2; yields are summarized in Tables 1, 2, and 3. In addition to these products, it was stated that considerable quantities of formaldehyde and water were formed, and that (at least for RDX), a considerable solid residue was found.

The early British closed literature includes a number of reports describing product distributions for HMX and RDX thermal decompositions; these will now be summarized.

Adams[9] described kinetic and product distribution studies on RDX decomposition above and below its melting point. The apparatus used for studies above the melting point is illustrated in Figure 1 of Reference 10, a copy of which is included as Figure 1 of the present report. 10 mg samples of RDX were used, and runs were carried out under 10 cm of H_2; use of 10 cm air instead of the H_2 did not affect the kinetics. Studies below the melting point were carried out using the apparatus described in Figure 1 of

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[7] A.J.B. Robertson, "The Thermal Decomposition of Explosives. Part II. Cyclotrimethylenetrinitramine and Cyclotetramethylenetetranitramine," Trans. Faraday Soc., Vol. 45, p. 85, 1949.

[8] A.J.B. Robertson, "The Thermal Decomposition of Explosives. Part I. Ethylenedinitramine and Tetryl," Trans. Faraday Soc., Vol. 44, p. 677, 1948.

[9] G.K. Adams, "The Thermal Decomposition of RDX," S.A.C. 5766, February 1944.

[10] G.K. Adams and L.A. Wiseman, "The Thermal Decomposition of PETN Alone and in the Presence of Metallic Oxides," S.A.C. 4258, June 1943.

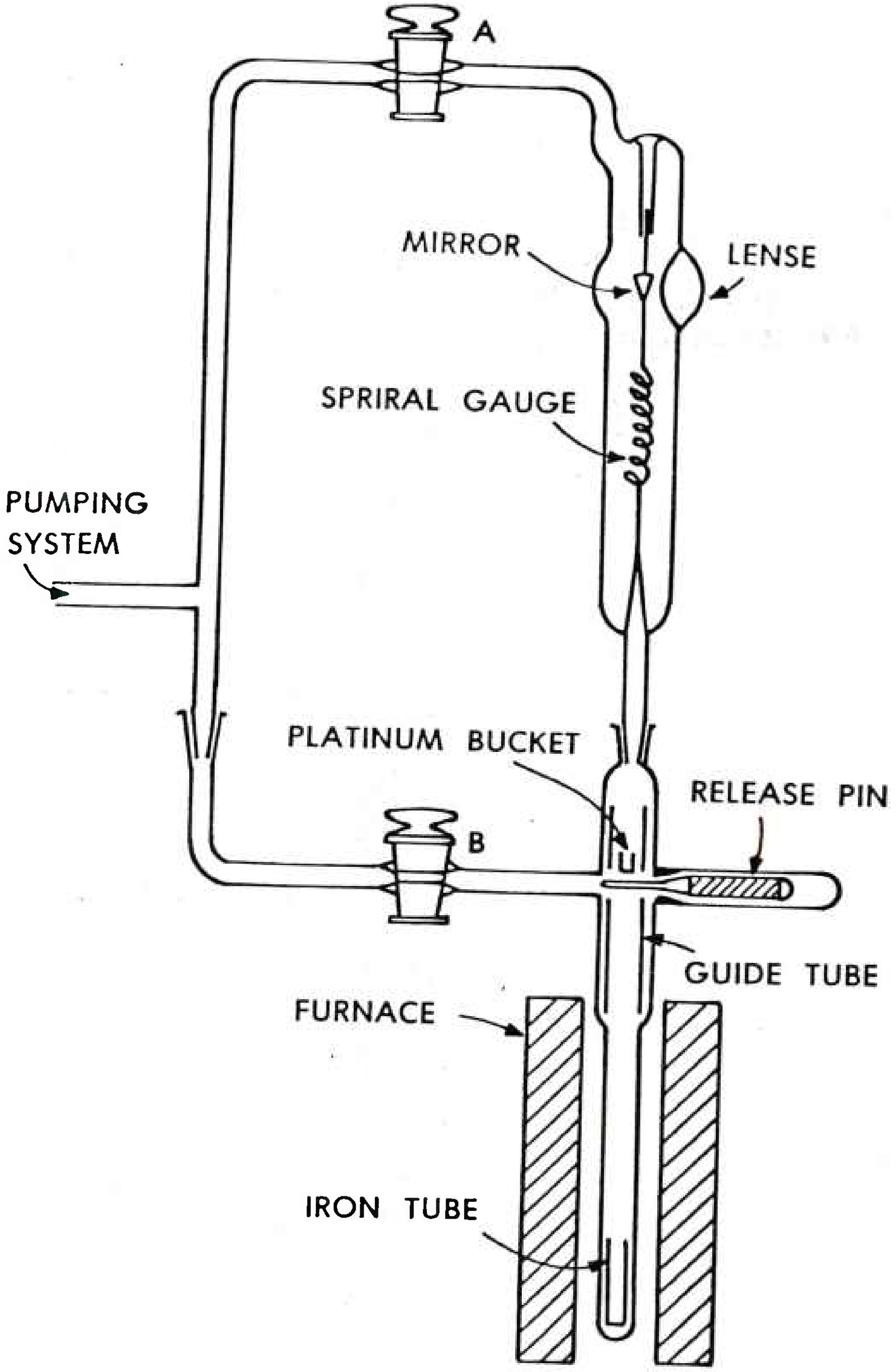

Figure 1. Experimental Apparatus Described in Figure 1 of Reference 10

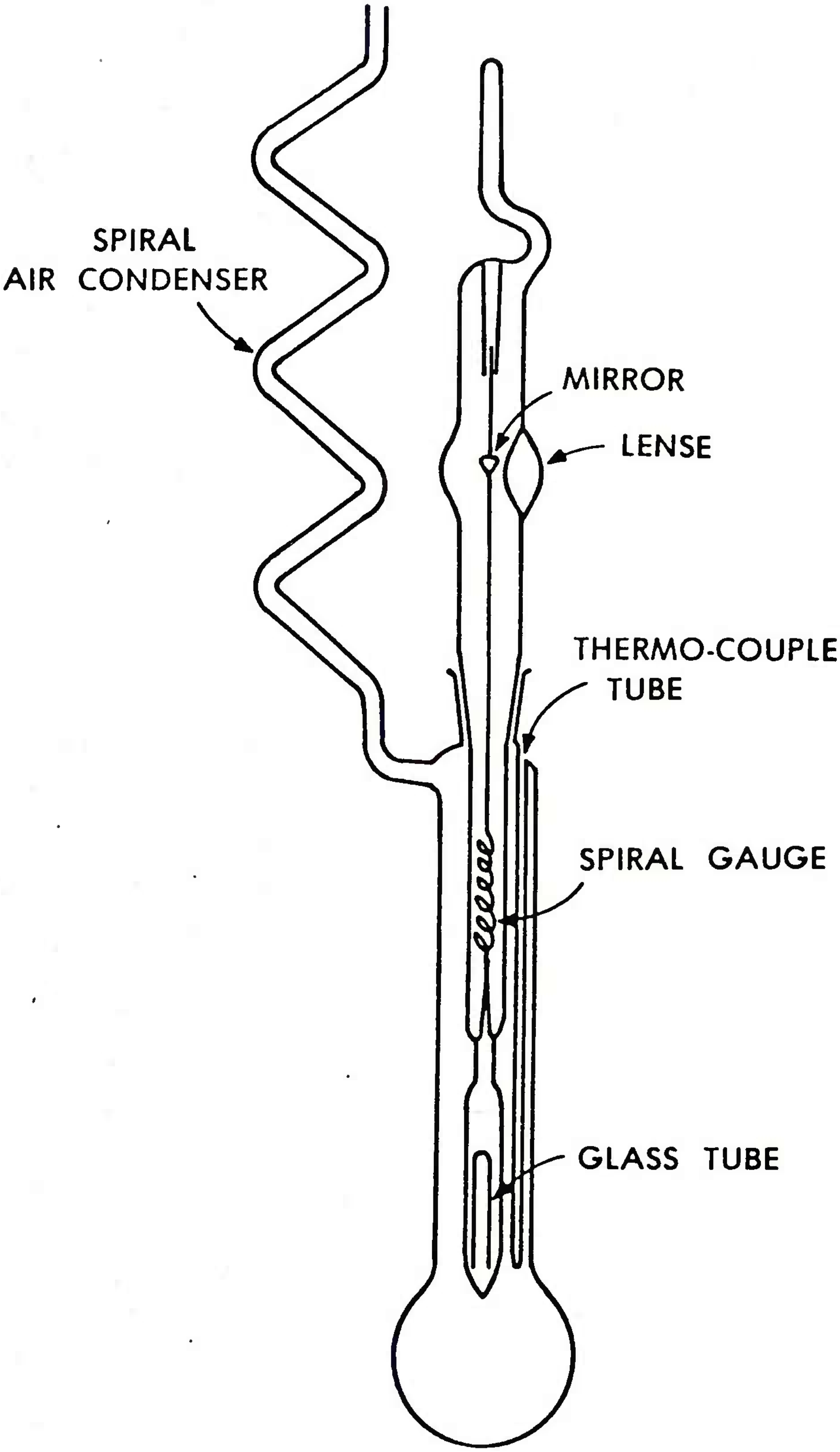

Figure 2. Experimental Apparatus Described in Figure 2 of Reference 11

Reference 11, a copy of which is also attached as Figure 2 of the present report. CO_2, CO, NO, N_2 and N_2O were determined by a method described in Reference 12, and the total carbon-containing gases were determined by a method described in Reference 13. It was stated that the RDX used was made at R.O.F. 37, and before use it was precipitated from acetone and dried in vacuo over phosphorus pentoxide. Two analyses of decomposition products of RDX (Moles per mole of RDX) are given in Table 3 of Reference 9. These were obtained at 206°C in sealed tubes. Products found are summarized in Table 1; they include NO, N_2O, N_2, CO, CO_2, and H_2CO. In addition, it was stated that water was formed.

Reference 14 describes the thermal decomposition of tetryl and RDX. It is stated (page 4 of Reference 14) that the decomposition of RDX is described in Reference 12; I assume that this report contains the experimental details on the work summarized below. However, I have been unable to obtain a copy of Reference 12.

It was stated[14] that analysis of the gaseous products showed that they consisted of N_2O, NO, N_2, CO, CO_2, H_2CO and traces of N_2.

The products of a decomposition at 192°C (ca 10°C below the melting point) were analyzed quantitatively; the composition of the gases (not percent yields based on RDX) was found to be 40.5% N_2O, 32.0% N_2, 8.5% NO, 5.5% CO and 13.5% CO_2. As the decomposition proceeds, the relative amounts of NO and N_2O decreased and CO_2 increased. Formaldehyde could be seen condensing on the apparatus and if the reaction was stopped just before the end, the brownish, resinous residue had a "fishy ammoniacal smell characteristic of an amine."

This report[14] also contains what seems to be a potentially very important observation on formation of NO_2. The products of a reaction at 202°C were trapped out in a liquid-air cooled trap, the contents of which were blue in color. The authors attribute this blue color to N_2O_3, but it is not clear to the present writer why NO, which is also blue in the liquid state[15] could not account for this. In any case, when the contents of the trap were warmed, a vigorous reaction took place. The authors felt that this was due to reaction between NO_2 and formaldehyde. The final products had the composition 30.7% N_2, 34.5% N_2O, 11.5% NO, 9.0% CO and 14.3% CO_2. These presumably represent

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[11] P.R. Rowland and L.A. Wiseman, "A Study of Possible Catalysts for the Thermal Decomposition of Ammonium Nitrate," S.A.C. 4257, June 1943.

[12] Bristol Research Report No. 6 (A.C. 242). No further information available; we were unable to obtain a copy of this document.

[13] G.K. Adams and L.A. Wiseman, "The Thermal Decomposistion of HMX in the Solid State (U)," S.A.C. No. 5149, Nov. 1943, Secret, AD-057 605.

[14] C.E.H. Bawn, J.K. Hays, and F.H. Pollard, "The Thermal Decomposition of Tetryl and R.D.X," S.A.C. No. 2025, 25 Apr 42.

[15] R.C. Weast, ed., "Handbook of Chemistry and Physics," 49th Edition, The Chemical Rubber Company, Cleveland, OH, 44128 Vol. 1968-9, p. B-224.

the gas-phase composition normalized to 100 percent. In view of the fact that the blue color can apparently be explained by NO alone (NO_2 itself condenses to form yellow or colorless materials),[15] and that the "vigorous reaction" could possibly be explained as being due to bubble action on vaporization of very volatile materials such as N_2, it seems that it might be a good idea to repeat this experiment with the aid of modern equipment and methods such as infrared spectrometry. This is especially true in view of the possibility that volume and heat effects due to reaction between gas-phase products could be a source of error in manometric and DSC kinetic studies, especially where the HMX/RDX decomposition is taking place in the vapor phase.

Rauch and Fanelli[16] obtained results allowing a comparison between the liquid and gas-phase reactions. They decomposed RDX samples of varying weights in reactors of different volumes, at five temperatures in the range 207-227°C. Products were analyzed by gas chromatography, infrared, ultra violet and mass spectroscopy. Production of N_2O, CO_2, H_2O, N_2, CH_2O, CO and NO was found to be independent of initial weight of RDX for a reactor of constant volume. When the initial weight of RDX was left constant and the reactor volume was varied N_2O and CO_2 were formed in a manner independent of reactor volume. However the yield-time profile of NO_2 varied with reactor volume; therefore the authors suggested that it is formed in a gas-phase reaction. The fact that N_2O and CO_2 have yield-time profiles that are independent of both reactor volume and sample weight suggests that they are formed in a reaction taking place in the liquid-phase RDX. On this basis, Rauch and Fanelli[16] suggested that the mechanisms in the gas and liquid phases differ from each other.

The present writer cannot help wondering whether the data necessarily require that all of the NO_2 be formed in the vapor phase. It is true that the observed dependence of NO_2 formation on reactor volume could be explained if NO_2 is formed only in the vapor phase, since the amount of NO_2 should then be proportional to reactor volume. However, it was noted[16,17] that NO_2 reacts further after being formed. Now, if NO_2 is formed in the liquid phase, escapes to the vapor phase and then reacts again with gaseous products or with the liquid RDX, the amount of NO_2 the system can accomodate might also be proportional to the reactor volume. Note that it is not being argued that there is no gas phase reaction; some gas phase reaction seems necessary to explain the results of Cosgrove and Owen (see below). Also, the other products (N_2O, CH_2O, N_2, etc.) are probably formed in the liquid phase, according to the reasoning of Rauch and Fanelli[16,17] summarized above. What is being raised is the possibility that the results may be consistent with the idea that some NO_2 is also generated in the liquid phase, quite possibly by

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[16] F.C. Rauch and A.J. Fanelli, "The Thermal Decomposition Kinetics of Hexahydro-1,3,5-Trinitro-s-Triazine Above the Melting Point: Evidence for Both a Gas and Liquid Phase Decomposition," J. Phys. Chem., Vol. 73, pp. 1604-8, 1969.

[17] F.C. Rauch and R.B. Wainwright, "Studies on Composition B," Final Report, Contract No. DAAA21-68-C-0334, American Cyanamid Company, AD-850 928, February 1969.

the same mechanism (N-NO_2 cleavage) suggested for the vapor phase by Rauch and Fanelli.[16,17] See also the discussion on pp. 78-80 of the present report.

Note that the amount of NO_2 present drops to zero by the end of the reaction, presumably because it reacts with other products or with unreacted RDX. Possibly the failure to detect NO_2 in many experiments is due to destruction of NO_2 through further reaction with the other products, or with unreacted HMX or RDX.

The above work is described in more detail in a series of three reports,[17-19] which also include considerable material not published in Reference 16. The overall object of this work was a basic and applied study of Composition B. (Composition B is a secondary explosive consisting of a 60:40 mixture of RDX and TNT, plus a small amount of wax).

The reaction was carried out under vacuum,[16-19] in reactors of varying volumes constructed so that the entire volume available to RDX or its gaseous decomposition products was held at the stated temperature. The RDX was decomposed at several temperatures in the range 207-227° C, and the disappearance of RDX was followed by gas chromatography. The decomposition followed first-order kinetics.

Ten gaseous products were identified by gas chromatography, IR, UV and mass spectrometry. These were (yields summarized in Table 1) as follows: N_2, N_2O, NO, CO_2, CO, HCN, CH_2O, and H_2O. NO_2 and a trace of HCOOH were also found. It was found that the ratios of these products were quite constant throughout the decomposition (See Table 5 of Reference 17) with the exception of NO_2, HCN and possibly H_2O, which increased and then decreased in the manner described above for NO_2. All other products exhibited yield/time curves similar to those obtained[16] for N_2O and CO_2; this suggests that they too are formed in a liquid-phase reaction.

In addition to these gaseous products, small amounts of more than ten relatively nonvolatile components were found; it was suggested that at least several (and possibly most) of these might be H_2CO and HCN oligomers and polymers.

From the production profiles of the gaseous products, it appeared that as much as 15% of the products might be in the solid phase at some stages of the reaction. It was suggested that some of the products might be HCN or H_2CO oligomers or polymers. However, three of them were present in sufficient quantity to obtain a limited amount of Mass Spectral data; these were identified as hexahydro-1,3,5-trinitroso-s-triazine (III) and hexahydro-1-nitroso-3,5-dinitro-s-triazine (IV). The identities of these products were

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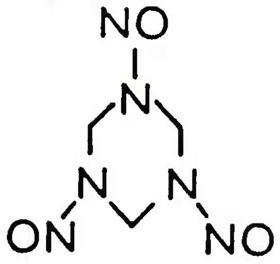
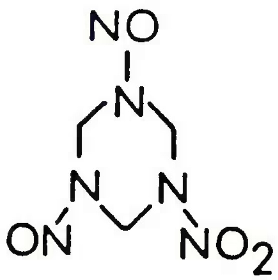
[18] F.C. Rauch and W.P. Colman, "Studies on Composition B," Final Report, Contract No. DAAA21-70-0334, American Cyanamid Company, AD-869 226, March 1970.

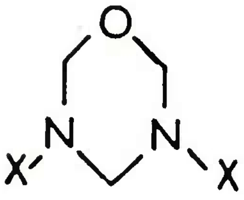
[19] W.P. Colman and F.C Rauch, "Studies on Composition B," Final Report, Contract NO. DAAA21-70-0531, American Cyanamid Company, AD-881 190, February 1971.



III



IV



(x = NO or NO_2)
V

confirmed by independent synthesis and matching of IR, Mass Spectral and Vapor phase chromatograph (VPC) data. A third product was not positively identified but it was suggested that it might be something like V.

The residue left at the end of the reaction is brown, insoluble in common solvents and contains CN unsaturation, as well as carbonate and/or nitrate anion according to IR.

Some effort was also expended[17,19] on analysis of impurities in military grade RDX and TNT. In view of the claimed isolation of the nitroso compounds III and IV, it seems worth mentioning that VPC analysis of military grade RDX does yield peaks with retention times characteristic of the nitroso compounds III and IV. Since III and IV are apparently present as impurities in military grade RDX it seems worthwhile at this time to give information from References 17 and 19 on the purification of the starting materials for the decomposition studies, and on analysis of impurities in military grade RDX.

RDX used in the investigation was recrystallized from γ-butyrolactone, then three times from aqueous acetone. It was stored under ethanol, then filtered and dried under vacuum. It melted at 204-205.5° C(dec). No impurities were detected chromatographically; the purity was estimated at greater than 99.5%.

Quantitative yields of the nitroso compounds III and IV are not given. However, the authors are obviously aware of the occurence of these compounds in impure RDX; and they state that the material used for their studies was more than 99.5% pure, no impurities being detectable chromatographically. Thus it seems reasonable to assume that the nitroso compounds found in the decomposition mixtures were authentic products of the decomposition of RDX and not artifacts resulting from use of impure RDX. However, since the nitroso compounds III and IV do occur in impure RDX, further confirmation of their formation in the thermal decomposition might be helpful, as well as studies to determine whether similar compounds are formed in decomposition of HMX.

The reason for dwelling so much on the question of the authenticity of the nitroso compounds III and IV is that as discussed earlier[2] and below, it seems possible that these compounds, if actually formed in the decomposition, may constitute important evidence as to whether at least some of the RDX (and by implication HMX) decomposes at least in part by N-NO_2 cleavage, or by a pathway involving early intermolecular loss of oxygen from a nitro group to give an isolable nitroso derivative as a primary product.

Preliminary studies of the decomposition of RDX/TNT mixtures were also reported;[18] the first-order rate constants for RDX decomposition were independent of TNT concentration, while the first order constants for TNT increased markedly with increasing RDX concentration. The gaseous products were stated to be superpositions of the RDX and TNT products, but higher intermediates, for example III and IV, were not observed from decomposition of the mixtures, even under conditions in which they were seen in RDX and TNT alone. The decompositions were followed by gas chromatographic analysis for RDX, TNT and decomposition products.

In the third and final report of the series,[19] an attempt was made to observe the decomposing RDX in a high temperature IR cell. The gases produced were found to include N_2O, HCN, CO_2, and H_2O, in agreement with previous results. Formaldehyde wasn't observed but it was suggested that it may have been polymerized. There was also observed a strongly absorbing and quickly reacting gaseous intermediate absorbing at 1620 cm^{-1}.

Cosgrove and Owen[20-22] studied the decomposition of solid RDX in the presence of RDX vapor at a temperature of 195°C, i.e., just a little below its melting point of 203-4°C. They found that the rate of RDX decomposition was (a) directly proportional to the volume of the reaction vessel; (b) for a constant volume independent of the amount of RDX present; and (c) retarded by the presence of inert gases such as nitrogen. From this they concluded that RDX does not decompose appreciably in the solid state at this temperature. Rather, it vaporizes, the vapor undergoes decomposition, and the products of this decomposition condense on the solid RDX and dissolve it, resulting in an

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[20] J.D. Cosgrove and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX)," Chemical Communications, p. 286, 1968.

[21] J.D. Cosgrove and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX) Part I: The Products and Physical Parameters," Combustion and Flame, Vol. 22, p. 13, 1974.

[22] J.D. Cosgrove and A.J. Owen, "The Thermal Decomposition of 1,3,5,trinitrohexahydro-1,3,5-Triazine (RDX). Part II. The Effects of the Products," Combustion and Flame, Vol. 22, p. 19, 1974.

accelerating reaction. Many of the earlier results of Batten[23-26] were rationalized with this approach. Batten[23-26] has also studied the decomposition of RDX below the melting point, and has interpreted the results in terms of positive or negative catalysis of the condensed phase decomposition by gaseous decomposition products. After the publication of Batten's work, Cosgrove and Owen[21] argued in favor of the gas-phase decomposition picture, saying that the results quoted by Batten are not at variance with their suggestion[20,21] that the gas-phase decomposition is important in the early stages of the reaction. In addition to the arguments of Cosgrove and Owen, this writer feels what it is worth noting that Batten[23] reported that with 0.4 g of RDX in a standard sample tube, the induction rate (in percent per minute) was one-half that with only 0.2 g RDX in the sample tube. Since the sample size was twice as great, this corresponds to a constant rate of decomposition in grams/minute. Since the same constant-volume reactor was presumably used for both experiments, this result seems more consistent with gas phase decomposition if it is considered that the second 0.2 g of RDX must lie underneath the first 0.2 g, and hence its vaporization is suppressed. In general, the present writer feels that the increase in rate with increasing reactor volume, or amount of free space, spreading, etc., and its independence of sample weight at constant volume, suggest that the gas phase decomposition is important in the early stages of the decomposition below the melting point. Note however that the decomposition residue is a positive catalyst, and that such products as formaldehyde, NO_2 and hydroxymethylformamide can catalyze the reaction either positively or negatively depending on the exact reaction conditions (see for example References 22 and 25). Thus it may well be possible to explain just about any set of results by some combination of positive and negative catalysis of the condensed phase reaction by gaseous products such as formaldehyde and NO_2, especially when the possibility of reaction between these products is considered.

One possible type of experiment that might help resolve this would be to use various amounts of sample in varying numbers of sample tubes of similar construction, in reactors of differing volumes but otherwise similar construction. This would make it possible to get a better idea of the effect

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[23] J.J. Batten and D.C. Murdie, "The Thermal Decomposition of RDX at Temperatures Below the Melting Point. I. Comments on the Mechanism," Aust. J. Chem., Vol. 23, p. 737, 1970.

[24] J.J. Batten and D.C. Murdie, "The Thermal Decomposition of RDX at Temperatures Below the Melting Point. II. Activation Energy," Aust. J. Chem., Vol. 23, p. 749, 1970.

[25] J.J. Batten, "The Thermal Decomposition of RDX at Temperatures Below the Melting Point. III. Towards the Elucidation of the Mechanism," Aust. J. Chem., Vol. 24, p. 945, 1971.

[26] J.J. Batten, "The Thermal Decomposition of RDX at Temperatures Below the Melting Point. IV. Catalysis of the Decomposition by Formaldehyde," Aust. J. Chem., Vol. 24, p. 2025, 1971.

of sample size, configuration, and reactor volume, separately. This should be done for HMX as well as for RDX. (See also the discussion on p. 27 of the work of Maksimov.)

Furthermore, just because it is said (literature summarized in References 3a and 3b) that the gas-phase decomposition seems important in decomposition of HMX and RDX below their melting points, it does not necessarily follow that true solid-state decomposition does not occur, or is unimportant under all conditions. In studies on HMX decomposition at 271, 273, and 276°C, Robertson[7] observed that some reaction appeared to take place before complete liquefaction; this seems consistent with the observation[27] of self-heating and increased evolution of product gases in the differential scanning calorimetry (DSC) and flow reactor mass spectrometry (FRMS) of HMX at temperatures just below its melting point. It seems uncertain whether this is due to a true solid state decomposition or to gas- and liquid state processes such as accumulation on the solid surface of liquid products of initial vapor-phase decomposition as suggested for the decomposition of RDX below its melting point.[20] This should be investigated, since it may well prove important to our understanding of the role of solid-state decomposition under combustion conditions.

The above discussion of gas- and liquid-phase vs solid-state decomposition in the region below the melting point was included because it will be referred to in later sections of the report. We now return to our discussion of the product distributions obtained by Cosgrove and Owen, for decomposition of RDX below its melting point.

Gaseous products were estimated on a mass spectrometer, residual RDX was estimated by non-aqueous titration or by separating and weighing the crystals; formic acid, formaldehyde and ammonia were analyzed by titration, and nitrite and nitrate were determined by the method of Morris and Riley (Reference given in Reference 21).

The products[21] were as follows: N_2, N_2O, NO, CO_2, CO, CH_2O, HCOOH, NH_3, NO_3^-, NO_2^-, H_2O, HCN, and hydroxymethyl formamide and similar components. Final product distributions are summarized in Tables 1-3. Due to the method of analysis used, it is possible that NH_3 and HCOOH were actually present in combined form, such as hydroxymethyl formamide or related polymers.

Products at various other reaction times were also reported[21] (Table 1 of Reference 21). Through the course of the decomposition, N_2O and H_2CO were in approximately 1:1 ratio to the amount of RDX decomposed. The N_2 was initially close to 1:1 but got larger as the reaction proceeded. NO, CO, HCOOH and NH_3 were found in greater proportion in the initial than the later stages of the reaction, while CO_2 exhibited the opposite tendency. Nitrogen recoveries were in the 90-100% range, while carbon recovery was almost 100% early in the decomposition but fell as low as 70-80% later in the decomposition. NO_2 was not isolated but it was suggested that the presence of NO_2^- and NO_3^- was

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[27] B.B. Goshgarian, "The Thermal Decomposition of Cyclotrimethylenetrinitramine (RDX) and Cyclotetramethylenetetranitramine (HMX)," AFRPL-TR-78-76, AD-B032 275L, October 1978.

consistent with its presence at some stage of the decomposition. In a reactor of constant volume, product distributions appear relatively independent of initial weight of RDX (Table 2 of Reference 21).

Liquid decomposition products condensed on the sides of the reaction flask; it was possible to collect enough of this liquid for analysis. The infrared spectrum of this liquid was similar to the spectrum of hydroxymethyl formamide ($HOCH_2NHCHO$) containing 10% nitric acid.[22]

These authors also studied the effects of products and of trinitrobenzene on the thermal decomposition of solid RDX in contact with the vapor at 195°C.[22] The product gases N_2, N_2O, CO_2, CO and H_2O were found to retard the reaction; this was attributed to physical retardation of the vaporization of RDX by the added gas. NO also retarded the decomposition, but its retardation was somewhat weaker than the other gases. H_2CO, $HOCH_2NHCOH$ and $HCONHCH_2NHCHO$, on the other hand, were found to enhance the rate, as did trinitrobenzene. The yields of NO, CO and CO_2 were enhanced by the presence of formaldehyde, while those of N_2 and N_2O were unaffected (Table 2 of Reference 22, Table 1 of Reference 21).

A later paper[28] from the same group describes product and kinetic studies on the decomposition of RDX in solution in 1,3,5-trinitrobenzene (TNB) at 173-84°C. Known amounts of RDX and TNB in spherical reaction flasks were decomposed in an oil bath thermostated at the required temperature, and then removed from the bath and rapidly cooled. They were then opened under vacuum, the total gas evolved was measured manometrically, and the N_2, N_2O, NO, CO and CO_2 were analyzed quantitatively by mass spectrometry. Formaldehyde was analyzed by heating the residue, trapping the evolved gases with sodium sulphite and titrating with 0.1N HCl. Hydroxymethylformamide ($HCONHCH_2OH$) was isolated and identified by thin layer chromatography, and analyzed by hydrolysis and analysis of the resulting HCOOH, H_2CO and NH_3. 2,4,6,3',5' pentanitrodiphenyl was isolated by thin layer chromatography and identified by comparison of its melting point, IR spectrum, R_F value and color reactions on a TLC plate with those of an authentic sample. RDX and 2,4,6,3',5'-pentanitrodiphenyl were analyzed quantitatively by UV analysis of a solution obtained by extraction of the material in their respective TLC spots.

The products isolated[28] from decomposition of RDX in TNB include N_2, N_2O, NO, CO, CO_2, HCN, H_2O, H_2CO, $HCONHCH_2OH$ (analyzed as HCOOH, H_2CO, and NH_3), 2,4,6,3',5'-pentanitrodiphenyl and a black unidentified solid residue. H_2 was sometimes seen in low yields (~1%). Products obtained at various stages of the decomposition in the absence of any reactants other than RDX and TNB are summarized in Table 1 of Reference 28; products near the end are tabulated in Table 3 of the present report. Note the formation of large amounts of N_2; this suggests that formation of increased amounts of N_2 from decomposition of RDX in solution in TNT may be due to the nitroaromatic nature of the solvent.

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[28] D.F. Debenham and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX) in 1,3,5-Trinitrobenzene," Proceedings of Symposium on Chemical Problems Connected with Stability of Explosives, No. 4, p. 201, 1977.

The effect of added H_2CO on the product distribution at various stages of the reaction is shown in Table 3 of Reference 28. The observations from the information in this Table include the following:

(a) Under the conditions of the study,[28] added formaldehyde retards the decomposition of RDX.

(b) Added formaldehyde increases the yield and rate of formation of pentanitrodiphenyl.

(c) Part of the added formaldehyde reacts.

(d) Added formaldehyde affects the composition of the gaseous products; in particular more N_2O and less NO and N_2 are formed than without added formaldehyde.

(e) In the early stages of the reaction with formaldehyde present, the fraction of nitrogen-containing products recovered is only about 60-70 percent, but improves as the reaction proceeds.

The authors also state[28] that at temperatures of 100°C to 140°C, formic acid, formaldehyde and ammonia readily form hydroxymethylformamide. No Reference is given; presumably they tried this experiment in their laboratory. This is not inconsistent with the idea that the hydroxymethylformamide is not primary product, but is formed by reaction among the other products.

Suryanarayana and coworkers[29] studied the decomposition of "β-HMX" (But was it converted to δ-HMX by the time it reached the temperature range (226-60°C) at which the experiments were carried out?).

Technical HMX was purified by Soxhlet extraction followed by three recrystallizations from acetone. The actual experiments were of two types: "gas accumulation" and "gas removal." In the gas accumulation experiments, 50 mg samples of β-HMX were heated at constant temperature in a vacuum system under 40 mm Argon (to eliminate sublimation). Samples for analysis on a mass spectrometer were taken through a 1 ml sampling volume. A single "gas removal" experiment was done, in which the system was kept under vacuum and the product gases diverted directly to a mass spectrometer. Maximum pressure was 2.5 mm, as opposed to 50 mm in the gas accumulation experiment. Analysis was by mass spectrometry, using previously determined calibration factors and known fragmentation patterns for the products.

The products were N_2O, HCHO, N_2, NO, CO, CO_2, and HCN, $(CN)_2$ and H_2. No higher mass peaks were reported, nor was m/e 46 (NO_2). Products were summarized in Table 2 of Reference 29; representative data are included in table 2 of the present report.

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[29] B. Suryanarayana and R.J. Graybush, "Thermal Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane (HMX): A Mass Spectrometric Study of the Products from β-HMX," Proceedings of 39th Congress on Ind. Chem., Gr. X-S.24-591, 1966.

About 90% of the nitro groups are recovered as $N_2O + N_2 + NO$ in the gas accumulation run, as opposed to 50% in the "gas removal" run and 90% in Robertson's[7] work. Thus it seems worth commenting that (a) Suryanarayana et. al. seem to have gotten a much larger N_2O/N_2 ratio than Robertson; and (b) in view of the discussion on pp. 21-23 it does not seem unreasonable to suspect that some of the decomposition described in Reference 29 may have taken place in the vapor phase rather than the solid phase.

Fogel'zang, Svetlov, Adzheman, Kolyasov and Sergienko[30] were concerned primarily with a comparison of combustion behavior of N-nitro and C-nitro compounds. The N-nitro compounds are found to burn faster than the C-nitro compounds; this was attributed[30] to formation of N_2O from the nitramines, with faster combustion of mixtures containing N_2O. However, some information on thermal decomposition was also given; this is summarized in Table 1 of Reference 30. The yields in percent of N_2, NO, N_2O, NO_2, CO and CO_2 from the indicated materials were as follows: RDX (solid) at 195°C, 36, 5, 37, 0, 11.2, 10.8; RDX (liquid) at 210°C, 38, 5.3, 33, 0, 12.7, 11; Cyclotrimethylenetrinitrosoamine at 110°C, 44.5, 49.5, 5.2, 0, 0, 0.8.

The yields given in this table are yields of gaseous products normalized to 100%; no indication of percent recovery is given. Other than the information given in the table, there is little indication of how the decomposition experiments were done. No mention is made of H_2O, H_2CO, HCN or NO_2, but it is possible that these may have been formed and lost due to polymerization or other further reaction.

In spite of the small amount of information as to the experimental details, some of the observed trends seem worth discussing further. For one thing, decomposition of RDX below its melting point (Gas and liquid-or solution-phase decomposition?)[20] gave an N_2/N_2O ratio of 36/37 = 0.97, while above the melting point (liquid phase decomposition) the N_2/N_2O ratio is higher (38/33 = 1.15). If the gas- and solution- phase decompositions are important in decomposition of RDX below its melting point, this is consistent with bimolecular abstraction of oxygen as discussed earlier,[2] since this would be expected to become more important in the liquid due to the greater concentration of RDX) in the liquid than in the gaseous or solution phases. This could lead to nitrosoamines which could decompose via nitroformimines ($H_2C{=}NNO$) rather than nitroformines (H_2CNNO). The nitrosoformimines could give N_2 on decomposition, rather than the N_2O formed from the nitroformimines. In agreement with this, the trinitroso analog of RDX was found to give more N_2 (445%) than RDX (38%) but only 5.2% N_2O as opposed to 33-37% for RDX, although without more information on product recovery the significance of this is uncertain. The trinitroso compound was presumably decomposing in the liquid phase at 110°C, since according to Beilstein (26, 6) it melts at 105-6°C.

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[30] A.E. Fogel'zang, B.S. Svetlov, V.Ya. Adzhemyan, S.M. Kolyasov, O.A. Sergienko and S.M. Petrov, "Combustion of Explosive Compounds with Nitrogen - Nitrogen Bonds," Fizika Goreniya I Vzryva, Vol. 12, No. 6, p. 827, 1974. English Translation, page 732.

Note also that the trinitroso compound gives much more NO than does RDX itself; this is consistent with decomposition of the trinitroso compound by N-NO cleavage, an analogy which suggests that N-NO_2 cleavage in RDX itself should at least be a readily accessible pathway.

Maksimov[31,32] studied the decomposition of nominally solid RDX (at 150-97°C) and HMX (176-230°C). Kinetics and Arrhenius parameters were studied, as were effects of additive gases such as NO and NO_2. The gas phase resulting from the decomposition of nominally solid HMX and RDX contained formaldehyde and NO, as did the gas phase resulting from decomposition of these same two compounds in solution in m-dinitrobenzene.

It was also reported that increasing the m/v ratio slows down the initial decomposition. Further information on this point is given by Reference 32 which appears to be a summary of the work described in Reference 31. Figure 1 of Reference 31 (Figure 60 of Reference 32) and accompanying discussion indicate that the rate of decomposition of RDX (at least at 190°C) (below its melting point) decreases with increasing mass/volume ratio, in agreement with the work discussed on pages 21-23 of the present report. The discussion on page 2 (accompanying Figure 3) of Reference 31 (page 91 of Reference 32) indicates that HMX exhibits this same tendency, but apparently to a lesser degree. These results are again in agreement with the idea that gas phase decomposition is important in the thermal decomposition of HMX and RDX at temperatures below their melting points, but possibly somewhat less important for HMX than for RDX.

B. Product Distributions: High Temperature and High-Heating-Rate Studies

Axworthy, Flanagan and Woolery[33] carried out high-temperature thermal decomposition studies on HMX, RDX and TAGN; only the HMX and RDX studies will be described here. Samples (ca 0.2 mg) were heated under a stream of helium (30 cm/sec flowrate) in a reactor shown in Figure 2 of Reference 33. The authors state that reaction temperature was reached in less than 1 second and the gaseous products remained in the heated zone for ca 0.25 sec. Analysis was by GC of the flowing gas stream (for N_2, N_2O, CO_2 and CO) and by wet chemical colorimetric means for HCN, NH_3, and H_2CO. NO and NO_2 were measured

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[31] Yu.Ya. Maksimov, "Thermal Decompositions of Hexogen and Octogen," Tr. Mosk. Khim-Tekhnol., Inst. No. 53, pp. 73-84, 1967 (Chem. Abstr., Vol. 68, p. 41742r). A translation is available: LA-TR-68-30, Los Alamos Scientific Laboratory, July 1968, translated by Helen J. Dahlby.

[32] K.K. Andreyev, "Thermal Decomposition and Combustion of Explosives," FTD-HT-23-1329-68, pp. 87-92 and 129, AD-693 600, 14 July 1969. References are given in a second volume, FTD-MT-24-147-70.

[33] A.E Axworthy, J.E. Flanagan, and D.O. Woolery, "High Temperature Pyrolysis Studies of HMX, RDX and TAGN," Proceedings of 15th JANNAF Combustion Meeting, Vol. I, p. 253, September 1978.

together by a procedure which the authors point out (page 257) would cause oxidation of NO to NO_2. Thus the reported yields of NO also include any NO_2 formed in the reaction.

The product distributions obtained are reported by the authors in Figures 3-6 of Reference 33 and in Table A of Reference 34a. The results at 300, 600 and 800°C are tabulated in Tables 1 and 2 of the present report in order to get a better idea of the temperature variation. The numbers were converted to moles of product/mole of HMX or RDX, by multiplying numbers read from Table A of Reference 34 (where possible), or from the appropriate Figure of Reference 33 by a factor of 3/100 for RDX or 4/100 for HMX, or by twice these numbers for NO (+ NO_2).

On examination of Reference 33, the following trends emerge: (a) The yield of HCN increases with temperature; (b) The yield of CO increases with temperature; (c) the yields of N_2O and of H_2CO decrease with temperature; and (d) Product recovery seems good, especially for HMX at 600°C, for which all products were studied. However, it seems low for the RDX study at 300°C. The low H_2CO yield here was apparently a real effect, since it was still found when HMX and RDX measurements were alternated.

Experiments were carried out in which NO or N_2O were used as carrier gases with HMX. NO had no effect on the yield of HCN from HMX, or on the yield of H_2CO at 300°C, but at 400° N_2O increased the yield of H_2CO from 6 percent to 16 percent. These were the only additive effect experiments performed.

The following year, at the 16th JANNAF Combustion Meeting, the same group described[34] a continuation of this work in which a second-stage reactor was added, downstream from the first-stage reactor described above. Residence time in the first stage was stated to be about 2.1 seconds, or ten times longer than the first stage. The second stage was held at a different (usually higher) temperature from the first stage. Variations in product distribution that result from variation in the first stage temperature alone may be attributable to the primary pyrolysis reactions, while any change in product yield that results from varying the second stage temperature only must of course result from the occurrence of secondary reactions.

HCN yields increased from <u>ca</u> 10 percent at 300°C to over 50 percent at 1000°C on single stage pyrolysis but at a constant first-stage temperature were independent of second-stage temperature. These results were held to indicate that HCN was formed in the initial pyrolysis stage, and that the yield increased with temperature. Rocchio and Juhasz (see below) also got more HCN at higher temperature but their yields dropped off at about 600°C; the Rocketdyne workers[33,34] state that they have demonstrated that HCN

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[34] (a) A.E. Axworthy, J.E. Flanagan, D.O. Woolery and J.C. Gray, "Kinetic-Combustion Interactions of Nitramines," Proceedings of the 16th JANNAF Combustion Meeting, Vol. III, p. 289, December 1978, CPIA Publication No. 308. (b) A.E. Axworthy, J.E. Flanagan, and J.C. Gray, "Interaction of Reaction Kinetics and Nitramine Combustion," AFATL-TR-80-58, AD-B052 861L, May 1980.

decomposes rapidly on metal surfaces at this temperature range, but experimental details are not given. HCN yields are summarized in Figures 2 and 3 of Reference 34.

Nitrous oxide yields (Figures 5 and 6 of Reference 34) tended to drop with increasing first stage temperature. They were independent of second stage temperature up to 600°C, then tended to drop.

Molecular Nitrogen (N_2) showed results which make it difficult to distinguish whether it is formed initially or in the following reactions. Possibly this is because there is some contribution from both.

NO (plus NO_2) increased slightly with increasing temperature at either stage; thus it seems difficult to link it to either stage alone, although the authors[34] concluded that most of the NO forms in the primary pyrolysis process. As with N_2, possibly both stages are involved in NO formation.

With regard to carbon oxides CO increased appreciably with temperature at either stage; this suggests that CO is actually dependent on the second stage temperature and hence is formed mainly in secondary reactions. It was hard to tell whether CO_2 formed mainly in primary or secondary reactions, although considerable CO_2 formed from HMX in the second stage at 1100°C (Figures 11 and 12 of Reference 34a).

Formaldehyde yields (Figures 14 and 15 of Reference 34) decreased with increasing temperature of the first stage. RDX gave unexpectedly low yields of H_2CO. This was felt to be a real effect since triplicate runs alternating between HMX and RDX were run. To account for the unexpectedly low formaldehyde yields from RDX, it was suggested that all C atoms in either compound with the exception of one in HMX must form H_2CO in competition with other products, while that one forms H_2CO exclusively.

A group at BRL[35-41] carried out pyrolysis, gas chromatography and mass spectrometric studies on HMX, nitrocellulose and HMX propellants. The portion of this work pertaining to pure HMX will now be summarized.

The experimental setup used in these pyrolysis/gas chromatography/mass spectrometry studies is described in References 35-37; the description given here is taken from Reference 36. The sample was pyrolyzed on a pyrolyzer capable of reaching 150-999°C/ for intervals from 20 msec to 20 sec. Heating rates were 100°C/sec to 20,000°C/sec. Products were separated by GC and the effluent from the GC was analyzed mass spectrometrically (capable of unit mass resolution in the range of 10-260 amu that was monitored in these studies). It was pointed out (Reference 36, p. 186) that any NO_2 formed in the decomposition would not have been detected, since NO_2 would react with the column packing. Gas Chromatography was carried out using a Gas Chromatograph having low temperature and multilinear temperature programs and equipped with both flame ionization and thermal conductivity detectors. A Porapak T column was used for formaldehyde separation and Porapak QS column for all other separations.

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[35] A.A. Juhasz and J.J. Rocchio, "Determination of the Gasification Products from Developmental Propellants Which are Self-Extinguishing at Atmospheric Pressure," Proceedings of 10th JANNAF Combustion Meeting, p. 341, August 1973.

[36] A.A. Juhasz and J.J. Rocchio, "Pyrolytic Fragmentation Studies," in "Army Material Command Program, The Fundamentals of Ignition and Combustion. Volume II: Combustion," I.W. May and A.W. Barrows, eds., BRL Report 1708, p. 179, April 1974. (AD-919 316L)

[37] J.J. Rocchio, "The Effect of Heating Rate on the Thermal Decomposition of Propellants," in "Army Material Command Program, The Fundamentals of Ignition and Combustion. Volume I: Ignition," I.W. May and A.W. Barrows, eds., BRL Report 1707, p. 327, April 1974. (AD-919 315L)

[38] J.J. Rocchio and A.A. Juhasz, "HMX Thermal Decomposition Chemistry and Its Relation to HMX-Composite Propellant Combustion," Proceedings of 11th JANNAF Combustion Meeting, p. 247, September 1974.

[39] A.A. Juhasz, "Nitramine Pyrolysis Mechanisms," in "1975 Annual Review of the ARMCOM Program, The Fundamentals of Ignition and Combustion," E. Freedman and K.J. White, eds., BRL Report 1883, AD-B011 644L, May 1976.

[40] J.J. Rocchio and R.A. Wires, "The Effect of Heating Rate on the Thermal Decomposition of Propellant Ingredients," in "1975 Annual Review of the ARMCOM Program, The Fundamentals of Ignition and Combustion," E. Freedman and K.J. White, eds., BRL Report 1883, AD-B011 644L, May 1976.

[41] J.P. Pfau, J.J. Rocchio, and R.A. Wires, "New Aspects of HMX Thermal Decomposition as Studied by Pyrolysis/Mass Spectroscopy," Proceedings of 15th JANNAF Combustion Meeting, p. 267, September 1978.

TABLE 4. EFFECT OF PYROLYSIS TEMPERATURE ON PRODUCT DISTRIBUTION (HMX)
(FROM TABLE 3 OF REFERENCE 38)

COMPONENT	RELATIVE PERCENT				
	271°	320°	350°	600°	800°
N_2	15.4	14.5	17.4	12.4	13.4
CO	3.8	3.5	3.6	5.0	12.1
NO	26.3	27.5	23.1	34.3	27.9
CO_2	4.2	3.9	4.2	9.5	7.2
N_2O	17.5	17.1	17.1	13.0	10.4
H_2O	18.7	18.5	15.4	18.8	21.1
HCN	14.0	15.0	19.2	7.0	8.0

TABLE 5. EFFECTS OF PYROLYSIS TEMPERATURE ON HMX PRODUCT RATIOS
(FROM TABLE 4 OF REFERENCE 38)

SPECIES	RATIOS AT INDICATED TEMPERATURE				
	278°	289°	320°	350°	600°	800°
CO/CO_2	0.92	0.93	0.90	0.85	0.52	1.7
$\frac{HCHO}{(CO+CO_2)}$	0.32	0.31	0.28	0.30	0.053	0.0029
NO/N_2O	1.4	1.3	1.6	1.4	2.6	2.7
$\frac{N_2O+NO}{N_2}$	3.0	3.1	3.1	2.3	3.8	2.9

TABLE 6. PRODUCTS FROM SAME SAMPLE OF HMX REACTED TWICE
(FROM TABLE 5 OF REFERENCE 38)
(T_{pyr}: 285°, 10 sec., 10 deg/ms)

PRODUCT	RELATIVE PERCENT	
	Run 1	Run 2
N_2	17.6	31.3
CO	4.7	6.0
NO	17.8	(<1)
CO_2	5.1	6.3
N_2O	25.1	33.2
H_2O	19.4	17.3
HCN	10.4	5.5

TABLE 7. PRODUCT RATIOS FROM THE SAME SAMPLE OF HMX REACTED TWICE
(FROM TABLE 6 OF REFERENCE 38)
(T_{pyr}; 285°, 10 sec., 10°/ms)

	Run 1	Run 2
CO/CO_2	0.93	0.96
$\frac{H_2CO}{CO+CO_2}$	0.40	0.77
$\frac{NO}{N_2O}$	0.71	$<1X10^2$
$\frac{N_2O+NO}{N_2}$	2.4	1.1

Reference 37 gives a list of products from HMX pyrolysis: H_2, CO, NO, CO_2, N_2O, H_2O, H_2CO, HCN and cyanogen (NC-CN). The effect of pyrolysis temperature on product distribution for HMX is given in Table 3 of Reference 38, and the temperature dependence of the product ratios is given in Table 4 of Reference 38 and reproduced as Tables 4 and 5 of the present report. The yields in Table 4 are relative yields, normalized to 100%.

Many of the general trends are in agreement with those reported by the Rocketdyne group.[33-34] For example, N_2O and formaldehyde yields decrease with increasing pyrolysis temperatures while CO increases. However, there are discrepancies also, for example the Rocketdyne group[33,34] reports much more CO relative to NO, and it was also reported that HCN increased rather than decreased with increasing pyrolysis temperature. (The Rocketdyne workers as mentioned above attribute the decrease observed at BRL to decomposition of HCN on the surface of the metal ribbon; they state that they have established that HCN decomposes rapidly on metal surfaces in the temperature range under study, but details are not given and no Reference is cited.)

When pyrolysis was interrupted and then resumed, the products of the second pyrolysis were richer in H_2CO relative to CO, and in nitrogen oxides relative to N_2. In the second pyrolysis, only a small amount of NO was formed relative to N_2O (Tables 5 and 6 of Reference 38), summarized in Tables 6 and 7 of the present report. This is in at least partial agreement with the later results of Goshgarian[42] who found an increase in m/e 29, 30, and 44 on pyrolysis of a thermally treated (150°C, 18 hr) sample of HMX. Later the BRL group described[39] further work on the medium and higher molecular weight products of the decomposition of HMX. Spectral data were given for a variety of unidentified products, and some were identified as CH_3CN, formaldehyde polymer $(CH_2O)_n$, and something with infrared spectral characteristics of aliphatic CH, triply bonded or allenic species and secondary amides. Possibly these could be explained by reaction of H_2CO, HCN, and H_2O to form something, possibly an oligomer or polymer related to the hydroxymethylformamide found by Cosgrove and Owen[22] in decomposition of RDX below its melting point.

The effect of heating rate on product distribution was also examined,[40] using a sample-decomposition technique in which thin films of HMX were deposited on the pyrolyzer ribbon by solvent evaporation; this method was stated to give improved accuracy and reproducibility. The products observed included (Table 1 of Reference 40) (Product, relative molar ratio): N_2, 0.22; CO, 0.07; NO, 1.00; CO_2, 0.14; N_2O, 0.36; H_2O, 0.14; H_2CO, unable to analyze accurately; cyanogen, 0.14; HCN, 0.34. Two organic molecules "A" and "B" were also found; it was stated that their identity was under study. Pyrolysis temperature for the above data was not given.

There did appear to be a heating rate effect on product distribution; (Figures 1 and 2 of Reference 40), the amount of NO relative to N_2O increased,

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[42] B.B. Goshgarian, "The Thermal Decomposition of Cyclotrimethylenetrinitramine (RDX) and Cyclotetramethylenetetranitramine (HMX)," AFRPL-TR-78-76, AD-B032 275L, October 1978.

and the amount of cyanogen and of "B" relative to HCN decreased with increasing heating rate, with most of the change occurring between 100° and 1000°C/sec.

Another paper[41] from this group describes further high-heating-rate studies, at rates of 188°, 860°, 1320°, 7045°, and 12,250°C/sec, with product analysis by a quadrupole mass spectrometer coupled to a laboratory computer. The pyrolysis was carried out using a platinum ribbon pyrolysis probe (Chemical Data Systems' Pyroprobe 100 Solids Pyrolyzer) located in the inlet chamber of a quadrupole mass spectrometer. A Mass Spectrometer Data Acquisition and Control System (MSDACS) controlled the quadruple, monitored m/e intensity and ribbon temperature and gave out the results as plots of m/e intensity vs time and/or temperature. The electron energy was 70 eV. Note that under the high-vacuum conditions of these experiments, there may be reason to question whether the sample ever actually reaches the stated temperatures, and whether it instead just vaporizes with or without decomposition at considerably lower temperatures.

The m/e observed included 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 37, 38, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 69, 70, 71, 72, 75, 76, 77, and 78 (sec).

Possible structures are given in Table 2 of Reference 41. Product concentrations were obtained as a function of time and of the temperature of the pyrolysis probe. One very interesting and possibly important observation was that m/e 46, (NO_2?), was observed and found to exit very early, at low probe temperature (Figure 12 of Reference 41). The temperature intensity profiles of the other species were also recorded.

It was found that there were five temperature ranges in which maximum intensities of the various m/e peaks occurred; these were 220-230, 330-340, 490-500, 740-750, and 930°C. The maximum for m/e 46, NO_2, occurs before that for m/e 75, protonated $H_2C{=}NNO_2$. This would appear to be evidence for formation of NO_2 by N-NO_2 cleavage at an earlier stage of the reaction than that at which $H_2C{=}NNO_2$ is formed. However, see the discussion on page 63 of the present report.

Reaction appeared to occur in two regions. One of these was between 220-550°C, and comprised the first three of the five temperature ranges listed in the preceeding paragraph; and secondly there was a high-temperature region from 650°C and 930°C, corresponding approximately to the highest two of the temperature ranges mentioned in the preceeding paragraph. To further substantiate the occurrence of a high- and a low-temperature reaction region, a sample was pyrolyzed to 545°C, then pyrolyzed a second time to 930°C at the same heating rate. These results are shown in Figures 13 and 14 of Reference 41. The material decomposing in the high temperature region is a hard, insoluble, possibly polymeric residue amounting to only 2-4% by weight of the original HMX. It has no apparent effect on the products of the initial decomposition.

The heating rate effect was studied by Kissinger plots ($\ln \phi/T_m^2$ vs $1/T_m$, where ϕ = heating rate and T_m is temperature at maximum intensity; the slope is equated to the activation energy for a homogeneous, first order reaction). Since the slopes of these plots were linear for m/e 27, 28, 29, 30, 44, and 46, it was argued that, in the low-temperature region, the activation energy must be independent of heating rate, hence the mechanism of reaction must also be the same for all heating rates considered. The results for m/e 30 and 44 would appear to be in conflict with the results described in Reference 40 (see above, pp. 33-34), which reported a heating rate effect on the NO/NO_2 ratio. This writer does not understand the reason for this discrepancy. It is true that Kissinger's method has often been found to give poor results when applied to DTA and DSC,[43-45] but it is not obvious whether the same problems would necessarily occur in the pyrolysis experiment here under consideration. In any case, the significant result may well be the constancy rather than the absolute magnitude of the slope.

Another piece of evidence suggesting that the decomposition mechanism at low temperature is independent of heating rate was also obtained. When the melting point was approached at 400° C/sec and at 1100° C/sec, the ratios of intensity vs time for m/e 28, 29, 30, 44, and 46, relative to 27, were the same for both heating rates.

Clearly there is a need for more work on the important question of the effect of heating rate on mechanism and product distribution in view of the apparent discrepancy between References 40 and 41.

Beyer and Morgan[46-48] studied heating-rate effects by laser pyrolysis studies on HMX and RDX decomposition; the products were studied by infrared and mass spectrometric methods. They studied HMX, RDX, nitrocellulose and HMX propellants; but only the work on pure HMX and HMX/polyurethane will be summarized here.

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[43] W.W. Wendlandt, "Thermal Methods of Analysis," 2nd ed., John Wiley and Sons, New York, NY, p. 187, 1974.

[44] J.H. Sharp, Differential Thermal Analysis, R.C. Mackenzie, ed., Academic Press, Vol. 2, Chapter 28. See especially page 55.

[45] R.N. Rogers and L.C. Smith, "Application of Scanning Calorimetry to the Study of Chemical Kinetics," Thermochimica Acta, Vol. 1, p. 1, 1970.

[46] R.A. Beyer, "Molecular Beam Sampling Mass Spectrometry of Fast Thermal Decomposition of HMX, Polyurethane and Nitrocellulose," Abstract of paper for presentation at the Fall Technical Meeting of the Eastern Section, The Combustion Institute, 10-11 November 1977.

[47] R.A. Beyer, "Molecular Beam Sampling Mass Spectrometry of High Heating Rate Pyrolysis: Description of Data Acquisition System and Pyrolysis of HMX in a Polyurethane Binder," ARBRL-MR-02816, AD-A054 328, March 1978

[48] C.U. Morgan and R.A. Beyer, "ESR and IR Spectroscopic Studies of HMX and RDX Thermal Decomposition," Proceedings of 15th JANNAF Combustion Meeting, pp. 359-366, September 1978.

The apparatus used for the infrared studies is diagrammed in Figure 1 of Reference 48. A gas-phase infrared cell was initially pressurized with one-half atmosphere of helium: the pressure rise on laser pyrolysis was 5-20 torr. The heating rate was estimated to be ⩾ 5000°C/sec. The laser was a 50 W CO_2 laser. For the mass spectral studies, the laser pyrolysis setup was combined with a time of flight mass spectrometer, and the spectra recorded on an oscilloscope and photographed as shown in the block diagram of Figure 1 of Reference 47.

Product distributions from mass spectrometric[46] and infrared[48] measurements are summarized in Table 8. Note that the numbers are only relative amounts; actual percentage yields are not given. The amount of HCN (42) given in Reference 46 was later[49] corrected to the number given in Table 8.

The following general observations on products were made.[46] (a) HMX gave the same products on pyrolysis with the CO_2 laser and with heating by a torch flame; (b) HMX and HMX/polyurethane gave the same products on CO_2 laser pyrolysis at 760 torr; (c) HMX/polyurethane gave the same products at 1 mTorr and at 760 Torr. Thus it appears that the product distributions are, to a first approximation, independent of heating rate, pressure up to atmospheric and inclusion of polyurethane.

Variations in formaldehyde yield were attributed to polymerization on the walls of the reaction vessel.

Time resolution of product appearance was also studied. The electronic data handling system[46,47] made it possible to follow the sequence of appearance of the products by mass spectrometry. Pure HMX was apparently not studied in this way, but rapid pyrolysis of HMX/polyurethane mixtures[47] gave double peaks for m/e 44, with the second peak corresponding to appearance of m/e 22; this suggests initial formation of N_2O, and later emergence of CO_2 formed in follow-up reactions, possibly between H_2CO and NO_2. The m/e 46 (NO_2) peaked early in the decomposition: this may be in agreement with initial formation of NO_2 by $N\text{-}NO_2$ cleavage. Note, however, that m/e 46 also appears in the mass spectrum of unreacted HMX and RDX themselves: thus the observed m/e 46 could possibly be due to HMX vapor. On the other hand, if formation of NO_2 is considered to be established by non-mass spectrometric studies (pp. 62-64), the behavior of the m/e 46 peak could be taken as evidence that the NO_2 is mostly formed <u>early</u> in the decomposition, as if by $N\text{-}NO_2$ cleavage of HMX or RDX, rather than of $H_2C{=}NNO_2$ formed later in the reaction. However, the m/e 46 pear (NO_2) showed a very long "tail."

The group at Thiokol/Huntsville[50] carried out a number of experiments involving pyrolysis of HMX on a wire screen located in the light path of a

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[49] R.A. Beyer, Ballistic Research Laboratory, private communication, 1980.

[50] D.A. Flanigan and B.B. Stokes, "HMX Deflagration and Flame Characterization Volume I: Phase II Nitramine Decomposition and Deflagration Characterization," Thiokol/Huntsville, AFRPL-TR-79-94, AD-B053 058L, October 1980.

TABLE 8. RELATIVE CONCENTRATIONS OF SOME DECOMPOSITION SPECIES OF HMX AND HMX/POLYURETHANE, FROM REFERENCES 46 and 48

SPECIES	THIS WORK	
	Mass Spectrum ($>$ 1 torr)	IR (1/2 atm press)
N_2O	100	Strong (50)
CO	---	Weak
HCHO	31	---
NO	59	Strong (56)
NO_2	44	Strong (26)
HCN	$>$80	Strong (100)
N_2	b	---
CO	b	Weak
H_2O	b	---

Fourier Transform Infrared Spectrometer. The screen was rapidly heated resistively, and the FTIR spectrum of vapors given off was recorded. The main infrared absorbers were N_2O and NO_2; there was also some formaldehyde but most of it apparently polymerized. The formation of NO_2 and N_2O and some $H_2C=O$ was taken as indicating initial formation of NO_2 by $N-NO_2$ cleavage. The brown color of NO_2 was also seen in color movies of decomposing HMX and RDX. Deepening of the orange-brown color appeared related to vary rapid catalytic decomposition of the nitramine melt.

C. Miscellaneous Studies on Products of Slow Thermal Decomposition of HMX and RDX: ESR and Isotope Labeling Studies

Beyer and Morgan[51-53] carried out ESR studies on decomposing HMX and RDX. The sample was heated under vacuum and the evolved gases swept out with argon and frozen onto a sapphire rod at 10-20°K. The matrix on the rod was studied by ESR. The species observed by ESR were NO_2 and H_2CN.[48,51-53] For HMX, the relative distribution of these species was as shown in Figure 2 of Reference 6. The change with tube length in the temperature dependence of $(NO_2)/(H_2CN)$ suggests that H_2CN is quite reactive, possibly losing H to the tube walls or to other molecules.

On the basis of the observations with a 38mm tube, it now appears[53] that the NO_2/H_2CN ratio does not change on going from below to above the melting point of HMX; this suggests that the basic chemical mechanisms of decomposition of HMX are similar above and below its melting point.

Also, RDX resembled HMX in that both showed substantial amounts of both H_2CN and NO_2. The relative amount of H_2CN was about the same for both compounds,[53] but RDX showed a larger absolute amount of NO_2 than HMX, possibly as a result of faster decomposition due to its lower melting point and resulting liquid-phase decomposition, or to higher vapor pressure and resulting increased vapor-phase decomposition.

Isotope labeling studies have been carried out on the thermal decomposition of HMX and RDX labeled with N-15 at the nitro group.[54,55] The results are summarized in Table 4 of Reference 55, and are reproduced below as Table 9 of the present report.

The percent composition of the products at 230°C was N_2O, 40; NO, 9.9; N_2, 9.6; HCN, 4.5; HCHO, 22.9; CO_2, 8.5 and CO, 4.1. The presence of N_2O as $NN^{15}O$ was indicated because there was no evidence of contribution of N_2O to mass 30, although a prominent peak at mass 31 was observed, consistent with

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[51] C.U. Morgan and R.A. Beyer, "Electron-Spin Resonance Studies of HMX Pyrolysis Products," Combustion and Flame, Vol. 36, p. 99, 1979.

[52] R.A. Beyer and C.U. Morgan, "ESR Studies of HMX Pyrolysis Products," ARBRL-MR-02921, May 1979.

[53] R.A. Beyer and C.U. Morgan, "Electron Spin Resonance Studies of HMX and RDX Thermal Decomposition," Proceedings of 16th JANNAF Combustion Meeting, CPIA Publication No. 308, Vol. II, p. 51, December 1979.

[54] B. Suryanarayana, R.J. Graybush, and J.R. Autera, "Thermal Degradation of Secondary Nitramines: A Nitrogen-15 Tracer Study of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane)," Chem. Ind., London, p. 2177, 1967.

[55] B. Suryanarayana, J.R. Autera, and R.J. Graybush, "Mechanism of Thermal Decomposition of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane)," DDC, AD-837 173, 9 August 1968.

TABLE 9
NITROGEN-CONTAINING THERMAL DECOMPOSITION PRODUCTS OF NITRO-N^{15}-LABELED δ-HMX AND RDX
(FROM TABLE 4 OF REFERENCE 55)

ISOTOPIC SPECIES		Percent Composition			
		δ-HMX			RDX
		230°	254°	285°	190°
N_2O[a]	$N^{14}N^{14}O$	--	--	--	--
	$N^{14}N^{15}O$	98-99	98	98	98-100
	$N^{15}N^{14}O$	--	--	--	--
	$N^{15}N^{15}O$	1-2	2	2	0-2
N_2[b]	$N^{14}N^{14}$	--	--	--	--
	$N^{14}N^{15}$	93-100	92	95	98-100
	$N^{15}N^{15}$	0-7	8	5	0-2
NO[b]	$N^{14}O$	0-7	0-5	0-5	0-5
	$N^{15}O$	93-100	95-100	95-100	95-100
HCN[c]	HCN^{14}	100	100	100	100
	HCN^{15}	--	--	--	--

$NN^{15}O$ and $N^{15}O$. These results indicate that NO comes from the nitro nitrogen, and that N_2 and N_2O are formed without intermixing of nitro and amino nitrogen. They also rule out the possibility that the N_2, N_2O and NO come from scrambling among low-molecular-weight products.

It was stated[54] that "at these temperatures, HMX exists as the δ-form," but it can also be seen (Reference 55, Table 3) that the products at 285°C are markedly different from those at 226-58°C; possibly this is due to some liquid-phase decomposition at 285°, as opposed to gas and/or solid decomposition at the below-melting point temperatures. In fact, when these results are tabulated along with other data (Table 2 of the present report), the product distributions at 285°C seem in many ways to have more in common with those from higher decomposition temperatures, including Robertson's[7] liquid-phase results at 280°C, than with the lower-temperature results from References 29, 54 and 55. This is an important point, as it is very helpful to have evidence for lack of scrambling between amino and nitro nitrogens in the _liquid phase_ decomposition, rather than just below the melting point. RDX was studied at 190°C, _ca_ 10-15°C below its melting point.

However, none of the above results give any information as to whether the nitro groups on different molecules scramble with each other. Some information on this point is provided by preliminary results from some very recent studies[56] on decomposition of mixtures of fully labeled (i.e., in both the nitro and amino groups) and unlabeled liquid HMX. It was found that N_2O was formed with a significant degree of scrambling (m/e 44, peak height 50; m/e 45, peak height 29, m/e 46, peak height 60).

A labeling study[55] using C-13 and O-18 labeled HMX was also carried out, using mixtures of HMX labeled separately with C-13 and O-18. More m/e 33 ($H_2C^{13}O^{18}$) than required on a random-mixing basis was found, possibly because the formaldehyde was in equilibrium with its polymer.

Studies on deuterium-labeled HMX indicate[56] that in the liquid-decomposition region, there is no indication of a primary isotope effect, although there is a noticeable effect on the induction period plots (solid phase). Studies on mixtures of un- and fully (all 8 nitrogens) ^{15}N-labeled HMX indicate _ca_ 20% scrambling in the N_2O formed.

D. Mass Spectrometric Studies on Decomposing HMX and RDX

There have been a number of mass spectrometric studies on the gaseous products emanating from the surface of decomposing solid or liquid HMX and RDX. Although, as will become clear below, these studies are capable of yielding useful information, it should be noted that they suffer from the serious deficiency that it is very hard to be sure which of the observed peaks correspond to parent peaks of true thermal decomposition products, and which ones are merely ion fragmentation peaks.

The present writer feels that more effort should be devoted to overcoming this deficiency. One way around the problem would be to work at low ionizing voltages and to study the effect of variations in ionizing voltage, (see the

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[56] R.J. Powers, AFATL, Eglin AFB, private communication, June 1980.

work of Farber, below) or to acquire an improved understanding of HMX and RDX fragmentation patterns by studies of metastable transitions and isotope labeling, as has been done for TNT.[57] Other approaches that should be considered include (a) increased use of techniques such as field ionization mass spectrometry, which would lead to reduced ion fragmentation; and (b) use of time-resolved laser spectroscopic techniques involving laser-induced multiphoton dissociation. (See for example Reference 58.)

However, it should be remembered that even the observance of a certain mechanism as an ion-fragmentation pathway may be evidence of a sort for its occurrence thermally, since there are many examples of analogous behavior in thermal and in mass spectrometric cleavage of molecules, although there are also a number of exceptions (see for example Reference 59). Nevertheless, due to time limitations, it has been necessary to limit the scope of this section of the present review to those papers and reports which address the question of the thermal decomposition of HMX and RDX; those concerned only with elucidation of ion-fragmentation pathways will not be explicity considered except as necessary for purposes of the discussion of the thermal-decomposition papers. It might well be worthwhile to carry out a separate review, considering together the purely mass-spectrometric and the decomposition mass-spectrometric studies, to get a better idea of what can be established from these studies, especially in the light of the results of the application of the metastable-ion and labeling techniques described in Reference 57 to HMX and RDX; the author(s) of such a review should probably have a background in mass spectrometry.

Mass Spectrometric studies on HMX or RDX decomposition fall into three general classes. By type A studies we will designate solid-probe-type studies in which the sample is held in a vacuum in a probe heated to a given temperature and the gases given off by the probe are sampled mass spectrometrically. Type B studies are effusion-cell studies, in which the sample is kept in a cell, referred to as an effusion cell, with a narrow opening through which product gases can escape. Differences between type B and type A studies are attributable to the fact that in the type A studies, product gases go directly to the detector, while in the type B studies, many collisions can occur before a molecule leaves the cell. Type C studies are flow-reactor studies in which the sample is heated to a given temperature under a current of inert gas, often helium, and the gas stream, downstream of the sample, is sampled mass spectrometrically. Differences between the results of type A and type C studies are due to the fact that in the type A

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[57] S. Bulusu and T. Axenrod, "Electron Impact Fragmentation Mechanisms of 2,4,6-Trinitrotoluene Derived from Metastable Transitions and Isotope Labeling," Organic Mass Spectrometry, Vol. 14, p. 585, 1979.

[58] B.H. Rockney and E.R. Grant, "Resonant Multiphoton Ionization Detection of the NO_2 Fragment from Infrared Multiphoton Dissociation of CH_3NO_2," Chem. Phys. Lett., Vol. 79, p. 15, 1981.

[59] R.C. Dougherty, "The Relationship Between Mass Spectrometric, Thermolytic and Photolytic Reactivity," Topics in Current Chemistry (Fortschritte der Chemischen Forschung), Vol. 45, p. 93, 1974.

studies, product gases go directly to the detector, while in the type C studies the molecules spend a long time in the gas stream. During this time they can undergo collisions with each other and with atoms or molecules of carrier gas.

We now begin our summary of the individual mass-spectrometric studies. We begin by pointing out that the studies by Pfau, Rocchio and Wires[41] and by Beyer,[46,47] summarized in the present report under the heading "High Temperature and High Heating Rate Studies," could also be considered as mass spectrometric studies on decomposing HMX and RDX.

Miller, Grigor, Musso and Yount[60] carried out mass spectrometric studies on the decomosition of HMX and of dimethyl N-nitroamine (DMN), nitroglycerin (NG), nitrocellulose (NC), ammonium perchlorate (AP), triacetin (TA), trimethylolethane trinitrate (TMETN) bis-(2,2-dinitropyl) acetal (BDNPA), and on mixtures and propellants containing these compounds. Only those results on pure HMX or in some way clearly related to decomposition of pure HMX will be summarized here.

Decomposition of HMX was studied under high vacuum (10^{-6}torr) at 190°C, and at atmospheric pressure at 280°C under a steam of inert gas. A splitter valve inlet system (Figure 8 of Reference 60) was used for the high vacuum studies. This writer is uncertain whether this system constitutes a type A or type B apparatus; the exact assignment would depend on the size of the opening at the needle valve and on the comlexity of the path to the mass spectrometer. For the atmospheric-pressure studies, the flow-reactor (type C) apparatus depicted in Figure 9 of Reference 60 was used. The mass spectrometer was a Bendix time-of-flight mass spectrometer. Ionizing voltage was 70 eV.

The peaks observed were, for the atmospheric pressure (type C) experiment, at m/e 12, 13, 14, 15, 16, 17, 18, 26, 27, 28, 29, 30, 31, 32, 40, 41, 42, 43, 44, 45, and 46. Under high vacuum (type A or B experiment) all of the above peaks were observed, as well as m/e 54, 55, 56, 57, 58, 59, 67, 68, 69, 70, 71, 72, 73, 74, 75, 81, 82, 83, 84, 85, 95, 96, 97, 98, 99, 102, 128, and 148. Relative abundances and tentative structural assignments are given in Table 15 of Reference 60.

The authors point out that although under high vacuum the mass spectra include many peaks at m/e up to 148, under atmospheric pressure all peaks above m/e 46 were missing.

The authors point out another interesting aspect of their results: under high vacuum, the m/e 46 (NO_2) peak is greater than the m/e 44 (CO_2, N_2O) peaks, but at atmospheric pressure the m/e 46 peak is much smaller than the m/e 44 peak. The authors attribute this to reaction of any NO_2 formed at atmospheric pressure with other HMX molecules or decomposition products, and

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[60] R.R. Miller, A.F. Grigor, R.C. Musso and R.A. Yount, "Combustion Mechanism of Low Burning Rate Propellant," Hercules Inc., AFRPL-TR-69-130, AD-502 957, May 1969.

call attention to a similar observation by Bernecker and Smith,[61] although these authors[61] worked only at atmospheric pressure or higher, and looked for NO_2 by visual identification of its brown color. It seems to the present writer that this apparent pressure-dependence of NO_2 formation should be kept in mind as a possible explanation for other apparent discrepancies with regard to formation or non-formation of NO_2 in decomposition experiments. However, it would be helpful to know whether NO_2 gave a parent peak under the condition of the experiments described in Reference 60, since Bernecker and Price[61] reported that their mass spectrometer did not give a parent peak for NO_2, and the mass spectra of HMX and RDX both give large peaks at m/e 46. (See for example References 62 and 63 and other References cited herein.) Thus it is hard to be sure that the m/e 46 results do not simply mean that more undecomposed HMX vapor reaches the detector in the type A and B experiments.

One other point seems worth mentioning: In addition to the m/e 75 peak, a peak at m/e 74 was observed. Thus there is apparently precedent for the observation by Farber and Srivastava[63,64] of peaks at m/e 74 in HMX and RDX decomposition.

Farber and Srivastava[64-67] carried out studies by two methods, an effusion-mass spectrometric method (Type B study) and a Langmuir evaporation-mass spectrometric method (Type A study). A diagram of the apparatus used is given in Figure 1 of Reference 65. The mass spectrometer was a dual-vacuum-chamber-quadrupole mass spectrometer.

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[61] R.R. Bernecker and L.C. Smith, "On the products Formed in the Combustion of Explosives. Freeze-Out of the Water-Gas Reaction," J. Phys. Chem., Vol. 71, p. 2381, 1967.

[62] S. Bulusu, "Electron-Impact Fragmentation of Some Secondary Aliphatic Nitramines. Migration of the Nitro Group in Heterocyclic Nitramines," Organic Mass Spectrometry, Vol. 3, p. 13, 1970.

[63] J. Stals, "Chemistry of Aliphatic Unconjugated Nitramines. Part 7. Interrelations Between the Thermal, Photochemical and Mass Spectral Fragmentation of RDX," Trans. Faraday Soc., Vol. 67, p. 1768, 1971.

[64] M. Farber and R.D. Srivastava, "Mass Spectrometric Investigation of the Thermal Decomposition of RDX," Chem. Phys. Lett., Vol. 64, p. 307, 1979.

[65] M. Farber, "A Mass Spectrometric Investigation of the Decomposition Products of Advanced Propellants and Explosives," Space Sciences, Inc., Annual Summary Report on Contract N00014-75-C-0986, AD-A074 963, August 1979.

[66] M. Farber and R.D. Srivastava, "Thermal Decomposition of HMX," Proceedings of 16th JANNAF Combustion Meeting, p. 59, September 1979.

[67] M. Farber and R.D. Srivastava, "A Mass Spectrometric Investigation of the Chemistry of Advanced Composite and Double Base Propellants," Proceedings of 15th JANNAF Combustion Meeting, September 1978.

In the effusion-mass spectrometric studies, the sample was heated in a closed cell (called the effusion cell) in the furnace chamber, and the vapors allowed to escape through an orifice (>1mm diameter). In the Langmuir evaporation method, the material was heated and allowed to enter the mass spectrometer directly. The two methods might be expected to give different results, since in the effusion cell the pressure can be three or more orders of magnitude higher within the cell than the surrounding vacuum; thus decomposition products have time to collide with each other, the walls and the condensed phase before escaping from the cell into the chamber. This may, cause secondary decomposition and fragmentation, whereas in the Langmuir effusion technique there is much less opportunity for secondary fragmentation as the sample can escape into the main spectrometer immediately. Unless otherwise specified, HMX and RDX studies described in References 64 and 65 were done in the effusion cell. These workers[64,65] recognized the need to ascertain that the measured ion intensities are from the parent species, not from fragmentation of larger molecules of intermediates. Thus the mass spectrometer was operated at an ionizing voltage only 1 or 2 eV above the appearance potential since it was felt that this would minimize or eliminate the detection of peaks other than parent peaks of true thermal decomposition products. Some illustrations of this effect are seen in Figure 3 of Reference 65. Note however that the exact ionizing voltage was often not stated; this could be important since appearance potential is expected to vary from species to species, and References 64-7 often report several species on one graph, without specifying the appearance potential for each.

However, it seems to the present writer as if there might still be problems of interpretation: when, for example, a voltage is reached at which m/e 46 appears, is the parent peak from product NO_2 being detected, or is something else ionizing, and then fragmenting to give m/e 46? In deciphering points such as this MS/MS studies of the type described in Reference 57 might be of use in unraveling the observed patterns.

It was stated that the β-form of HMX (which is stable at room temperature) was used, although presumably this had transformed to β-HMX by the time the studies at temperatures higher than 190-200°C were done.

Product distributions were studied mass spectrometrically, using the effusion cell described above. Between 175 and 200°C, sublimation of unchanged HMX was predominant (Figure 11 of Reference 66 in agreement with effusion-cell measurements at 98-130 C and 188-213°C by Rosen and Dickenson, and by Crookes and Taylor respectively (References 14 and 18 of Reference 65).

As the temperature approached 225°C, considerable decomposition occurred, as shown in Figures 12-14 of Reference 66. The peaks observed were at m/e 148, 128, 120, 102, 74, 56, 46, 44, 32, 30, 28 and 18. It is not stated specifically what happened to the peak at m/e 222 in Figure 11 of Reference 66; presumably it also appeared at the higher temperatures.

Farber and Srivastava also worked[64] on RDX decomposition. RDX was decomposed below the melting point at 200° and above it at 220°C.

Peaks seen below the melting point were at 28, 30, 42, 44, 56, 74, 82 and 83; and peaks seen above the melting point were m/e 28, 30, 42, 44, 46, 74, 82, 83, 102, 120, 128, 132, and 148. Note the presence of the nitrosoamine

132 above the melting point and absence below; this is consistent with formation of nitrosoamines preferentially in the liquid phase, possibly by radical abstraction of a nitro oxygen as discussed earlier or by $N-NO_2$ cleavage followed by equilibration. Note also that these workers see the peak at m/e 74 but no m/e 75 peak; observation of m/e 74 is not unprecedented, as mentioned above.

Langmuir evaporation studies on decomposing HMX were also done.[66] At a low ionizing energy, the only peak (other than m/e 296) from the Langmuir evaporation studies on decomposing HMX was at m/e 148 (Figure 4 of Reference 66).

Bradley, Butler, Capey and Gilbert,[68] carried out mass spectrometric studies on the decomposition of RDX over the temperature range 130-230°C, using a combination of open and two-stage cells that enabled condensed-and vapor phase reactions to be distinguished. The open cell was a type A experiment consisting of a pyrex tube 5 mm long and 0.5 mm internal diameter. The two-stage cell was a sort of two-stage type A experiment an open cell over which was fitted a second chamber of 0.3 cc volume with an outlet orifice 015 mm in diameter, whose temperature could be measured independently of the open cell. The distance of the cells from the ion source could also be varied. The mass spectrometer was a quadrupole mass spectrometer.

Product Studies. The experiments performed are summarized in Table 1 of Reference 68, a copy of which is given below as Table 10 of the present report. The experiments of series I were used to assign peaks to the individual components of a mixture. Changes in spectra in series II can be attributed to processes occurring in the solid phase. Series III was intended to indicate whether any products of the solid-phase reaction remained in the solid phase for a significant time, although it was stated that it would only indicate species with lifetimes of some minutes. Changes occurring during Series IV could be attributed to the gas-phase processes. The authors state that Series V was of value only as a way of associating different mass peaks with separate mechanisms. Series VI was intended to study the effect of keeping RDX and its products together for substantial times above the melting point.

These results were combined and used to identify specific mass spectrometric peaks with processes occurring in the solid and gaseous phases, as shown in Figure 3 of Reference 68, a copy of which is included as Figure 3 of the present report. The authors concluded that at least four different mechanisms were distinguishable: one taking place in the gas phase and giving rise to m/e 42, 46, 56, 75; one taking place in the solid phase and giving rise to m/e 80, 98, 120; and two groups (m/e 82, 83; and m/e 71) were formed by both gas- and solid-phase routes, although not by the same mechanism.

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[68] J.N. Bradley, A.K. Butler, W.D. Capey, and J.R. Gilbert, "Mass Spectrometric Study of the Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX)," J. Chem. Soc., Faraday Trans. Pt. 1, Vol. 73, p. 1789, 1977.

Table 10. Summary of Experimental Observations, from Reference 68.

Series	Reaction Cell	Description of Experiment	Effect on Peak Height (relative to m/e 128)
I	open cell	temp. held at 170°C separation from ion source varied	57, 82, 83 decreased with increasing separation.
II	open cell	temp. varied between 130 and 170°C	71, 80, 98, 102, 120 increased with increasing temp. 42, 46, 56, 75, 81, 148 showed no change 30. 82, 83 decreased with increasing temp.
III	open cell	temp. cycled 130 to 150 to 130°C	30, 83, increased after cycle 71, 102, 148 showed no change
IV	two-stage cell	temp. first stage held at 175°C temp. second stage varied from 175 to 225°C	30, 42, 46, 56, 71, 75, 81, 82, 83 increased with increasing temp. 80, 98, 102, 120, 148 showed no change
V	two-stage cell	temp. first stage varied from 160 to 195°C temp. second stage held at 195°C	42, 46, 56, 71, 75, 102, 148 increased with increasing temp. 30, 80, 81, 98, 120 showed no change 82, 83 decreased with increasing temp.
VI	two-stage cell	temp. both stages held at 206-208°C followed variation with time	132 appeared and increased linearly with time

Peak heights underlined can confidently be attributed. The other peak heights tend to behave as indicated.

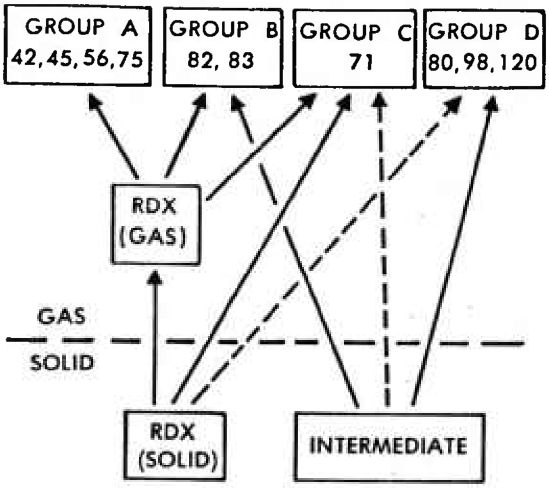


Figure 3. Summary of Decomposition Mechanisms, from Reference 68.

The peak at m/e 83 was attributed to 1,2-dihydro-sym-triazine, formed by stepwise loss of NO_2 or HONO from RDX. Accurate mass analysis identified the m/e 46 as NO_2; others were m/e 75 - $CH_3N_2O_2$, m/e 56 - $C_2H_4N_2$ and m/e 42 - C_2H_4N. These were considered to arise from a molecule $C_2H_4N_2O_2$ three isomeric forms of which were given.

The authors conclude by noting that when RDX was kept above the melting point for long periods a new peak at m/e 132 was observed; Goshgarian[42] also observed the appearance of this peak in RDX decomposition when the melting point was reached, and attributed it to a nitroso derivative such as N-Nitro-N'-nitroso-1,3 diazacyclobutane or a ring-opened form thereof. Farber and Srivastava[64] reported similar observations. These observations suggest that some aspect of the liquid state renders it particularly conducive to the formation of nitroso compounds, possibly by free-radical deoxygenation of nitro groups, or by N-NO_2 cleavage and recombination of NO_2 and denitro-HMX or -RDX radical, as discussed earlier.[2] Another less straightforward possibility might be combination of NO with the cyclic imino compound resulting from HONO elimination: These possibilities will be discussed below, Section III. B.

One important thing about Reference 68 may well be that, although the gas-and liquid-phase reactions apparently proceed at appreciably faster rates than the reaction in the solid state, the results described in Reference 68 would appear to suggest that there is a definite (although apparently small relative to the gas and liquid phases) amount of decomposition in the solid phase in the 200°C temperature range.

Goshgarian[42] also carried out mass spectrometric studies on decomposing HMX and RDX. The mass spectrometric system included a gas chromatograph, quadrupole mass analyzer and computerized data system. Operating parameters were as shown in Table 1 of Reference 42.

Two methods were used for introducing samples into the ion source. These were a solid probe (2-mm glass tube at tip of probe, 10^{-7} torr vacumm) (Type A experiment), and a glass flowreactor (type C experiment, shown in Figure 1 of Reference 42), maintained in the GC oven for temperature control and connected to the jet separation mass spectrometer/gas chromatograph interface.

The elemental composition of ion masses observed were determined by combining methane chemical ionization mass spectra and electron impact ionization data. The m/e values and elemental compositions are given in Table 5 of Reference 42 (included as Table 11 of the present report), and the structures assigned are given in Figures 16a and 16b of Reference 42 (included as Figure 4 of the present report). It seems that in many (but not all) cases, open-chain forms might be chemically more appropriate than the ring forms given; this has also been pointed out to this writer by Goshgarian in private discussions. For example m/e 132 might be better represented by $CH_2N(NO_2)CH_2N(NO)$ than by the cyclic form given in Figure 4. The reason for this is that the ring in HMX undoubtedly cleaves in forming, for example m/e 222 from HMX, and a separate ring closure step would have to be postulated in order to get to the closed-ring forms. In many cases, especially the 3- and 4-membered rings, this seems unlikely although the possibility that these diradicals might cyclize cannot be ruled out rigorously. In other cases, however, for example the product of HONO elimination from RDX (m/e 175, Figure 4), the cyclic form given seems more reasonable.

Although m/e 74 is listed[42] among the ions seen, the accompanying discussion makes it evident that m/e 75 (protonated 74?) must have been much more intense than m/e 74.

Decomposition products of HMX were studied both (a) below the melting point in the range 220°-80°C (Figure 17 of Reference 42, copy attached as Figure 5 of the present report) and (b) during melt and deflagration (281-5°C) (Figure 18 of Reference 42, copy attached as Figure 6 of the present report).

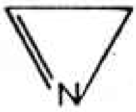
Below the melting point, m/e 46 was seen but was attributed to cleavage of m/e 75, apparently on the basis of similarity in the shapes of the temperature-intensity curves, and of the detection of NO_2 and HCN in decomposing HMX by Beyer and Morgan[46-49] at BRL. However, it seems to this writer that this might also be explained by formation of NO_2 and $H_2C{=}NNO_2$ in the same process, e.g., Scheme III of Reference 2.

During melt and deflagration, m/e 46 was also seen. Another interesting thing was that m/e 132 ($CH_2N(NO)CH_2N(NO_2)$), 70 (C_2H_2NNO), and 58 ($H_2C{=}NNO$) increased during RDX and HMX melting. The formation of these nitrosoamines was attributed to coupling of NO with nitrogen-centered radical formed from N-NO_2 cleavage. However, very recent isotope-labeling studies[56] now indicate the oxadiazole structure for m/e 70, although it is possible that it may still be a fragmentation peak or decomposition product from a nitrosoamine.

It seems possible on the basis of the discussion in Reference 2 (Schemes VII-XIII of Reference 2 and accompanying discussion) that formation of nitrosoamines might actually be evidence for either deoxygenation of the nitro groups by free radical intermediates formed in the decomposition, or for the occurence of some combination of N-NO_2 cleavage and HONO elimination, since the increase in nitrosoamines on melting might suggest the deoxygenation due to the greater concentration of unreacted HMX/RDX seen by intermediate radicals in the liquid than in the vapor phase, and the m/e 205 peak might suggest addition of NO to the imine formed by HONO elimination (assuming m/e 205 is a true thermal decomposition peak).

Table 11. Elemental Composition of Ion Masses, From Reference 42

m/e	Elemental Composition	m/e	Elemental Composition
18	H_2O	68	$C_3H_4N_2$
27	HCN	70	C_2H_2NNO, $C_2H_2N_2O$
28	N_2, CO, H_2CN	71	$C_2H_3N_2O$
29	CHO	74	CH_2NNO_2
30	CH_2O, NO	75	CH_2NHNO_2, CH_3NNO_2, CH_2NNO_2H
40	C_2H_2N	81	$C_3H_3N_3$
41	C_2H_3N	88	$C_2H_4NNO_2$, CN_2O_3
42	C_2H_4N, NCO	102	$C_2H_4N_2NO_2$
43	HNCO, C_2H_5N	104	$C_2H_4NONO_2$
44	N_2O, CO_2, CH_2NO	120	$CH_2NN_2O_4$
45	$HCONH_2$, CH_3NO	128	$C_3H_4N_3NO_2$
46	NO_2	132	$C_2H_4N_2N_2O_3$
52	C_2N_2	148	$C_2H_4N_2N_2O_4$
54	$C_2H_2N_2$	175	$C_3H_5N_3N_2O_4$
56	$C_2H_4N_2$	176	$C_3H_6N_3N_2O_4$
58	CH_2NNO, CONO	205	$C_3H_5N_3N_3O_5$
59	HCONO	222	$C_3H_6N_3N_3O_6$
67	$C_3H_3N_2$	296	$C_4H_8N_4N_4O_8$



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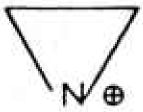

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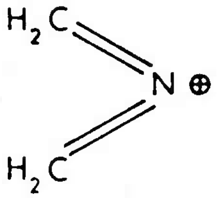
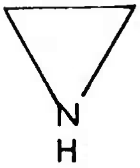


42

$HN=C=O$

43

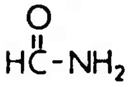


43

$O=C=O$

$N\equiv N\rightarrow O$

44



$H\overset{O}{\overset{\|}{C}}-NH_2$

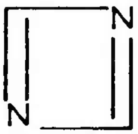
45

$H_2C=N-OH$

45

$N\equiv C-C\equiv N$

52



54

$HN=CH-N=CH_2$

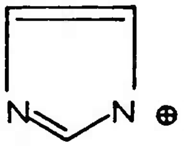
56

$H_2C=N-N=O$

58

$O=CH-N=O$

59



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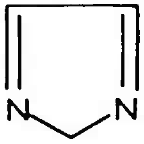

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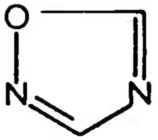

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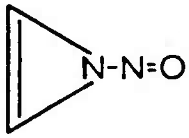

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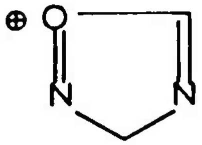

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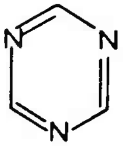
Figure 4. Probable Structures for RDX and HMX Fragments, from Reference 42.

$H_2C=N-NO_2$

74



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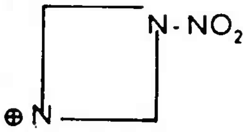

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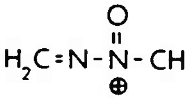
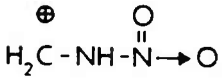


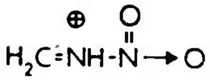
$H_2C=N-\overset{O}{\underset{\oplus}{N}}-CH$

75



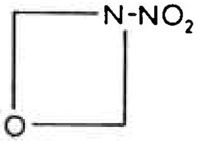
$\overset{\oplus}{H_2C}-NH-\overset{O}{N}\rightarrow O$

75



$H_2\overset{\oplus}{C}=NH-\overset{O}{N}\rightarrow O$

75



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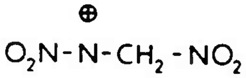
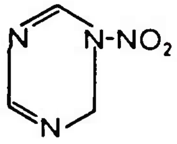


$O_2N-\overset{\oplus}{N}-CH_2-NO_2$

120



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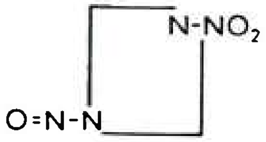

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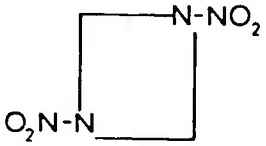

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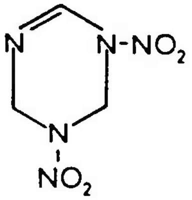

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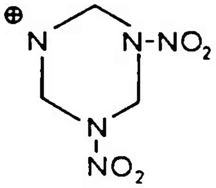

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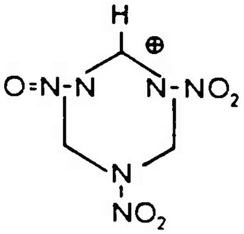

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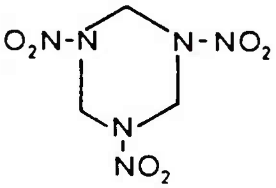

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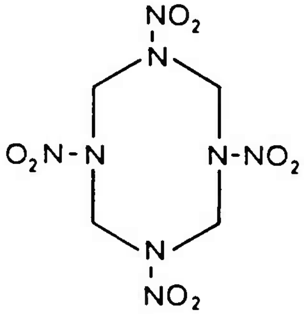

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Figure 4 (cont'd). Probable Structures for RDX and HMX Fragments, from Reference 42.

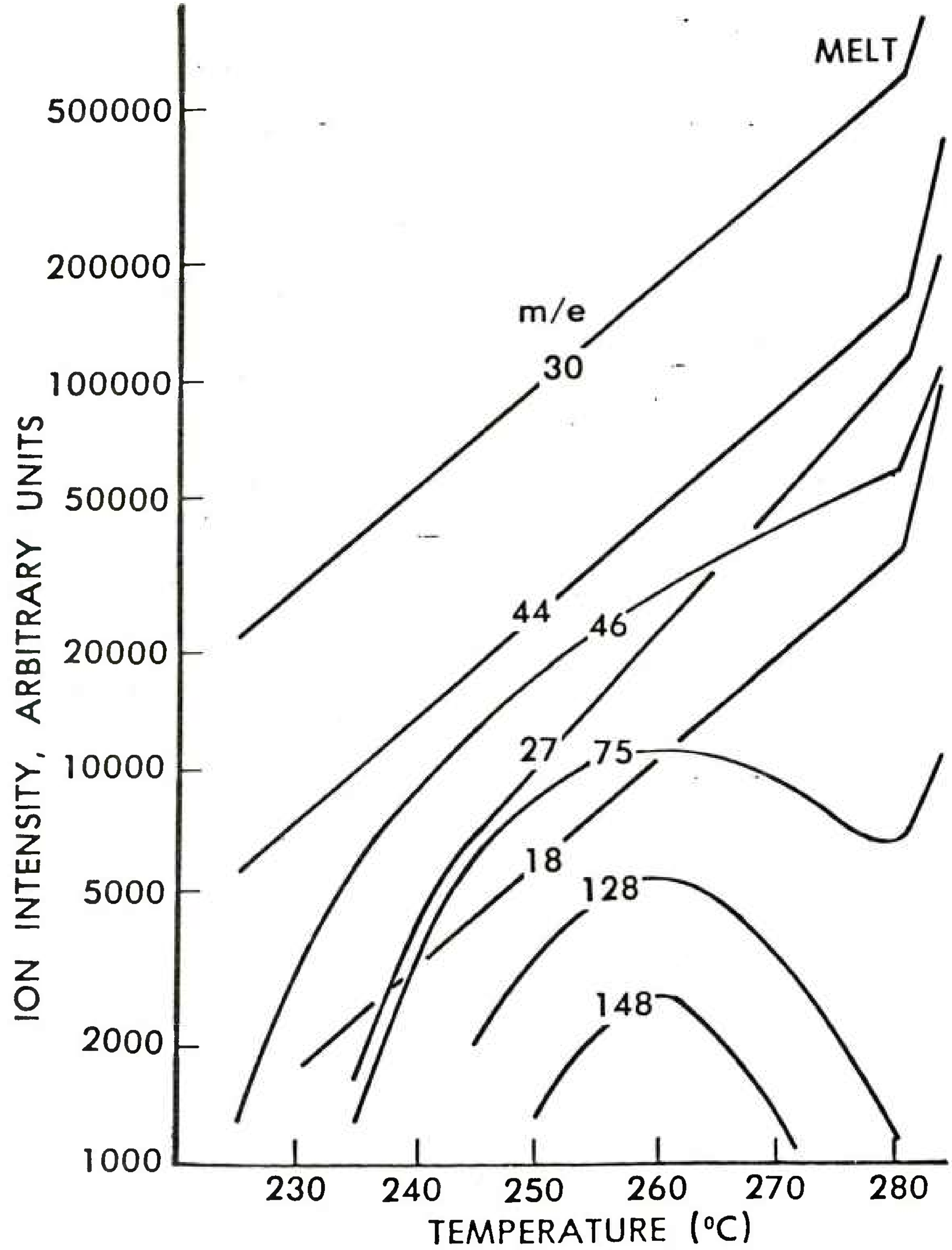

Figure 5. Changes in HMX Decomposition Products with Temperature - FRMS, from Reference 42.

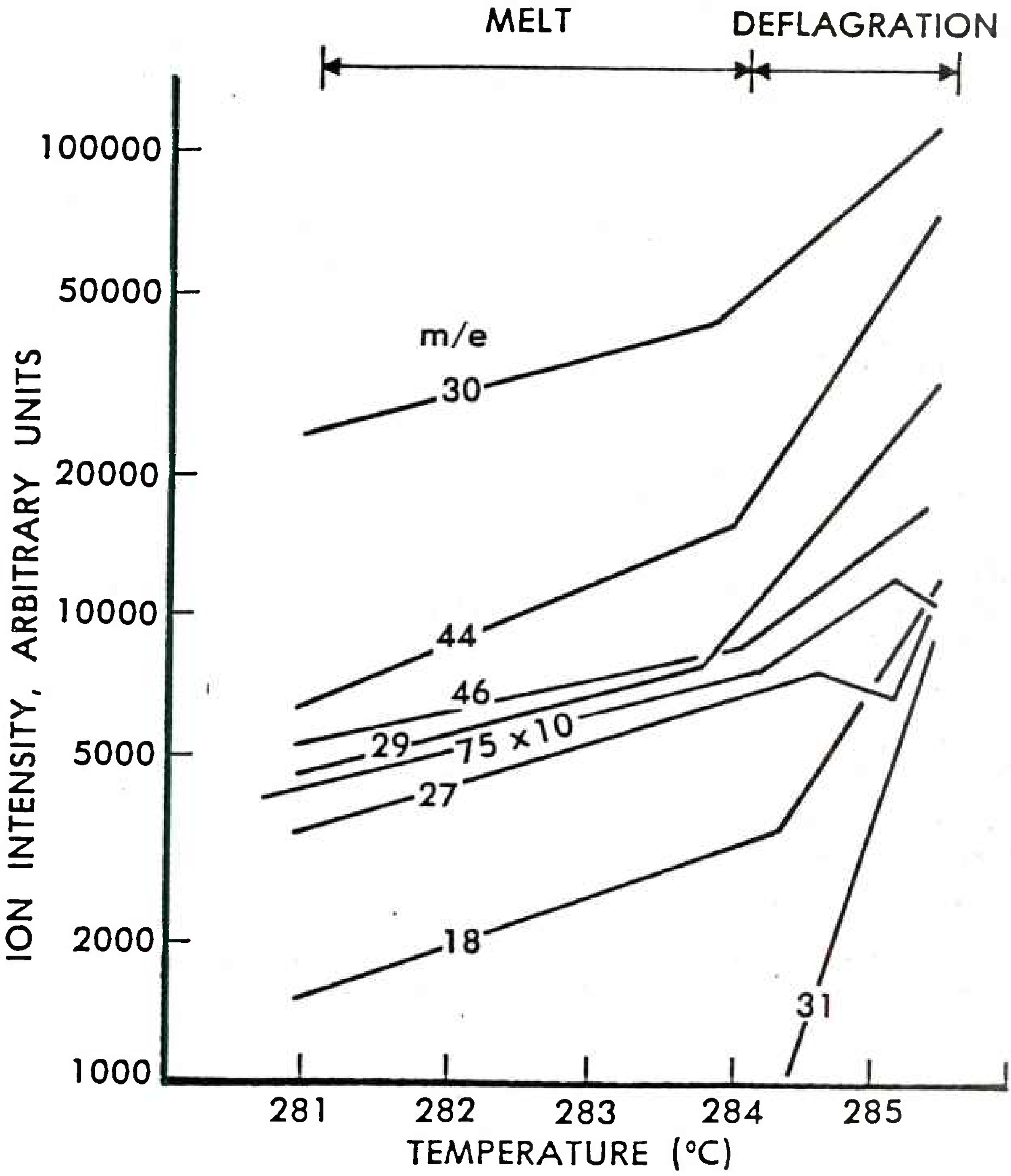

Figure 6. Changes in HMX Decomposition Products During Melt and Deflagration, from Reference 42.

Figure 19 of Reference 42 (copy attached as Figure 7 of the present report) shows the RDX decomposition products as studied by FRMS below (160-200°C) and above the melting point (ca 200°C). It was suggested that sublimation accounted for the smooth transition from below- to above-the-melting point decomposition; the increase in nitrosoamine (m/e 132) when the melting point is reached was also pointed out.

The solids probe results for α-RDX, β-, and δ-HMX are compared in Figure 23 of Reference 42 (copy attached as Figure 8 of the present report. The results were obtained at 10^{-7} torr; hence gas-phase interactions are minimized and ions detected are due primarily to condensed-phase reactions and to sublimation.

The spectra of β- and δ-HMX under solid-probe conditions differ slightly from each other.[42] The β- and δ- forms were distinquished on the basis of whether the probe temperature was above or below the transition temperature of about 200°C.

The products of flowreactor and solid probe studies on HMX are compared for HMX in Figure 20 of Reference 42 and for RDX in Figure 21 (copies attached as Figures 9 and 10 of the present report. In both cases, low molecular weight species seem to predominate at atmospheric pressure (Flowreactor, FRMS), although higher molecular weights become more important at high (10^{-7} torr) vacuum (solid probe, SPMS). This is especially true for HMX, Figure 9. This is in qualitative agreement with the results of the Hercules work[60] in which high-molecular weight ionic species were found at high vacuum but at atmospheric pressure the heaviest peak was m/e 46, NO_2.

Also in qualitative agreement with the Hercules work,[69] much more m/e 46 (NO_2) was observed at high vacuum (SPMS, Figure 9) than at atmospheric pressure. However, RDX, which was not studied by the Hercules workers, gave equal amounts of NO_2 at high vacuum and under flow reactor (atmospheric pressure) conditions.

The mass spectra of liquid RDX and liquid HMX are presented in Figure 22 of Reference 42 (copy attached as Figure 11 of the present report). High molecular-weight products are more important for RDX than for HMX, possibly because of higher temperature in the molten HMX.

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[69] R.R. Miller, A.F. Grigor, R.C. Musso and RA. Yount, "Combustion Mechanism of Low Burning Rate Propellant," Hercules Inc., AFRPL-TR-69-130, AD-502 957, May 1969.

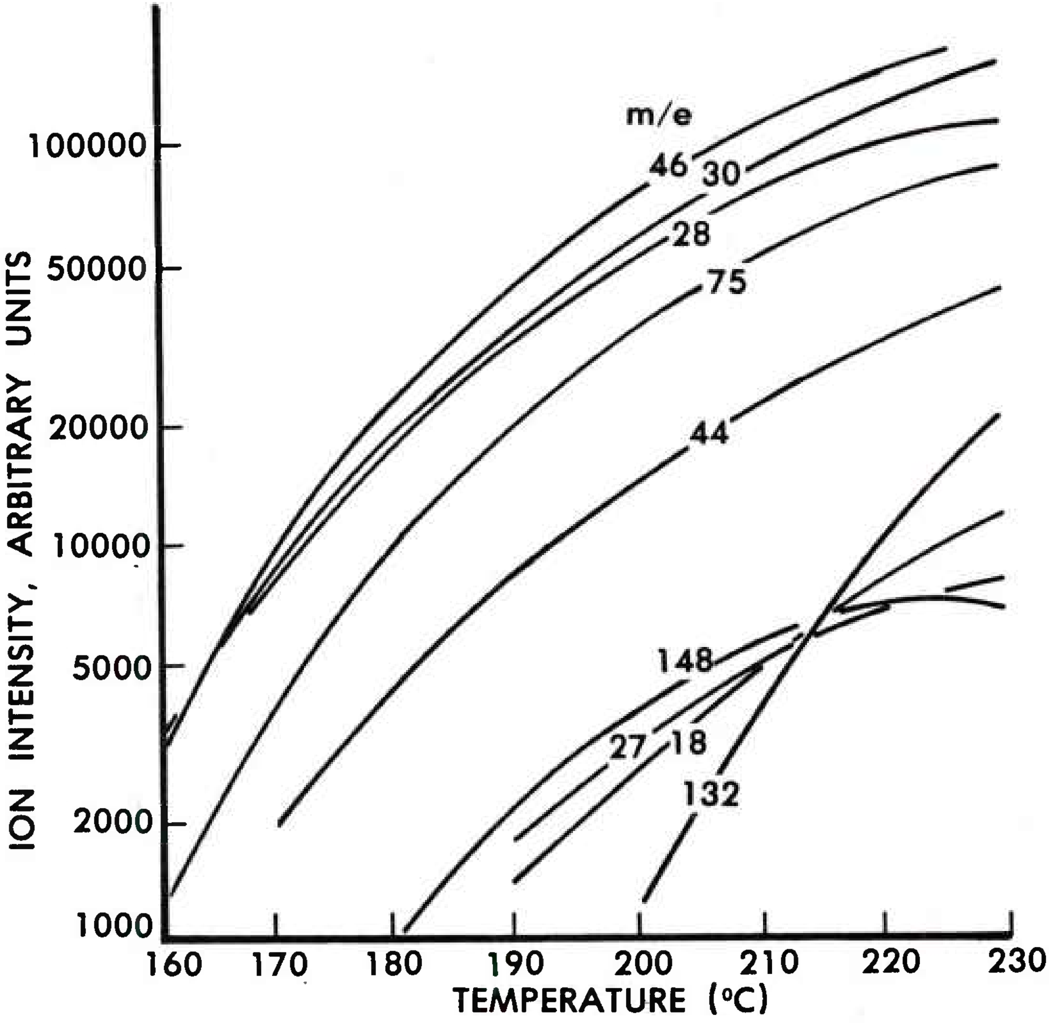

Figure 7. Changes in RDX Decomposition Products with Temperature - FRMS, from Reference 42.

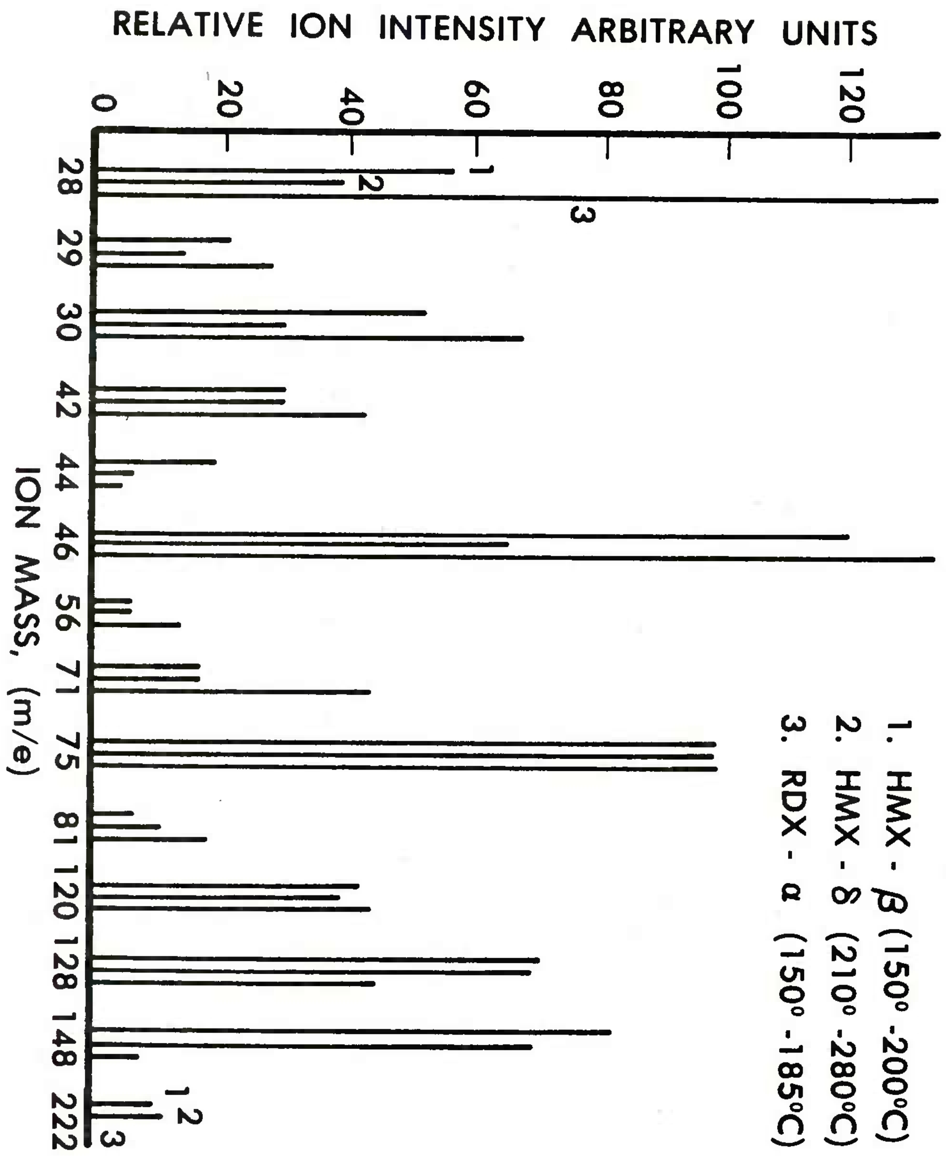

Figure 8. Ion Mass Comparison Between α-RDX, β-HMX, and δ-HMX Solid Probe Mass Spectral Data, from Reference 42.

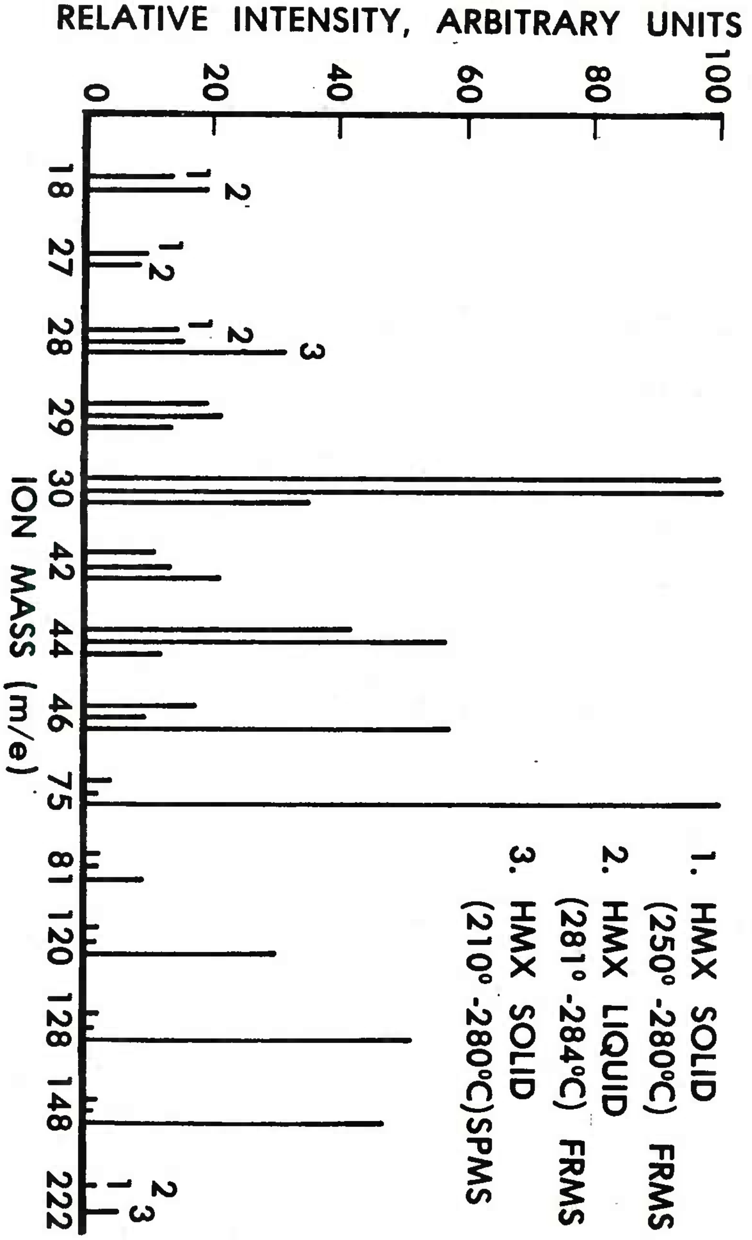

Figure 9. FRMS and SPMS Data Comparison for Solid and Liquid HMX Thermal Decomposition,from Reference 42.

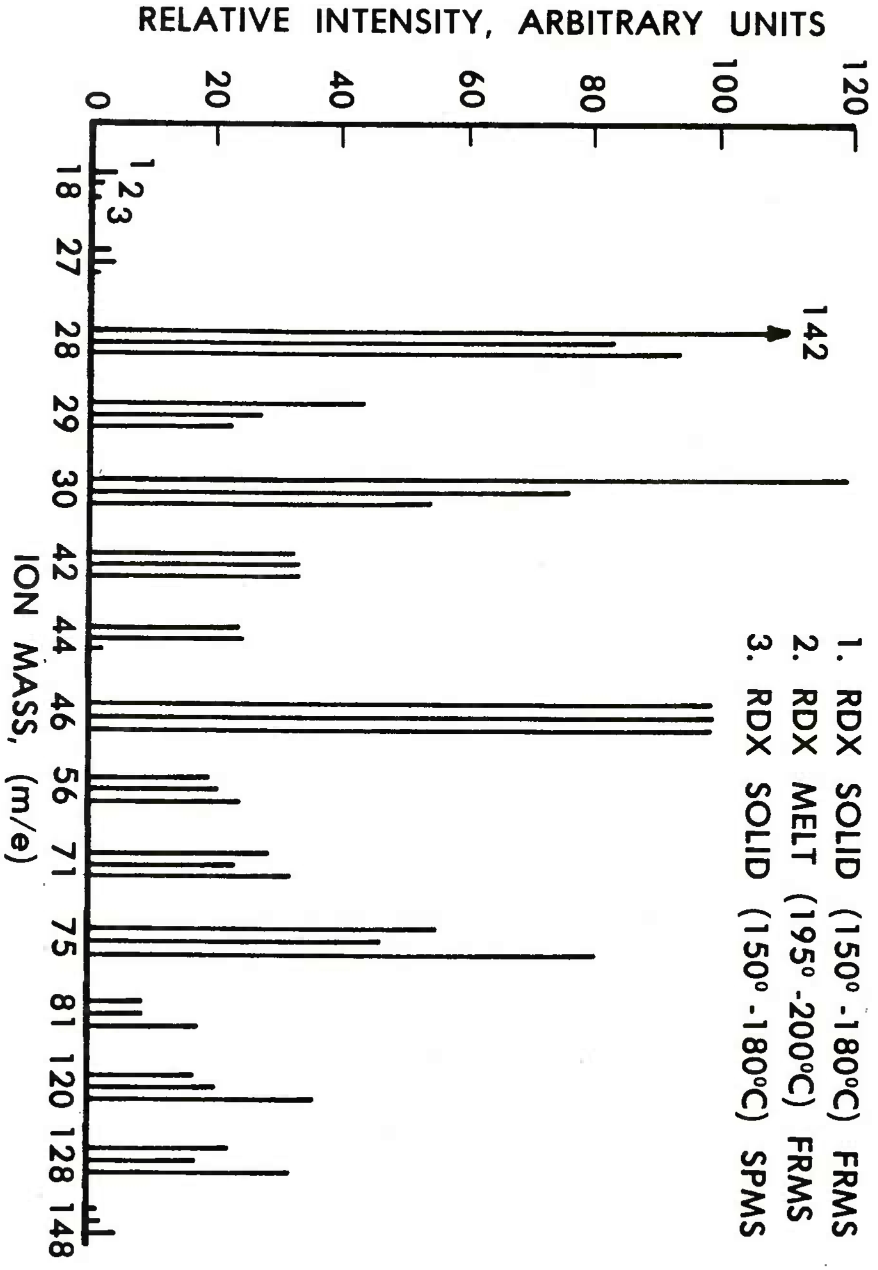

Figure 10. FRMS and SPMS Data Comparison for Solid and Liquid RDX Thermal Decomposition, from Reference 42.

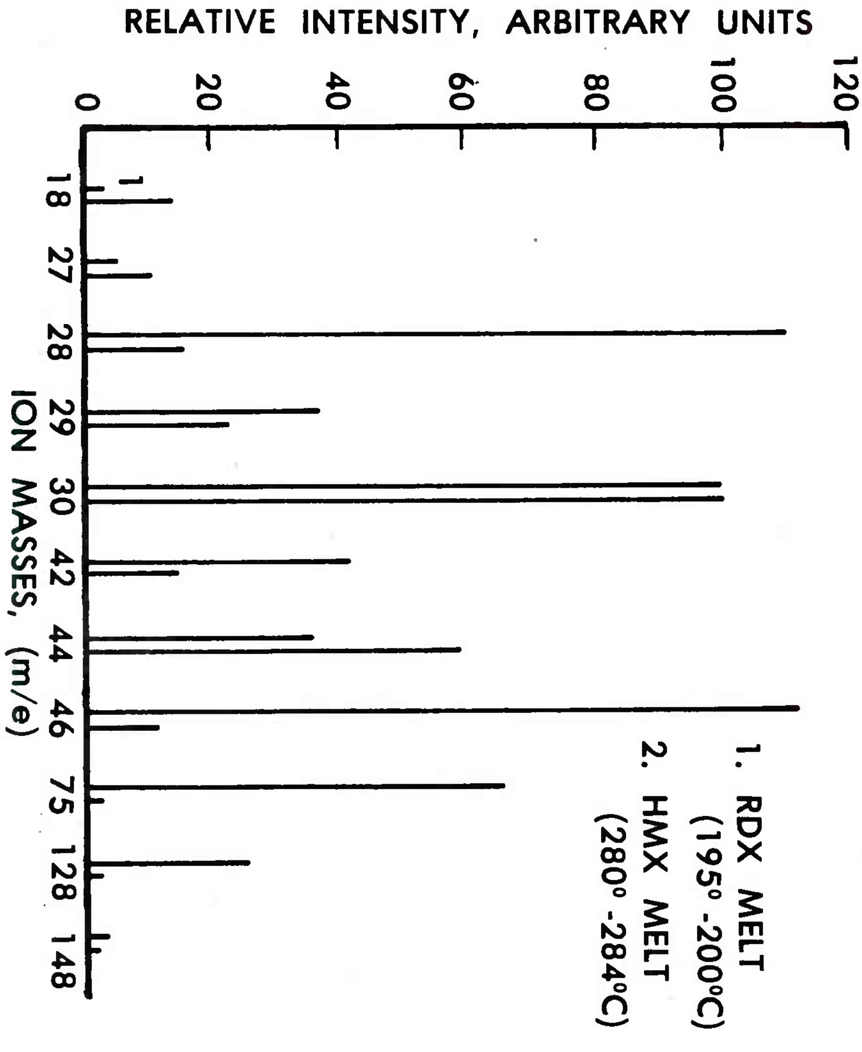

Figure 11. Ion Masses Detected from Liquid RDX and HMX Thermal Decomposition - FRMS, from Reference 42.

McCarty[70] reported Time-of-Flight mass spectrometric studies on HMX and several other nitramines. The peaks are summarized in Table 3 of Reference 70, which also gives relative intensities. The peaks observed for HMX were at m/e 12, 13, 14, 15, 16, 17, 18, 19, 20, 22, 26, 27, 28, 29, 30, 31, 32, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 55, 56, 57, 58, and 69. Further details on the apparatus are not given.

E. Effect of Pressure on HMX and RDX Decomposition.

There are several papers and reports describing pressure effects on HMX and RDX thermal decomposition. In order to help emphasize the need for more work on this area, the summary of this work is incorporated into section 5, "Suggestions for future work."

III. DISCUSSION OF POSSIBLE CHEMICAL MECHANISMS

A. Summary of Literature Information on Formation of Individual Products of Potential Mechanistic Significance.

In this section of the report, individual products of HMX and RDX decomposition will be discussed individually with regard to their occurrence and possible chemical mechanisms for their formation.

Molecular Hydrogen, H_2. Molecular hydrogen has been reported in relatively small amounts ($<$ 0.1 mole/mole of RDX decomposed) from the decomposition of neat liquid RDX, or of RDX in dibutylphthalate[7] (Tables 1 and 3), and in somewhat larger amounts (0.2-0.3 moles/mole of RDX decomposed) from decomposition of RDX in solution in TNT.[7] Other authors have reported the presence of H_2, without giving quantitative data; it has been reported formed from RDX decomposition in trinitrobenzene,[71] from decomposition of HMX below its melting point[29] and under high-heating-rate conditions[37] (600°C max temp., 20°C/msec, 20 sec total time). Failure of a given paper to report H_2 should not be taken to mean it was not formed, as it is often not made clear how much, if any, effort was expended looking for it.

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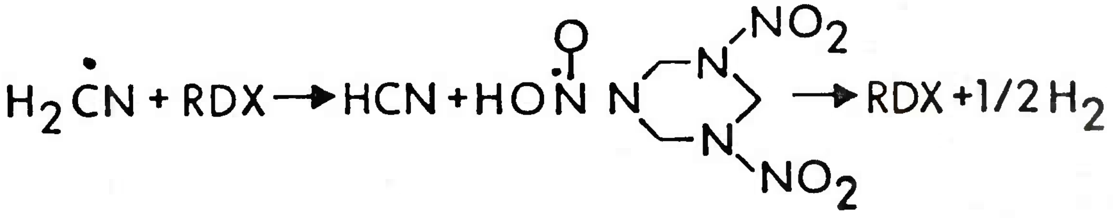
[70] K.P. McCarty, "HMX Propellant Combustion Studies. Phase II. Ballistic Modeling and Phase III. Nitramine Propellant Combustion Investigation," AFRPL-TR-78-73, AD-B034 774, November 1978.

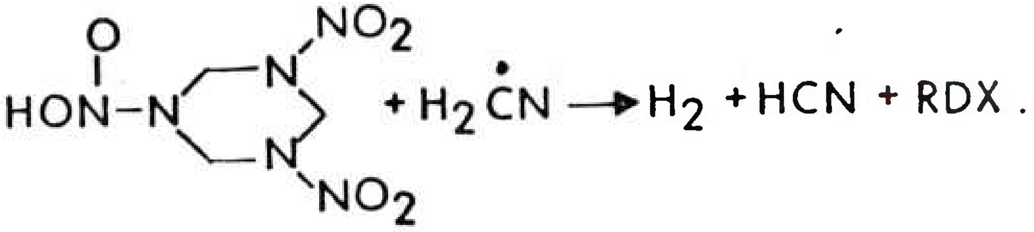
[71] D.F. Debenham and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX) in 1,3,5-Trinitrobenzene," Proceedings of Symposium on Chemical Problems Connected Stability Explosives, Vol. 4, p. 201, 1977.

Some possible mechanisms for formation of H_2 include the following:

$$2H_2\dot{C}N \rightarrow H_2 + 2HCN \qquad (1)$$



(2)



(3)

There are many other possible sources of H_2; for example, similar mechanisms involving HCO can also be written. The actual mechanism of formation of H_2 seems uncertain; however its presence would appear to suggest the presence of free radicals formed during the decomposition.

<u>Ammonia, NH_3</u>. Ammonia is formed (Tables 1-3) (about 0.3 - 0.9 mole/mole of RDX decomposed), when RDX is decomposed at a temperature of 195°C (just below its melting point),[21] or in trinitrobenzene as a solvent.[71] Ammonia was also formed (*ca* 0.1 mole/mole of HMX decomposed) when HMX was decomposed at 600°C in a high-temperature flowreactor.[33] Formation of *m/e* 15 is also mentioned in some of the mass spectrometeric studies.[60,70]

The ammonia is probably formed from the amino rather than the nitro oxygen since labeling studies[54,55] indicate that NO, N_2 and N_2O are each formed with incorporation of one nitro nitrogen, and these products together account for more than 90 percent of the nitro nitrogens in those experiments where NH_3 was reported (Tables 1-3).

The mechanism of formation of NH_3 is uncertain. It may well be present in the reaction mixture in the form of hydroxymethylformamide or some polymer or other compound related thereto. In view of this uncertainty, ammonia and formic acid (also formed on hydrolysis of hydroxymethylformamide) will not be discussed further, although it might be that some formic acid might be formed by deoxygenation of nitro groups of starting material, by formyl radical HCO.

Hydroxymethylformamide, $HCONHCH_2OH$. This compound has been reported formed in the decomposition of both RDX and HMX, in the temperature region near or just below their melting points.[20-22,72] It has been regarded as a true primary decomposition product,[22,72] but the possibility should be considered that it might be formed from water, ammonia, HCN, formaldehyde and/or formic acid at the temperatures of these studies. Studies on decomposition of mixtures of for example, unlabeled and fully carbon-labeled, or on mixtures of carbon-labeled and nitrogen-labeled HMX and RDX, might be helpful in distinguishing between these possibilities; hydroxymethylformamide formed as a primary product would be unscrambled, while any formed form primary products such as HCN, H_2CO and H_2O subsequent to primary decomposition would have the labels scrambled.

Cosgrove and Owen[20] have suggested that hydroxymethylformamide may be responsible for accelerating the decomposition of RDX below its melting point, by condensing on and dissolving the solid RDX, the decomposition of which then accelerates presumably due to faster reaction in the liquid or dissolved state than in the solid state.

Nitrogen Dioxide, NO_2. NO_2 appears to be formed in the decomposition of RDX[16,17,41,46,53,60] possibly from the gas-phase decomposition,[16,17] although (see pp. 80-82 of the present report), the results do not seem inconsistent with some liquid-phase formation of NO_2 as well.

Note that the NO_2 reacts further immediately on formation[16,17] and in fact appears to be gone by the time the decomposition is over. Further evidence for this is provided by the violent reaction (NO_2-H_2CO?) observed (pp. 17-18 of the present report) when the frozen products of RDX decomposition were allowed to warm to room temperature. Thermochemical estimations[2] and available literature analogies (see for example Reference 73) suggest that abstraction of hydrogen from RDX or HMX by NO_2 is a reasonable reaction; NO_2 might also abstract oxygen (References summarized in Reference 2) from a nitro group of HMX or RDX. Experimentally, NO_2 has been reported to accelerate[31] and to retard[25] the decomposition of HMX and RDX, and to

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[72] J. Kimura and N. Kubota, "Thermal Decomposition Process of HMX," Propellants and Explosives, Vol. 5, p. 1, 1980.

[73] J.C. Dechaux, "Nitration of Alkanes in the Gas Phase," Oxidation and Combustion Reviews, Vol. 6, 1973.

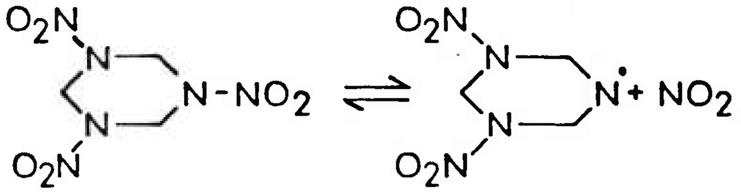
accelerate the decomposition of other nitramines.[74,75] More work is needed on the effect of NO_2 on decomposition of nitramines, including HMX and RDX.

In view of the tendency for NO_2 to react with products (and possibly starting HMX or RDX as well), it seems likely that in those studies where it was only detected and no attempt was made to detect it during the reaction, it probably was present but was not detected because it reacted further. In addition, Rocchio[36] pointed out that in their pyrolysis-GC experiments, NO_2 would avoid detection by reaction with the column packing, and the Rocketdyne workers[33,34] pointed out that their analytical procedure analyzed NO and NO_2 together; both were reported as NO. Thus it seems likely that NO_2 is formed but often evades detection by reacting further.

Some indication that NO_2 may be formed in an early stage of the reaction is provided by a report[41] that in a high-heating-rate mass spectrometric study, m/e 46 appeared at an early stage, before m/e 75 (protonated $H_2C{=}NNO_2$). However, m/e 46 is strong in the mass spectrum of HMX and RDX themselves.[62,63] Consequently, it is hard to be sure that the m/e 46 is not due to vaporized HMX. If the formation of NO_2 is considered to be established by the other studies,[16,17,46-53,60] the above result could be taken as meaning that NO_2 is not formed after the m/e 46 in Figure 12 of Reference 41.

Nitrogen dioxide seems to be formed in greater amounts in high-temperature and high-heating-rate experiments; but it is hard to be sure whether this is due to formation of more nitrogen dioxide, or to freezing-out when the reaction is quenched.

Possible pathways for formation of NO_2 include but are not limited to the mechanisms shown in schemes (4 - 7) for



(4)

The N-NO_2 cleavage pathway of scheme 4 would appear to be favored by the early appearance of the m/e 46 peak[41] (second preceding paragraph).

$$H_2C=N-NO_2 \rightleftharpoons H_2\dot{C}N + NO_2 \qquad (5)$$

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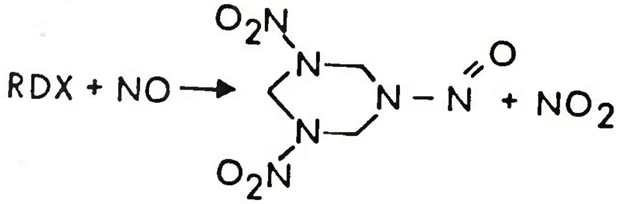
[74] B.L. Korsunskii and F.I. Dubovitskii, "Thermal Decomposition Kinetics of N,N-Dimethylnitroamine," Dokl. Akad. Nauk. SSSR, Vol. 155, p. 266, 1964.

[75] B.L. Korsunskii, F.I. Dubovitskii, and E.A. Shurygin, "Kinetics of the Thermal Decomposition of N,N-Diethylnitroamine and N-Nitropiperidine," Izv. Akad. Nauk. SSSR, Ser. Khim., p. 1452, 1967.

Cleavage for $N-NO_2$ bond in N-nitroformimine (Scheme 5) seems less favored, on the basis of the report[41] that m/e 46 appeared before m/e 75, although thermochemical estimates[2] suggest that it might become more important at higher temperatures.

$$2\,HONO \rightleftharpoons H_2O + NO + NO_2 \qquad (6)$$

This one, (scheme 6) is a little harder to judge, although again the early appearance[41] of m/e 46 would appear to be a point against it.


(7)

Another possibility might be oxygen abstraction by NO (Scheme 7); but again, the early appearance of m/e 46 argues against this.

The mechanism of Scheme (4) seems favored by the early appearance of m/e 46; but note that other mechanisms including those of schemes 5-7, cannot be ruled out.

Some possible further reactions of NO_2 include reaction with $H_2C=O$ or with unreacted HMX or RDX; these are discussed in Section III B and in Reference 2; see also pp. 89-92 of the present report.

Nitrite Anion and Nitrate Anion. These have been reported[21] from the decomposition of RDX just below its melting point. As pointed out,[21] these suggest the presence of NO_2; possibly they are formed via H-abstraction from starting material or from formaldehyde, or by abstraction of nitro oxygen in the case of NO_3, or via combination of NO_2 or NO with hydroxyl radical.

N-Nitroformimine, $H_2C=NNO_2$. Although this has apparently never been prepared, let alone isolated from decomposition of HMX or RDX, it seems appropriate to discuss at this point the evidence concerning its occurrence as an intermediate in HMX and RDX decomposition.

Examination of Tables 1-3 suggests that the sum of the N_2 and N_2O obtained from HMX or RDX decomposition is between 2 and 3 moles per mole of RDX, in many cases approaching 3. This is consistent with formation of N_2 and N_2O from nitroso- and nitroformimine respectively. The formimines could be formed by "unzipping" reactions such as those presented in Reference 2 from starting material and from nitrosoamines formed in the course of the decomposition provided we consider the lack of scrambling in the isotope-labeling (singly-labeled) results[54,55] described on pp. 38-40, and consider approximately one $H_2C=NNO_2$ unit per molecule of starting material to be broken up by either unimolecular or bimolecular initiation of the "unzipping" of that particular molecule. Another item consistent with this is the thermochemical estimations described on page 22 of Reference 2; these suggest that the "unzipping" step should be appreciably faster than the initial step. These estimations have since been (hopefully) improved (p. 87 of the present report), but note that they are still crude, and involve neglect of such factors as conformational effects, electrostatic effects, medium effects, etc. Other evidence consistent with this picture includes the observation (p. 75) of peaks at m/e 74 (H_2C=N-NO_2) and m/e 75 (protonated H_2C=N-NO_2), and of series of peaks differing by increments of 74 (e.g., 102, 28; 222, 148, 74) observed in mass spectrometric studies of decomposing HMX and RDX; even if these prove to be ion-fragmentation peaks rather than parent peaks of true thermal decomposition products, the analogy to thermal decomposition would still be relevant. The observation of N_2, N_2O and H_2CO in the products of HMX and RDX decomposition are also consistent with this since nitro- and nitrosoformimines are known[2,76-79] to decompose thermally yielding N_2O or N_2 respectively, and formaldehyde, at least at low temperature.

Also, the data summarized in Section IIA of the present report indicates that formaldehyde, H_2C=O, and nitrous oxide, N_2O, are important products of the decomposition, often being formed in amounts of two or more moles per mole of HMX or RDX decomposed. Now, H_2C=NNO_2 itself has apparently never been prepared. The closest analogy available appears to be the dimethyl derivative $(CH_3)_2C$=NNO_2, which has been reported[76] to decompose thermally into acetone and N_2O; the analogy between these two compounds would appear to sugest that H_2C=NNO_2 should decompose thermally to H_2C=O and N_2O. In general, N-nitro- and N-nitrosoimines appear to decompose to the corresponding carbonyl compound and N_2O (nitroimines) or N_2 (nitrosoimines),[76-79] although the more sterically hindered compounds show increasing tendency to give N-N cleavage to NO or NO_2 and an iminyl radical.[77,80] Crude thermochemical estimations[2] raise the possibility that at higher temperatures(ca 700-1100°K), N-NO_2 cleavage of even unhindered nitrimines might become faster than the decomposition to N_2 and H_2C=O. This might account for the apparent tendency for formation of larger amounts of NO_2 and HCN in decomposition of HMX and RDX at higher heating rates.

Finally, it seems worth mentioning that reasonable organic mechanisms for formation of H_2C=NNO_2 by radical β-cleavage reactions can be written[2] as follow-ups to the most reasonable initial steps for HMX and RDX decomposition;

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[76] J. Burdon and A. Ramirez, "Reaction of Gem-Nitronitroso Compounds with Triethyl Phosphite," Tetrahedron, Vol. 29, p. 4195, 1973.

[77] J. Jappy and P.N. Preston, "Reaction of Group IV Organometallic Ketimines with Nitrosyl Chloride. Comment on the Thermolysis of the Product N-Nitrosoketimines," Tetrahedron Letters, p. 1157, 1970.

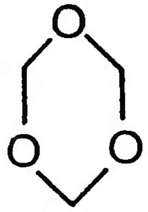
[78] K. Akiba and N. Inamoto, "Chemistry of N-Nitrosoimines," Heterocycles, Vol. 7, p. 1131, 1977.

[79] C.L. Coon, Lawrence Livermore Laboratories, private communication, 1980.

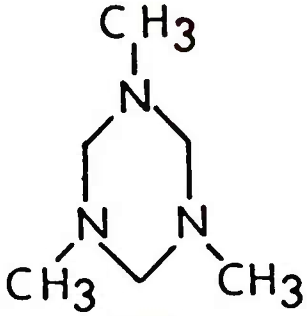
[80] G. Buchi and H. Wuest, "Transformation of Nitrimines to Acetylenes and Allenes. 1,3 Rearrangement of N-Nitroenamines to C-Nitro Compounds," J. Org. Chem., Vol. 41, p. 4116, 1979.

and rough thermochemical estimations (Reference 2 and pages 87-88 of the present report) suggest that these can proceed at rates fast enough to allow their occurrence.

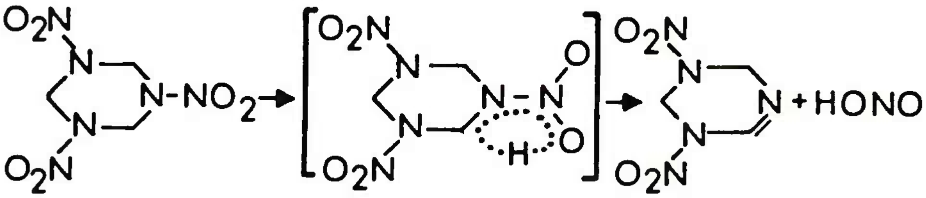
It should also be remembered that HMX and RDX can be regarded as a cyclic tetramer and trimer, respectively, of $H_2C{=}NNO_2$, in the same way that trioxane (VI) can be regarded as a cyclic trimer of $H_2C{=}O$, and 1,3,5-trimethyl-1,3,5-triazine (VII) as a cyclic trimer of N-methylformimine. Note however that the well-known depolymerization reactions of compounds such as VI and VII (see for example Reference 81) do not necessarily constitute a straightforward analogy to HMX and RDX decopmposition, due to the presence in the latter of nitro groups, which (a) would be expected to exert a substituent effect on the depolymerization reaction; and (b) render the molecule capable of undergoing decomposition by pathways such as $N{-}NO_2$ cleavage (Scheme 4) and HONO elimination (Scheme 8), which are not available to VI and VII.



VI



VII



(8)

Apart from the limited speculation in the preceding paragraphs, it is difficult to say much about temperature-dependence of the formation, occurrence and fate of $H_2C{=}NNO_2$, since it has been detected directly only as

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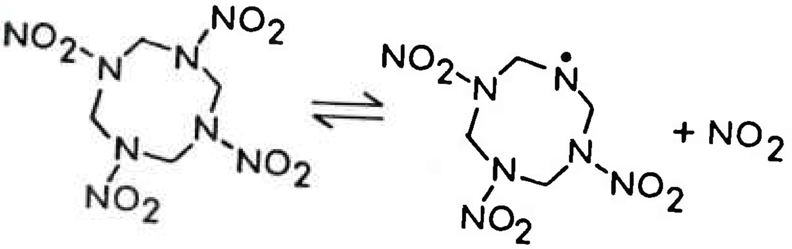
[81] B.G. Gowenlock and K.E. Thomas, "The Gaseous Equilibrium of 1,3,5-Trimethylhexahydo-1,3,5-Triazine and N-Methylenemethylamine," J. Chem. Soc., Vol. B, p. 409, 1966.

m/e 74 and m/e 75 in the mass spectrometric studies (Section II. D. of the present report); thus it is hard to separate the thermal and ion-fragmentation contributions to its formation.

Nitrous Oxide, N_2O. This material is formed copiously in thermal decomposition of HMX and RDX (Sections IIA-IID, Tables 1-3), often in amounts significantly greater than one mole of N_2O per mole of HMX or RDX decomposed, and in some cases more than two moles were obtained per mole of HMX or RDX.

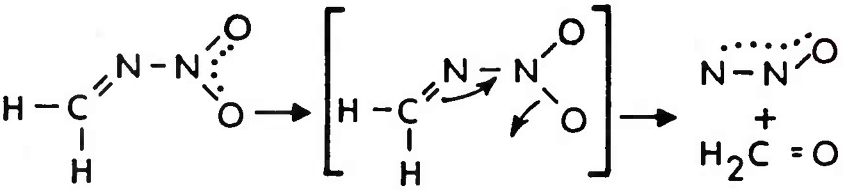
The yield of N_2O appears to decrease somewhat with increasing temperature of pyrolysis, when temperature is varied between 200°C and 800°C (Section IIIB). Two-stage pyrolysis experiments[34] suggested that much of the N_2O was formed in primary rather than secondary reactions.

Labeling studies[54,55] indicate that the N_2O is formed with almost complete retention of one nitro nitrogen; this is based on studies of HMX decomposition at 230-285°C and of RDX at 190°C; thus it is apparently formed from two nitrogens that were joined in the starting material. Very recent studies[56] on mixtures of fully (all nitrogens, both nitro and amino, in all positions of the molecule) and unlabeled HMX give appreciable (ca 20-30 percent) scrambling, presumably due to the equilibrium

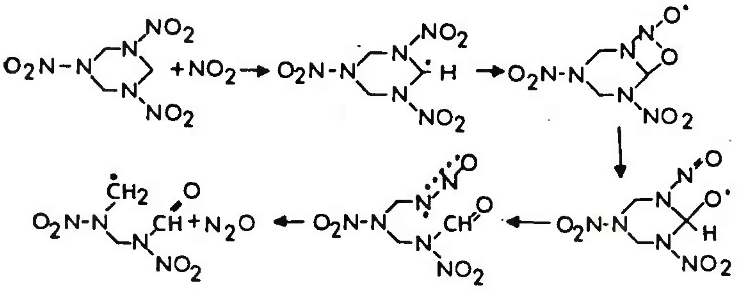

(9)

preceding the decomposition of the nitrogen-centered radical.

N_2O is most likely formed from thermal decomposition of N-nitroformimine (Scheme 10)


(10)

although it is possible to write other pathways for its formation, for example


(11)

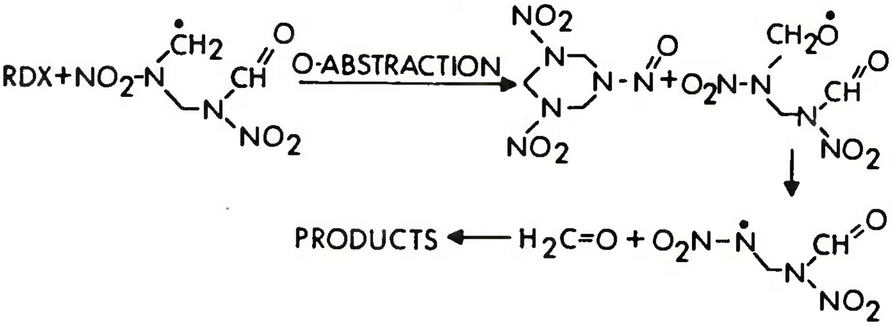
Further comments on formation of N_2 will be found in the section on molecular nitrogen, N_2.

Formaldehyde, $H_2C=O$. Formaldehyde is also reported as a product in nearly all of the studies (Section II, Tables 1-3). Even those studies that do not give quantitative data on formaldehyde, sometimes mention it as being present. One problem sometimes mentioned is that formaldehyde polymerizes, interfering with the analysis.

In the one labeling experiment reported for formaldehyde,[55] a coprecipitated mixture of C-13 and O-18 labeled HMX was studied; it gave some scrambling but was considered by the authors to be inconclusive due to the possibility of exchange via polymerization/depolymerization.

When decomposition temperatures are increased from 200-300°C to ca 600-800°C, the yield of formaldehyde decreases greatly[33,34,38] (Section IIB and Tables 1 - 3 of the present report), possibly due to reaction with NO_2 or N_2O.

Most of the formaldehyde is most likely formed from $H_2C=NNO_2$ or $H_2C=NNO$, in the same step (Scheme 10) as N_2O or N_2 respectively. Other possibilities include disproportionation or abstraction reactions among radicals such as HCO, H_2CN, H, or possibly HCO might abstract a hydrogen from starting material. Another possible type of pathway is illustrated below, starting with one of the radicals involved in Scheme 11.



(12)

Molecular Nitrogen, N_2. This gas is formed in yields of up to one mole and more per mole of HMX or RDX decomposed. Up to two moles of N_2 may be formed when RDX is decomposed in nitroaromatic solvents; since RDX induces decomposition of TNT,[19,82-84] it may be that this nitrogen does not arise from RDX but from TNT; thus it will not be discussed further at this time.

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[82] J. Wilby, "The Thermal Decomposition of RDX/TNT Mixtures. Part 2," RARDE Report (X)7/63, June 1963.

[83] J. Wilby, "Thermal Decomposition of RDX/TNT Mixtures. Part 1," A.R.D.E. Report (MX)16/59, AD-225 991, August 1959.

[84] J. Wilby, "Thermal Stability of RDX and HMX Compositions, Particularly Their Mixtures with TNT," Proceedings of Symposium on Chemical Problems Connected Stability of Explosives, p. 51-65, 1968.

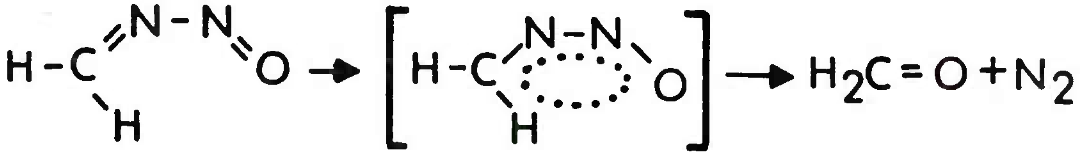
With regard to high-temperature decomposition, it is hard to distinguish any particular trend in N_2 formation (Tables 1-3, and Section IIB).

Nitrogen-15 labeling studies[54,55] show that nitro-N15 labeled HMX (decomposed at 230°, 245°, or 285°C) or RDX (decomposed at 190°C) gave N_2 which still retained over 90 percent of the N-15; thus nitrogen must be formed with the N-NO_2 bond still intact.

There are two principal types of pathways by which N_2 could be formed; these are (a) removal of oxygen from N_2O, with or without a free radical

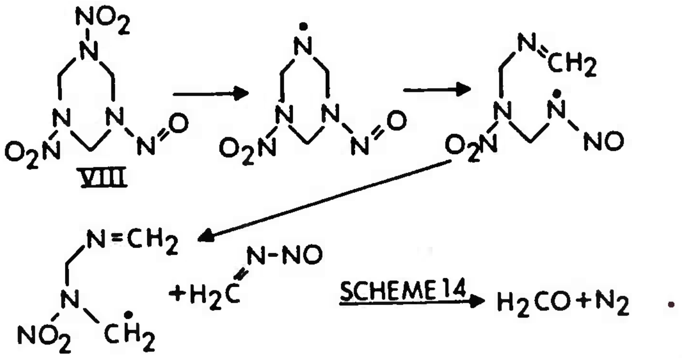
$$R\bullet + N_2O \longrightarrow \left[RON_2^{\bullet}\right] \longrightarrow RO\bullet + N_2 \qquad (13)$$

and (b) rearrangement of N-nitrosoformimine by a pathway analogous to that given in Scheme 10 for N-Nitroformimine



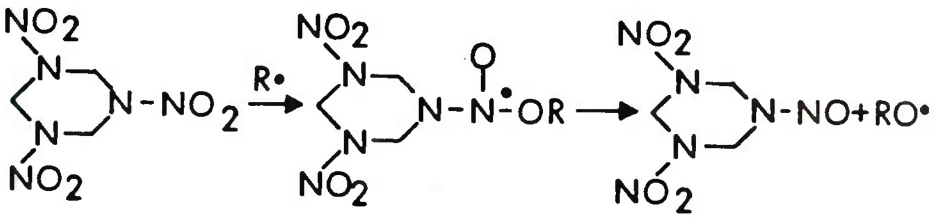
(14)

The nitrosoimine might be formed by β-cleavage of an intermediate radical formed from a nitrosoamine, e.g.,



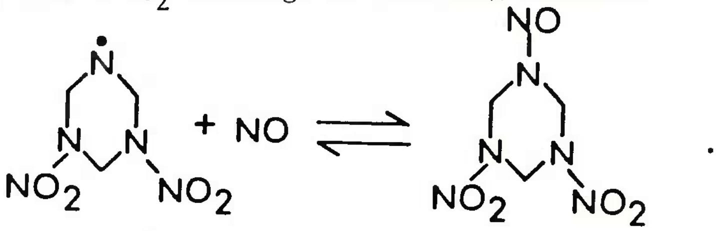
(15)

It is known[78] that nitrosoimines generally decompose thermally to give N_2 and carbonyl compounds. The nitrosoamine VIII might be formed by deoxygenation of a nitro group of HMX or RDX by a free radical intermediate, as suggested earlier.[2]



(16)

Alternatively, the nitrosoamine might be formed by combination of NO with the radical formed from $N-NO_2$ cleavage of starting material



(17)

Further discussion of these pathways is given in Reference 2.

The exact mode of formation of molecular nitrogen is uncertain, but the following observations are consistent with the idea that at least some of it is formed via mechanisms similar to those given in Schemes 16, 15, and 14. We begin the discussion by noting that if it occurs at all, the deoxygenation reaction of Scheme 16 is expected to be favored in neat liquid HMX or RDX, since in the neat liquid an intermediate radical would be surrounded by HMX or RDX nitro groups to a much greater degree than in the gas phase or in solution in an inert solvent.

(a) Peaks at m/e 132 and 58, attributable to the nitrosoamine-containing fragments $H_2C{=}NNO$ and $CH_2N(NO_2)CH_2NNO$, appear in the mass spectra of decomposing HMX and RDX, when the temperature is raised above the melting point.[27,64,68]

(b) Thermal decomposition of neat liquid RDX at 225°C yields[7] N_2/N_2O ratios of $1.16/0.98 = 1.18$, while decomposition in solution in dicyclohexylphthalate gave $N_2/N_2O = 0.89/1.13 = 0.79$.

(c) When RDX was decomposed below its melting point,[21] the N_2/N_2O ratio was found to be lower in the early stages of the decomposition (Table 1, First two columns) and in flasks of large volume (Table 1, column 2) than for almost-complete reaction in a 150 ml flask (Table 1, column 3). This is consistent with greater oxygen abstraction (Scheme 16) in the liquid phase, if one accepts the conclusion[20-22] that under these conditions the early phases of the decomposition take place primarily in the vapor phase, and hence involve less opportunity than the liquid phase for oxygen abstraction (Scheme 16). Presumably the concentration of RDX in the liquid phase increases toward the end of the reaction.

(d) When HMX is decomposed below its melting point,[29] (Table 2, first two columns) the N_2/N_2O ratio is lower than when it is decomposed in the liquid state[7] (Table 2, column 3). The interpretation here runs parallel to that in (c) above, assuming that HMX below its melting point also vaporized and subsequently decomposed to some extent in the gas phase in the early stages of the decomposition.

(e) When pyrolysis of HMX is interrupted and then resumed,[38] the second pyrolysis shows a higher N_2/N_2O ratio than the first, consistent with the idea that the second pyrolysis may have involved nitrosoamines left from the first. However it is hard, on this basis, to understand why the second pyrolysis gave very little NO, since pyrolysis of cyclotrimethylenetrinitrosamine[30] gave product gases containing 49.5% NO, although without more information on product recovery it is difficult to evaluate this information.

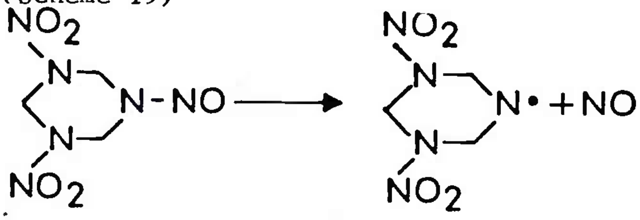
Nitric Oxide, NO. This material is also formed in yields of up to one mole or more per mole of HMX and RDX decomposed (Section II, and Tables 1-3). On high-temperature pyrolysis, the yield of NO increased somewhat with both first and second-stage temperature (Section IIB), leading the Rocketdyne workers[34] to suggest it is formed as a primary product.

Labeling studies indicate that each molecule of NO incorporates a nitrogen from a nitro group of a molecule of HMX or RDX.

Possible mechanisms for formation of NO include the following (see also discussion on pp. 65, 80-82).

$$2\,HONO \rightleftharpoons H_2O + NO + NO_2 \qquad (18)$$

The HONO could arise by cyclic elimination from starting material, or from hydrogen abstraction by NO_2 from starting material or from some intermediate or product such as $H_2C{=}O$. NO could also be formed by N-NO cleavage in a nitrosoamine (Scheme 19)



(19)

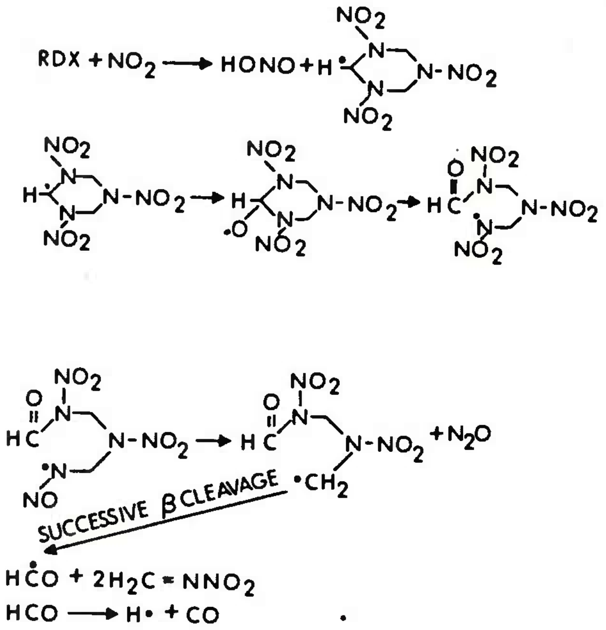
or nitrosoformimine (Scheme 20). Nitrosoamines could arise from oxygen abstraction (Scheme 16).

$$H_2C=N\text{-}NO \rightleftharpoons H_2\dot{C}N + NO \qquad (20)$$

By analogy with NO_2 formation from $H_2C{=}NNO_2$ (pp. 64-65), the reaction of Scheme 20 seems more likely at higher than at lower temperatures.

Carbon Oxides, CO and CO_2. As shown in Tables 1-3 and in Section II, CO and CO_2 are also formed in amounts of up to one mole per mole of HMX or RDX decomposed. In general, yields of CO and CO_2 seem to remain constant or increase with increasing pyrolysis temperature (Section IIB).

CO and CO_2 are most likely secondary products, possibly formed by oxidation of $H_2C{=}O$ by other products such as NO_2, although it is possible that some CO might form by a pathway such as



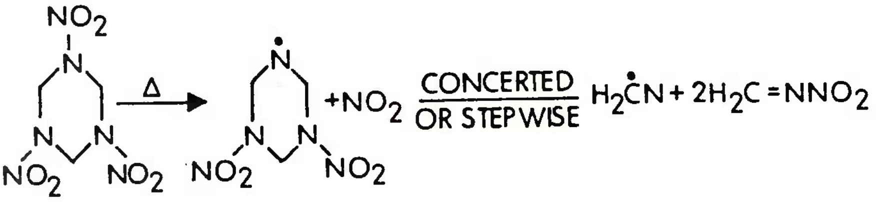
(21)

Hydrogen Cyanide, HCN. This compound is formed in low yield if at all during low-temperature pyrolysis (Tables 1-3, Section II), but the exact significance of this is uncertain since yield-time curves and Tables[17,18] show that HCN reacts further during the decomposition.

Isotope labeling studies[54,55] indicate that HCN incorporates an amino nitrogen from HMX at 230°, 254° and 285° C, and from RDX at 190°C (Section IIC, Table 9).

At higher temperatures, the yield of HCN appears to increase (Section IIB), although since HCN reacts further during slow decomposition,[17,18] it is not rigorously clear whether this is a real effect or is merely due to "freezing out" of HCN before it has a chance to undergo polymerization or other further reaction. Two-stage pyrolysis[34] suggests than HCN is formed in the primary pyrolysis reaction.

The most straightforward pathways for formation of HCN involve loss of a hydrogen atom from H_2CN radical. Possible modes of formation of H_2CN radical (detected by ESR[51-53] at BRL, see Section II) include those in Schemes 22 and 23 (see Reference 50 and Scheme III of Reference 2).



(22)

$$H_2C = NNO_2 \longrightarrow H_2\dot{C}N + NO_2 \tag{23}$$

At lower temperatures, formation by the mechanism given in Scheme 22 seems more likely, since $H_2C=NNO_2$ probably decomposes to $H_2C=O$ and NO at these temperatures. At higher temperatures, however, thermochemical estimations suggest the possibility that the reaction of Scheme 23 may become important (see Reference 2 for further discussion of these points). Note (Tables 1 and 2) that at 600 and 800° C, more than one mole of HCN is reported[33,34] to be formed per mole of HMX or RDX decomposed; this result suggests that $H_2C=NNO_2$ may be undergoing some $N-NO_2$ cleavage (Scheme 23) at least at higher temperatures, since the mechanism of Scheme 22 allows formation of only one mole of H_2CN from one molecule of HMX or RDX.

N-Nitrosoamines. More information is needed on nitrosoamine formation in HMX and RDX decomposition, in view of their possible importance to our understanding of the N_2/N_2O ratios from HMX and RDX decomposition (see above discussion under molecular nitrogen) and to our understanding of the question of $N-NO_2$ cleavage in the initial step, and of the possible occurrence of bimolecular followup steps involving free-radical deoxygenation of nitro groups (see Reference 2, pp. 61-71 and 89-90 of the present report for further discussion of these points).

The American Cyanamid workers[4,17-19] isolated the mono- and trinitrosoanalogs of RDX from liquid-phase decomposition of RDX; but when RDX was decomposed in TNT solution, no intermediate products were found.[19] In addition, as mentioned above (pp. 48-49), nitrosoamines at m/e 58 ($H_2C=NNO$) and m/e 132 ($H_2CNNO_2CH_2NNO$) have been reported to start appearing when HMX or RDX reach their melting point and rapid decomposition begins.[27,64,68] A peak at m/e 70 was also mentioned,[27] but it now appears[56] that this has an oxadiaxole rather than a nitrosoamine structure; this conclusion is based on isotope labeling studies.

For further discussion on mechanisms of nitrosoamine formation see above under "Molecular Nitrogen" and in Reference 2.

It seems worthwhile to mention some very interesting work on the occurrence of nitrosoamines in significant amounts in RDX decomposition at elevated temperatures (J.C. Hoffsommer, Naval Surface Weapons Center, White Oak, Maryland, private communication, 1981). The mono-, di- and trinitroso derivatives were formed in that order; the nitroso compounds increased and went through a maximum, in some cases reaching a concentration higher than the remaining RDX. If confirmed, these are important observations, since as discussed earlier[2] the formation of nitrosoamines can be explained most easily by either $N-NO_2$ cleavage or by deoxygenation of nitro groups, probably be free radicals formed in the decomposition. As far as this writer is aware, this is the first time nitrosoamines have been isolated from HMX and RDX decomposition in such large amounts, although they have been detected in smaller amounts[4,17-19] and detected in mass spectrometric studies on decomposing HMX and RDX.[27,64,68]

There is a need for more work on the nature, occurrence and futher reactions of nitrosoamines in HMX and RDX decomposition. Labeling studies will be especially helpful; see Reference 2 for further discussion of this point.

Mass Spectral Peaks of Particular Mechanistic Significance. In this section, some of the peaks observed in mass spectrometric studies of decomposing HMX and RDX (Section IID) will be discussed. Note that the comments are few and general; it is not claimed that all peaks of mechanistic significance are being discussed here. A number of mechanistically significant peaks are undoubtedly being omitted because of uncertainty as to whether they originate from thermo-or ion-fragmentation, and because time limitations prevented a more thorough review of the several, often rather complicated data sets. Note the comment (Section IID, second paragraph) about a separate, interpretative review on the mass spectrometric studies. Note also that the following should be read in the light of the comments in the first three paragraphs of Section IID.

Peaks at relatively high m/e seem to be observed only in low intensities, if at all. In particular, the mass spectrum of decomposing HMX shows little ion current from ions of m/e higher than 222. It seems uncertain whether this is due to actual failure of the parent radicals to form thermally, to their decomposition while passing from the reactor to the mass spectrometer, or to their failure to exhibit a parent peak. More information on this point would be very useful in evaluating the likelihood of initial steps such as $N-NO_2$ and HONO elimination. Studies of the effect of flow rate and of reactor-detector and of ionization-detector distance might be helpful here.

m/e 148 and m/e 222. These peaks correspond to loss of m/e 74 ($H_2C=NNO_2$) from RDX and HMX respectively. If these could be conclusively shown to be parent peaks of true thermal decomposition products, it would be a point in favor of initial C-N cleavage, since it is difficult to write mechanisms for getting from HMX or RDX to (parent - 74) starting with HONO elimination or $N-NO_2$ cleavage.

m/e 58, m/e 70 and m/e 132 are apparently thermal in origin, since their appearance seems to be associated with melting or with the onset of rapid decomposition upon melting. See the discussion above under Nitrosoamines and under Molecular Nitrogen.

m/e 74 and m/e 75. These peaks are generally attributed to N-nitroformimime and its protonated form respectively; to the extent that they constitute parent peaks of true thermal decomposition products, they constitute evidence for occurrence of $H_2C=NNO_2$ as a decomposition intermediate.

Nonvolatile Decomposition Residue. Fully decomposed HMX and RDX both leave behind a noticeable residue. Robertson[7] noted the formation of a "considerable" residue from RDX decomposition. Rauch and Colman[18] estimated from kinetic data and product production profiles that at some stages of the decomposition, as much as 15 percent of the products might be in the condensed phase. If the reaction was allowed to proceed to completion, a "small amount" (quantitative data not given) of brown residue, virtually insoluble in common solvents, was obtained. Infrared spectral data indicated general C=N unsaturation, as well as presence of nitrate and/or carbonate anion.

In the case of HMX, it was reported[29] that the residue composed about 4 percent by weight of the starting HMX. It was also reported[41] that the material decomposing in the higher temperature region (see p. 34 of the present report) constituted 2-4 percent by weight of the original HMX.

The residue is of interest because it appears to have autocatalytic properties,[27,29] at least in the case of HMX. The RDX residue also probably has true chemical autocatalytic properties, as shown by the reports[7] that the spent solvent from decomposition of RDX in dicyclohexyl phthalate catalyzed the decomposition of a fresh sample of RDX, and that the residue catalyzed[25] the decomposition of liquefied RDX.

The exact nature of the residue is uncertain, but it is presumably polymeric in nature. The nature of autocatalysis by the residue is uncertain; possibly it is due to the presence of aldehyde groupings, since formaldehyde and hydroxymethylformamide have both been reported[22] to accelerate the decomposition of RDX below its melting point. Note however that formaldehyde has also been reported[28] to retard the decomposition of RDX in solution in trinitrobenzene. Possibly this descrepancy is due to the fact that the second[28] study involved decomposition in a homogeneous liquid solution while the first[22] may have involved complexities due to vaporization followed by gas-phase decomposition.

B. Chemical Mechanisms of Thermal Decomposition of HMX and RDX.

In this section we will consider systematically the decomposition mechanisms of HMX and RDX. In reading this section, it should be remembered that the decomposition of these compounds is complex, involving concurrent gas, liquid and solid decomposition; when solid phase is present there is presumably some degree of solid decomposition taking place, especially at temperatures near the melting point of HMX. Furthermore, at least some of the products (NO_2 and $H_2C=O$) are known to react rapidly at even the relatively low temperatures (150-300°C) at which the decomposition is usually studied.[73,85] There also seems to be a possibility that some of the products (for example NO_2) or radicals formed during the reaction may react with starting material; some examples of such reactions are given in Reference 2, and are discussed below. Possibly reactions such as these are responsible for the apparent autocatalysis that has been reported in decomposition of HMX, RDX and other nitramines.[3]

Furthermore, the mechanism may change with temperature and pressure; for example in the case of dimethylnitramine, and by extension HMX, it has been

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[85] D. Barton, "Deuterium Isotope Effects in the Gas Phase Oxidation of Formaldehyde by Nitrogen Dioxide," J. Phys. Chem., Vol. 65, p. 1831, 1961.

suggested[86] that the first step of the decomposition is HONO elimination at low temperatures and N-NO_2 cleavage at higher temperatures, the crossover occurring at about 300°C. Thermochemical estimates[87] are also in agreement with this idea.

These complexities should be kept in mind, because a mechanism shown to be operating under one set of conditions may not be operating under some different set of conditions.

In the following sections, we will consider in turn the initial step, unimolecular follow-up steps and bimolecular follow-up steps.

Initial Step. Shaw and Walker[87] have reviewed eight possible steps that have been proposed for the initial step of HMX decomposition. These include the following (original References given in Reference 87): (a) Unimolecular N-NO_2 cleavage; (b) Five-center elimination of HONO; (c) Four-center elimination of HONO; (d) Unimolecular homolytic cleavage of a single C-N bind; (e) Elimination of one molecule of $H_2C{=}NNO_2$; (f) Concerted depolymerization of HMX to four $H_2C{=}NNO_2$; (g) Insertion of an oxygen atom from a nitro group into an adjacent C-N bond; (h) Heterolytic cleavage of a C-N bond. The same listing encompasses the specific mechanisms that have been proposed for the first step of RDX decomposition, except that (i) Bimolecular attack by a nitro oxygen on a CH_2 grouping in a neighboring molecule has been proposed for the decomposition of neat liquid RDX,[18,25] and it also seems[2] worth considering the possibility of (j) Initial electron-transfer between two molecules of HMX or RDX, leaving one of them as a radical cation and the other as a radical anion.

Neighboring-group or anchimeric assistance is a widespread phenomenon in heterolytic solvolysis and carbonium-ion chemistry. In free radical chemistry such assistance is much less favored due to orbital-energy considerations, but some examples are known.[88] The unexpectedly large ($\log A \simeq 18$) frequency factors[3] observed for decomposition of neat liquid HMX and RDX suggest that anchimeric assistance by nitro groups in steps such as (d) is probably not important, since cyclic association in the transition state should lead to negative entropy of activation, and hence, much lower frequency factors, probably in the range $\log A \simeq 14$ or lower. Low frequency factors observed in the gas phase may be due to HONO elimination (mechanisms (e) or (c)).

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[86] D.F. McMillen, J.R. Barker, K.E. Lewis, P.L. Trevor, and D.M. Golden, "Mechanisms of Nitramine Decomposition: Very Low-Pressure Pyrolysis of HMX and Dimethylnitramine," Final Report on SRI Project PYU 5787, June 1979. (AD-A039 019)

[87] R. Shaw and F.E. Walker, "Estimated Kinetics and Thermochemistry of Some Initial Unimolecular Reactions in the Thermal Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetraazacycloctane in the Gas Phase," J. Phys. Chem., Vol. 81, p. 2572, 1977.

[88] M.T. Reetz, "Anchimerically Accelerated Bond Homolyses," Angew. Chem. Int. Ed. Engl., Vol. 18, p. 173, 1979.

Furthermore, frequency factors for bimolecular reactions are much lower (as low as log A = 8-11) than for unimolecular reactions;[89] consequently the high frequency factors[3] (log A = 13-20) observed would appear to argue against bimolecular initial steps such as (i) or (j) in the liquid or vapor phase at moderate temperatures and pressures. Note however that the first step may not be the rate-determining step. However, it should be remembered that these steps might conceivably become important in solid-state decomposition, or under conditions of very high pressure, especially shock or detonation conditions. Note that here and later in the current report, results that are actually obtained in and most valid for the gas phase will be compared with liquid phase results; this has been done previously for HMX and RDX decomposition (see for example Reference 87) and does not seem unreasonable, since Benson[90] points out that experience shows that relatively nonpolar reactions in condensed phases between non- or slightly-polar molecules do not differ greatly from gas-phase reactions. However, the reader should understand that this assumption underlies much of the reasoning that follows. This assumption is, of course, not valid for ionic reactions in solvents of high dielectric constant[90] and the possibility should always be considered that it may not even be valid for reactions among molecules as polar as HMX and RDX, in solvents as polar as liquid HMX and liquid RDX.

Heterolytic cleavage of a C-N (h) or $N-NO_2$ or C-H bond seems likely to be unimportant in solvents no more polar than liquid HMX of RDX, or the other solvents (e.g. TNT, TNB, dicyclohexylphthalate) used in studies on HMX and RDX decomposition in solution, although in very polar solvents such as melted salts it is possible this situation could change. The oxygen-transfer mechanism ((g), scheme 23) could take place either in a concerted cyclic mechanism similar to that accepted for rearrangements of N-nitro and N-nitrosoamindes (see for example Reference 91), or by unimolecular C-N cleavage followed by attachment of the CH_2 at the oxygen. The latter reduces to a special case of unimolecular C-N cleavage, (d), and the former seems unlikely at least in the neat liquid, because the high frequency factors[3] seem inconsistent with a cylic mechanism. In the gas phase, it seems inconsistent with the reported formation of 80 percent N-nitrosodimethylamine from thermal decomposition of gaseous N-nitrodimethylamine,[92] a compound whose decomposition might be expected to parallel HMX and RDX in many ways, although it has been noted[86] that dimethyl N-nitroamine apparently shows more of a tendency for wall reactions than does HMX. Furthermore the β-cleavage reactions giving $H_2C=NNO_2$ have no parallel in the case of dimethylnitramine.

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[89] S.W. Benson, Thermochemical Kinetics, John Wiley & Sons, Chapter IV, 1976.

[90] S.W. Benson, Thermochemical Kinetics, John Wiley & Sons, p. 3, 1976.

[91] E.H. White and D.J. Woodcock, "The Chemistry of the Amino Group," S. Pataz, ed., Interscience, Chapter 8, 1968.

[92] J.M. Fluornoy, "Thermal Decomposition of Gaseous Dimethylnitramine", J. Chem. Phys., Vol. 36, p. 1106, 1962.

The remaining pathways then include N-NO_2 cleavage (a); the two HONO elimination pathways (b) and (c); and the three C-N cleavage pathways (d), (e) and (f), involving respectively cleavage of one or two C-N bonds, or complete synchronous depolymerizaton.

It is not easy to distinguish among these possibilities. The evidence does seem consistent with the idea that N-NO_2 cleavage (a) and HONO elimination (b) and (c) are important under some conditions, although it is difficult to rule out the C-N cleavage pathways (d), (e), and (f). We will now discuss these pathways in more detail. Note that this is not intended to be a final, definitive discussion but rather a summary of what this writer sees as the general picture at the present time; both the picture itself and the author's view of it are of course subject to change as more work and more thinking are done.

Note also that in many of the experiments, more attention should be paid to the possibility of the experimental results being affected by extraneous factors and sources of error. One example of this is the possible effect of wall reactions on gas-phase kinetic studies; another is possible false indications of NO_2 due to reaction of NO with any traces of atmospheric O_2 left in the system, or by reaction (6),[93] the HONO possibly being formed by a cyclic elimination from starting material. This seems especially pertinent in view of reports[25,31] that colorless product gases turned brown on opening the reaction vessel. A third example is the possibility that chain reactions and other kinetic complexities might influence the gas-and liquid phase kinetics and activation parameters.

This discussion will be limited to the vapor and liquid phases since at present it seems to this writer[2,3] that for decomposition below the melting point the decomposition probably involves the vapor and liquid phases, in addition to- if not essentially instead of- true solid-state decomposition; thus the situation is complex and the true solid-state decomposition is not understood, since further work is needed to separate it from concurrent gas- and (after liquefaction) liquid- or solution-phase decomposition.

A very important problem in trying to write a discussion of the first step of HMX and RDX decomposition is that the complexity of the systems involved makes it difficult to be definitive; observations that at first glance seem to resolve the question almost always turn out, on closer examination, to be subject to multiple interpretations. This is illustrated several times in the following discussion.

Vapor-Phase Decomposition of HMX and RDX. The vapor phase decomposition of HMX and RDX is currently not well understood; there is a great need for more research on both kinetics and products distributions. A number of discussions of the gas-phase decomposition center on N-NO_2 cleavage as the initial step. One plausible mechanistic picture[86] involves a combination of HONO elimination and N-NO_2 cleavage, with the former predominating at lower

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[93] E.W. Kaiser and C.H. Wu, "A Kinetic Study of the Gas Phase Formation and Decomposition Reactions of Nitrous Acid," J. Phys. Chem., Vol. 81, p. 1701, 1977.

temperatures and the latter at high temperatures, due to its higher[2,7,86,87] activation energy. This picture is based on the following: (a) Activation energies and frequency factors for gas-phase decomposition in the lower temperature region are in a range (log A(sec^{-1} = ca 12, E_a = 30-35 kcal/mole)) that is lower than expected (log A(sec^{-1} = ca 16, = ca 50 kcal/mole)) for N-NO_2 cleavage, but more appropriate for a process such as HONO elimination, which involves assisted N-NO_2 cleavage and a transition state more ordered than the starting HMX or RDX; (b) thermochemical estimates based on studies of dimethylnitramine decomposition predict crossing points for HONO elimination and N-NO_2 cleavage of ca 600°K (300°C)[86] and 333°K (60°C).[87] In view of (a), the latter estimate may be low, but both taken together seem consistent with the idea that the crossover may well occur at a temperature lower than those typical of combustion; if this is the case, the predominant reaction at combustion temperature and low pressure would probably be N-NO_2 cleavage; (c) in a mass-spectrometric study[86] of dimethylnitroamine decomposition, it was found that the ratio of N-NO_2 cleavage product to HONO elimination product could be seen to increase as the temperature was raised; note however that this is based on a study of dimethylnitramine, not HMX or RDX.

It should be remembered that there has been no experimental demonstration of the "crossover" phase; the above picture is based largely on thermochemical estimates and on relatively crude gas-phase data, some of which was taken by DSC.[2,3] In particular, factors such as the following should be kept in mind: (1) The effect of such factors as wall reactions and chain reactions on these values is not well understood; on the basis of an examination of the data the possibility was raised[3] that wall reactions may not be as important for HMX and RDX as for dimethylnitramine, but more work giving close attention to these factors is clearly required. (2) Changes in current thermochemical estimates or inclusion of such factors as electrostatic interactions (Reference 89, p. 163) between the decomposing N-NO_2 group and the other nitramine groupings in the HMX or RDX molecule could affect the expected enthalpies of reaction. (3) The change from low-pressure at 200-300°C to the higher pressures and temperature characteristics of combustion in guns and rockets may affect the mechanisms of decomposition.

Also with regard to the predominance of HONO elimination at lower temperatures, it should be remembered that there has been a suggestion[16,17] that NO_2 is formed from the gas-phase but not from the liquid-phase decomposition of RDX, since when liquid RDX decomposes in a sealed container the amounts of NO_2 present increase with increasing container volume. However, it seems to this writer that there is a good possibility that some NO_2 may also have originated in the liquid phase, since if the NO_2 originated in the liquid phase and escaped to the gaseous phase and reacted there or with the liquid RDX, the total NO_2 capacity of the system might be expected to depend on volume in such a way as to produce results similar to those described in the Figures of References 11 and 15.

The following seems at least consistent with the idea that some of the NO_2 may have originated in the liquid phase. If some of the NO_2 were originating in the liquid phase, the maximum concentration in moles/liter might be expected to increase with increasing sample size and to decrease with increasing container volume. To get an idea of what actually happens consider the following Table; the numbers here were read from Figure 12 of Reference 17.

TABLE 12. Volume and Sample Size Dependence of NO_2 Maximum.

Reactor Volume (ml)	Sample Size		m/v (mg/ml)	NO_2 Maximum			
	mg	mmoles		Time (sec)	mmoles per mmole RDX	mmoles ($X10^3$)	mmoles x 10^3 per ml
26	40	0.18	1.5	90	0.030	5.4	0.21
26	26	0.12	1.0	90	0.045	5.4	0.21
26	12.5	0.0563	0.48	275	0.073	4.1	0.16
100	40	0.18	0.4	80	0.063	11	0.11
300	40	0.18	0.13	590	0.188	34	0.11

The concentrations (mmole/ml) at maximum (last column) tend roughly to decrease with decreasing mass/volume (m/V) ratio, with decreasing sample size for constant (26 ml) volume and with increasing container volume for constant (40 mg) sample size. In other words, the NO_2 concentration at maximum (not total yield per mole of RDX) tends to increase somewhat with increasing sample size and to decrease with increasing volume of the container. This would seem to suggest that a good deal of the NO_2 might come from liquid-phase decomposition, in agreement with the observation[50] that the liquid phase shows a brown color during decomposition. However, it is difficult to rule out conclusively the possibility that the NO_2 does come from gas phase decomposition, but that the RDX does not vaporize or diffuse fast enough to reach its equilibrium vapor pressure throughout the container. It is true that the numbers in the last column decrease only by a factor of about 2 while m/V decreases by a factor of ca 10, but this might be due to, for example, slower disappearance of NO_2 by second order reactions at lower partial pressure. Thus, while the results in References 16 and 17 are not inconsistent with formation of at least some NO_2 in gas phase reaction, they also do not seem inconsistent with the idea that liquid-phase decomposition may also generate some NO_2.

Actually, at least some gas-phase formation of NO_2 seems likely, since as discussed in the enclosed write-ups, the mechanisms usually discussed for gas-phase decomposition usually involve either $N-NO_2$ cleavage (expected to give NO_2 as an initial product) or HONO elimination (yielding HONO, which could react further[93] to give one-half mole each of water, NO and NO_2). In agreement with this, References 16 and 17 describe a single experiment in which decomposition of RDX under 400 mm of Helium (rather than in vacuum, as in the other experiments) caused a shift of the maximum NO_2 concentration to longer time, while the rate of reaction remained constant. However, the numbers in columns 4 and 8 of Table 12 (concentration (mmoles/ml) of NO_2 at maximum decreases with decreasing m/v) would seem to suggest some contribution due to NO_2 formed from the liquid phase decomposition.

Thus, possibly the real meaning of this part of the work is that (1) as pointed out[16,17] the major part of the decomposition takes place in the liquid phase and produces the products (N_2O, CO, CO_2, NO, CH_2O, etc.) whose rate of formation curves are independent of volume; and (2) NO_2 is formed but reacts further; and that some (but not necessarily all) of the NO_2 is formed in the vapor phase. Note also the possibility that any NO_2 escaping from the liquid phase may be only a small fraction of that originally formed; the majority of the NO_2 formed in the liquid-phase decomposition might react further without ever leaving the liquid phase.

Before leaving the subject of the gas-phase reaction, it seems worth repeating for emphasis, that there is a need for more work in this area, since as discussed above the picture presented, such as it is, of the gas-phase reaction, is based mainly on thermochemical estimates and on crude data which may well be subject to errors due to such factors as wall reactions chain reactions and other forms of kinetic complexities.

Liquid-Phase Decomposition of HMX and RDX. It seems reasonable to conclude that at least part of the reaction goes via $N-NO_2$ cleavage. This is based on the following: (a) Reports of detection of NO_2 as a product of the reaction (References 41, 46-53, also References 16 and 17 together with the above discussion of the possibility that the results might be partially explainable in terms of escape of NO_2 from the liquid phase followed by reaction in the gas or with the liquid phase); (b) The observation[50] of an orange-brown color (characteristic of NO_2) in the liquid phase of decomposing liquid HMX and RDX (with regard to both (a) and (b)), it should be remembered that the NO_2 might arise from pathways other than initial $N-NO_2$ cleavage, for example from HONO[93] (Scheme 6) or from $H_2C=NNO_2$ (Scheme 5); (c) the activation energies for decomposition of neat liquid HMX and RDX are in a range (ca 50 kcal/mole) that seems characteristic, according to thermochemical estimates,[87] of $N-NO_2$ cleavage although it should be remembered that one is here comparing gas-phase thermochemical estimates with liquid-phase experimental data, and also that electrostatic effects,[94] chain reactions, and other kinetic complexities[95] may be playing a role here. Electrostatic effects (Reference 94) also probably deserve more consideration than they have received so far. Another possibility is that the activation energies are somewhat higher[3] ($\log A(\sec^{-1}) = 18-21$) than predicted[87] ($\log A(\sec^{-1}) = 16.4$) for $N-NO_2$ cleavage, but this could possibly be explained in terms of short, fast chain or other bimolecular followup reactions, or in terms of "cage effects."[96]

If the above (pp. 79-82) is accepted, it suggests that within the 200-300°C temperature range, the mechanism might be different in the liquid phase ($N-NO_2$ cleavage) and in the vapor phase (HONO elimination). This does not necessarily seem unreasonable, since this region is fairly close (within ca 50-100°C) to the estimated[86] gas-phase crossover point, and the rates for the two reactions would be within an order of magnitude or so of each other; this can be seen for example from Figure 1 of Reference 87. Solvent effects on free radical reactions are smaller than for ionic reactions, but rates can still vary by as much as an order of magnitude and even more, among common solvents and the vapor phase.[97,98] It is hard to be sure that neat liquid HMX or RDX (considered as a "solvent") might not exhibit similar effects. Thus, if gas-phase rates of HONO elimination and of $N-NO_2$ cleavage are close to each other in the 200-300°C range in which most of the studies have been done it does not seem unreasonable to suppose that there might be a shift in mechanism from $N-NO_2$ cleavage in the liquid phase to HONO elimination on going from the neat liquid phase to the vapor phase, or even just to a different solvent.

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[94] S.W. Benson, Thermochemical Kinetics, John Wiley & Sons, Eq. (4.17), p. 163, 1976.

[95] P.J. Robinson and K.A. Holbrook, "Unimolecular Reactions," Wiley-Interscience, 1972.

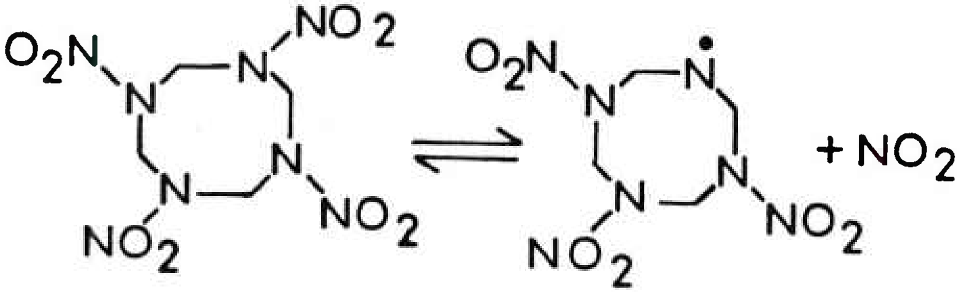
[96] R.A. Fifer, "Cage Effects in the Thermal Decomposition of Nitramines and other Energetic Materials," Proceedings, 19th JANNAF Combustion Meeting, Greenbelt, Maryland; October 1982, Volume I, CPIA Publication 366, p. 311-319.

[97] W.A. Pryor, Free Radicals, McGraw-Hill, New York, 1966. See for example Tables 12-3 and 12-6 and accompanying discussion.

[98] J.C. Martin, "Solvation and Association," Free Radicals, Volume II, Chapter 20, 1973.

However more work is obviously needed. Note that this suggestion rests on the closeness of the rates for HONO elimination and N-NO_2 cleavage in on going from the neat liquid phase to the vapor phase, or even just to a different solvent. Note that this rests on the closeness of the rates for HONO elimination and N-NO_2 cleavage in this temperature range; it would not seem nearly as reasonable to make such a suggestion involving cleavage of a single C-N bond, which according to Figure 1 of Reference 87 has a predicted rate much slower than N-NO_2 cleavage at 500-600°K. Note also that as discussed above (p. 80-82), the results of Rauch and Fanelli[16,17] are not necessarily inconsistent with formation of some NO_2 in the liquid-phase decomposition, if it is assumed that most NO_2 formed in the liquid phase reacts before escaping to the vapor phase, and if it is remembered that gas-phase reaction of NO_2 could also cause a volume dependence similar to that observed by Rauch and Faneli.

Probably the most conclusive evidence for some form of N-N cleavage in liquid phase decomposition comes from the isotope-labeling studies of Powers[56] at Eglin AFB, who decomposed, in a flowreactor, a mixture of un- and fully-N-15 labeled HMX, and found that the N_2O that was given off exhibited a significant amount of scrambling, as shown by the presence of some m/e 45. Presumably most of the decomposition occurred in the liquid phase, subsequent to melting or liquefaction this seems most straightforwardly accounted for by assuming an equilibrium dissociation of HMX into NO_2 and nitrogen centered radical (Scheme 24). The results could also be rationalized in terms of HONO elimination, followed by formation of NO_2 from the HONO and addition across the C=N double bond, followed by further reaction, but this seems unlikely since thermal decomposition of liquid, fully deuterated HMX did not show a primary isotope effect.[56]


(24)

In summary, the liquid-phase decomposition seems best represented at present by initial N-NO_2 cleavage, but there are still some questions to be answered. One of these is whether the scrambling observed by Powers occurred as a result of N-NO_2 cleavage in the starting HMX (Scheme 4) or at the N-nitroformimine stage of the decomposition (Scheme 5). Another concerns the analogy to trioxane decomposition.

Analogy to Trioxane Decomposition. The above discussion involves the assumption that HMX and RDX decomposition occurs in a manner similar to that expected for dimethylnitramine, i.e. by some combination of N-NO_2 cleavage and HONO elimination or (less likely) by cleavage of a C-N bond. However, there is some reason to consider another type of pathway. There are a number of reports (see for example References 99-105, esp, Reference 101, pp. 114-117) of unexpectedly low (ca 45 kcal/mole) activation energies and frequency factors (log A(sec^{-1}) = ca 15) for depolymerization of the formaldehyde trimer trioxane. Since trioxane (III) and derivatives are related to formaldehyde in the same way as RDX is related to N-Nitroformimine ($H_2C{=}N{-}NO_2$), and since the authors of Reference 101 suggested that the decomposition of the trioxane derivatives was concerted (the enthalpy of one-bond ring opening is expected to be about 80 kcal/mole), these results might be explainable by a concerted ring cleavage of some sort. Judging from the parameters given in Reference 101, it does not seem too unreasonable that the rate for this depolymerization reaction might be high enough for it to predominate under some conditions, although the above discussion would seem to indicate that NO_2 formation is also important. Note however that if concerted ring-cleavage of any kind is involved in HMX and RDX pyrolysis, it is apparently not all 3-bond (for RDX) or 4-bond (for HMX) cleavage; there must be some fragments formed that incorporate more than one nitroformimine unit. This follows from the observation of a peak at m/e 132[27,68] which since it does not appear until (or at any rate increases greatly when) temperature above the melting point are reached, is presumably from a product of some thermal decomposition process which does not set in until (or whose importance increases greatly when) the sample melts.

The existence of this possible concerted pathway makes it very difficult to decide between the various C-N and N-N cleavage pathways. For example, comparison of observed activation energies for the decomposition with those estimated for various possible pathways is not conclusive, since it is

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[99] B.G. Gowenlock and K.E. Thomas, "The Gaseous Equilibrium of 1,3,5-Trimethylhexahydro-1,3,5-Triazine and N-Methylenemethylamine," J. Chem. Soc. B., p. 409, 1966.

[100] W.K. Busfield and D. Merigold, "Gas-Phase Equilibrium Between Trioxane and Formaldehyde: The Standard Enthalpy and Entropy of the Trimerization of Formaldehyde," J. Chem. Soc., A, p. 2975, 1969.

[101] S.W. Benson and H.E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS 21, United States Department of Commerce, Washington, pp. 314-17, 1970. We thank Dr. D.F. McMillen for calling this Reference to our attention.

[102] W. Hogg, "The Pyrolysis of 1,3,5-Trioxan," J. Chem. Soc., p. 1403, 1961.

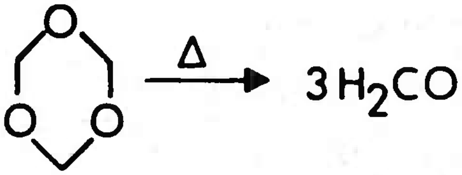
[103] R. le G. Burnett and R.P. Belt, "The Decompostion of Gaseous Trioxymethylene and Paraldehyde," Trans. Faraday Soc., Vol. 34, p. 420, 1938.

[104] C.C. Coffin, "Studies on Homogeneous First Order Gas Reactions," Can. J. Res., Vol. 7, p. 75, 1932.

[105] C.C. Coffin, "Studies on Homogeneous First Order Gas Reactions. IV. The Decompostion of Para-n-Butyraldehyde and Para-Isobutyraldehyde," Can J. Res., Vol. 9, p. 603, 1933.

difficult to know how to estimate values for the hypothetical concerted pathway for HMX or RDX, analogous to the one suggested[101] for trioxane. The formation of NO_2 does not alone indicate primary N-N cleavage, as it could be formed from HONO[93] after HONO elimination or after single-bond or concerted C-N cleavage by a β-cleavage reaction. It has recently been reported[106] that when RDX was decomposed in solution in TNT, NO_2 did not appear until late in the decomposition; its appearance was correlated with disappearance of another radical species, but this does not necessarily rule out initial $N-NO_2$ cleavage, as it could be that NO_2 formed early in the decomposition reacts very quickly, possibly with formaldehyde, delaying buildup until the later stages of the decomposition. Note that References 16 and 17 report formation of NO_2 early in the reaction followed by its disappearance at a rate apparently comparable to the rate of the decomposition itself; possibly this rapid disappearance provides a means of reconciling the discrepancy with regard to early or late detection of NO_2. Mass spectrometric studies on decomposing HMX and RDX (see for example Reference 27; other References summarized above **(p. 40-61, 74) show peak** at m/e 148 and 222 (from HMX), consistent with elimination ot $H_2C{=}NNO_2$, but these results, while possibly suggestive, tend to be hard to interpret due to such factors as the question of whether they are due to parent peaks of true thermal decomposition products, or to ion-fragmentation peaks of some sort.

In addition to these uncertainties, it should be remembered that there is a possibility that the mechanisms of thermal decomposition may vary with reaction conditions; examples of this include the possible shift with increasing temperature from HONO elimination to $N-NO_2$ cleavage, as mentioned above. Another such shift to a mechanism analogous to that of Scheme (25) may be suggested by the report (R.N. Rogers, Los Alamos Scientific Laboratory, Private Communication, 1979) of experiments involving both programmed-temperature decomposition under flowing helium, and isothermal heating in a static helium atmosphere. When the heating was fast enough to cause very rapid, abrupt HMX decomposition, gaseous products were introduced into an attached gas chromatograph as a single slug, with very little time for secondary, gas-phase reaction; under these conditions, "nearly a quantitative" yield of formaldehyde and N_2O was obtained.



(25)

Although as discussed above, $N-NO_2$ cleavage or a combination of $N-NO_2$ cleavage and HONO elimination seem most likely under at least some conditions, the exact nature of the first step of HMX and RDX thermal decomposition is still uncertain, and in fact there are probably several mechanisms, almost certainly chosen from $N-NO_2$ cleavage, HONO elimination, cleavage of one C-N bond or some form of concerted, unimolecular ring cleavage. It should be

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[106] H.L. Pugh, L.P. Davis, J.S. Wilkes, W.R. Carper, and R.C. Dorey, "Thermal Decomposition of RDX Below the Melting Point," Proceedings of 7th Symposium on Detonation, Preprints, Vol. I, p. 45, June 1981.

remembered that the exact mechanism most likely changes with conditions, and establishment of a given mechanism under one set of conditions would by no means indicate that the mechanism operates under any other set of conditions. More work is clearly needed on the first step of HMX and RDX decomposition, and in fact this forms the basis of several of the recommendations for future work at the end of this report.

Follow-up Steps: Unimolecular. Some possible unimolecular follow-up steps were discussed in a preliminary report on this review.[2] In addition to ring opening by β-elimination following N-Nitro cleavage (Scheme 15, see also Scheme III of Reference 2), possible unimolecular followup steps include loss of $H_2C{=}NNO_2$ by a β-elimination reaction (Schemes 11,15,21; see also Reference 2, Schemes II-IV).

Crude estimates of relative rates of C-N bond β-cleavage were presented in Reference 2; it appeared that these reactions were expected to proceed at rates orders of magnitude faster than the initial steps. A possibly improved, although still crude, estimate can be obtained as follows:

The activation energy for the β-cleavage is estimated by taking the difference between bond energies of the breaking C-N single bond and the forming C-N π-bond in the $H_2C{=}NNO_2$ or ring opened amine being formed in the reaction. The energy of the breaking C-N bond is estimated as 63 kcal/mole, considering it equal to the bond energy of a single C-N bond in HMX estimated by Shaw and Walker[87] with omission of their 3 kcal/mole H_2C-N resonance correction. The bond energy of the forming π-bond is estimated as being equal to the π-bond energy in $H_2C{=}NH$. This quantity can be estimated from the heats of formation of CH_3NH_2, CH_2NH_2 and CH_3NH given in Tables A.11 and A.12 of Reference 107, together with the heat of formation of $H_2C{=}NH$ (22.6 kcal/mole) (calculated at 298°K as the sum of $\Delta H_f(C_d H_2)$ = 6.26 kcal/mole, and $\Delta H_f(N_I(H))$ = 16.3 kcal/mole, Reference 107, Tables A.1 and A.3). The C-N π-bond energy (estimated from these numbers as given in Reference 107, pp. 63-5) comes out to be 61 or 62 kcal/mole, depending on whether the CH or NH bond of CH_3NH_2 is cleaved first. When the experimental[102] values of 94.6 for $D(H\text{-}CH_2NH_2)$ and 103 for $D(H\text{-}NHCH_3)$ are used, the same values or values as high as 65 kcal/mole, are obtained for the C-N π-bond energy. These values suggest, in agreement with our earlier[2] estimates, an activation energy of nearly zero for C-N cleavages of this type. If a frequency factor (log A(1/sec) = 14-16) is assumed as before, the cleavage rates estimated earlier should still be valid. Note that this estimate applies strictly to the ring-cleavage of the nitrogen-centered radical only; for the subsequent "unzipping" steps the activation energy will be *ca* 9 kcal/mole higher due to the fact that it is no longer necessary to consider the ring strain energy.

The N-nitroformimine ($H_2C{=}NNO_2$) formed in these cleavage reactions probably decomposes to H_2CO and N_2O, at least at lower temperatures. At higher temperatures, thermochemical estimates[2] suggest that this may still predominate, but the estimated relative rates are such that the possibility of $N\text{-}NO_2$ cleavage to H_2CN and NO_2 should be considered.

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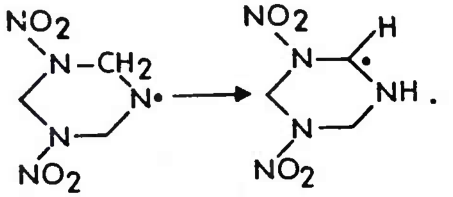
[107] S.W. Benson, *Thermochemical Kinetics*, John Wiley and Sons, New York, 1976.

The above paragraphs are intended to be read together with the discussion of "N-Nitroformimine, $H_2C{=}NNO_2$" on pages 64-67 of the present report, where further discussion of some of the above points will be found.

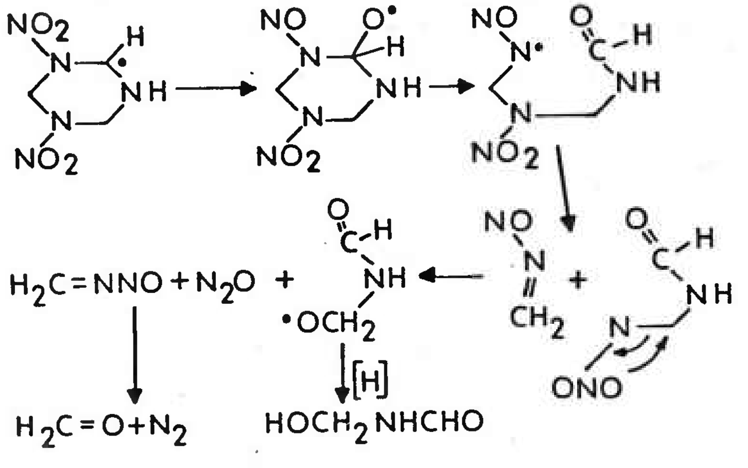
Another possible type of unimolecular followup step that should be considered is exemplified (Scheme 26) by rearrangement of a hydrogen atom from carbon to nitrogen-centered radical formed from N-NO_2 cleavage of RDX or HMX via the mechanism of Scheme (4) or (9)



(26)

This does not seem like an unreasonable type of reaction to consider, especially since the dissociation energy of an N-H bond with four-hydrogens might be expected to be about 100 kcal/mole, judging from the values given[108] for ammonia, methylamine and dimethylamine, while the dissociation energy for the C-H bonds in HMX and RDX can be estimated (although without allowance for conformational effects and medium effects etc.) as being about 86 kcal/mole, in view of the values for methane (104 kcal/mole) and methylamine (94.6 kcal/mole); the frequency factor for this migration is probably lower that for unimolecular ring cleavage. If this hydrogen atom migration does take place, it might lead to a new set of reaction pathways characteristic of the carbon-centered radical; however it might also just lead to a mechanism similar to that of Scheme (22), except for ending in HCNH instead of H_2CN.

One possible follow up to the mechanism of Scheme (26) might be the following (cf References 22 and 72), which can be regarded as a combination of various unimolecular steps discussed above and in Reference 2.



(27)

As mentioned above, isotope scrambling studies might distinguish between formation of hydroxymethylformamide by the mechanism of Scheme (27), and its formation from primary products formaldehyde, HCN and water.

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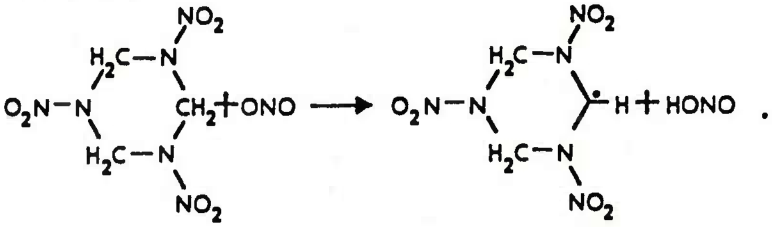
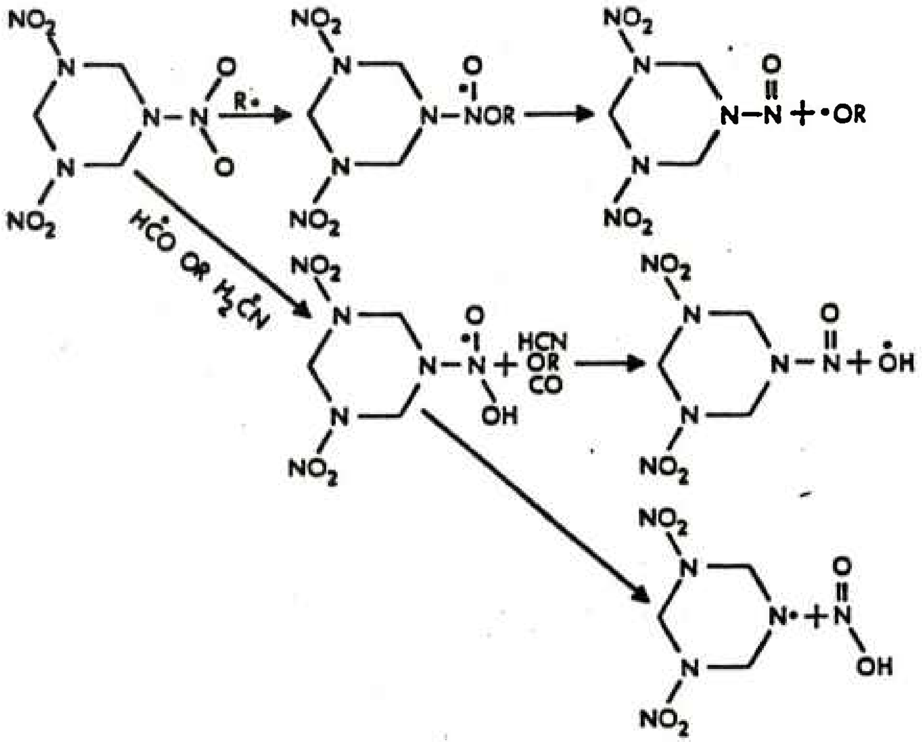
[108] R.C. Weast and M.C. Astle, Eds., CRC Handbook of Chemistry and Physics, 62nd Edition, Chemical Rubber Publishing Company, p. F-191, 1981.

Follow-up Steps: Bimolecular. Some possible bimolecular follow-up steps were discussed previously;[2] these include abstraction of hydrogen from unreacted HMX or RDX by NO_2, OH or other free radicals formed in the decomposition (scheme 28)



(28)

The discussion and thermochemical estimations presented in Reference 2 would seem to suggest that hydrogen abstractions of this type deserve serious consideration, although the present writer is not aware of any conclusive evidence for or against their occurrence in HMX or RDX decomposition. Note that the operation of hydrogen-abstraction from unreacted HMX or RDX probably depends on ability of starting material to compete with formaldehyde, for whatever radicals (NO_2, NO, OH, etc.) are present in the system under a given set of conditions. Note also that the activation energies estimated for hydrogen abstraction from HMX or RDX may be minmum values, subject to increase due to, for example, conformational factors in the HMX and RDX rings, and to decreased lone-pair conjugative stabilization of the radical center resulting from resonance between the nitro group and the amine lone pair of electrons. Another possibility is attack of free radicals formed in the decomposition on the oxygen atoms of the nitro groups in unreacted HMX or RDX. (Scheme 29)



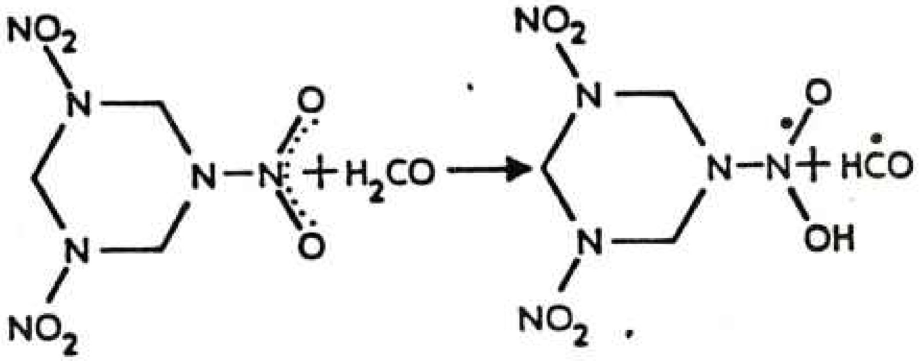
(29)

The previous discussion[2] tended to emphasize (Scheme 29) cleavage of the resulting alkoxynitroxide, but other possible outcomes worthy of consideration include N-N cleavage of the alkoxynitroxide (Scheme 29), as well as the possibility that the alkoxynitroxide might be stable enough to result in essentially nothing more than solvent-stabilization of the intermediate radicals by a specific solvation effect. Formation of nitroso compounds by bimolecular mechanisms (see for example Reference 109) should also be considered.

The discussion in Reference 2 would seem to suggest that radical abstraction, or at least addition, involving oxygen from a nitro group should also be considered seriously. Note however that while the References cited in Reference 2 would seem to suggest that free radical deoxygenation (or at least addition) involving oxygen atoms of nitroaromatics and nitroaliphatic compounds apparently can take place easily, the present writer is not aware of any case in which addition of free radicals to the nitro groups of a nitroamine has been reported or even knowingly attempted. Note also that addition of a free radical to nitro oxygen need not necessarily lead only to deoxygenation of the nitro group. The alkoxy or hydroxynitroxide could undergo other reactions too, for example (Scheme 29) N-N cleavage to give a nitrogen centered radical.

Apart from the fact the certain observed variations in the N_2/N_2O ratio from HMX and RDX decomposition are at least consistent with radical deoxygenation (pp. 71-72), the present writer is not aware of any evidence for or against mechanisms involving free-radical addition to or deoxygenation of the nitro groups in HMX or RDX decomposition. Even these variations are not conclusive, due to the possibility that the intermediate nitrosoamine may be formed by recombination equilibria similar to that of Scheme 17. Isotope scrambling studies such as those carried out at Eglin AFB[56] may also shed light on this point, as discussed in References 2 and 110.

Such reactions as abstraction of hydrogen from formaldehyde by a molecule of unreacted HMX or RDX (Scheme 30) are difficult



(30)

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[109] L. Lunazzi, F. Placucci, and N. Ronchi, "Alkoxy Nitroxide Radicals from Photolysis of Nitropyridines: A Kinetic Investigation by Electron Spin Resonance Spectroscopy," J. Chem. Soc., Perkin Trans., Part II, p. 1132, 1977.

[110] M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Some Suggestions for Needed Research Work," ARBRL-MR-03181, June 1982.

to evaluate but seem unlikely, since they would be expected to proceed at rates comparable to a similar reaction between two RDX or HMX molecules; since this type of reaction apparently proceeds at a rate slower than the first step of HMX decomposition the same is probably true of reaction between RDX and formaldehyde, in view of the close similarity between the C-H dissociation energies in formaldehyde (87 kcal/mole, Reference 108) and the value estimated for HMX or RDX (86 kcal/mole, Reference 2). Note however that the value for HMX or RDX may be a minimum value due to conformational factors in the HMX or RDX rings, and to decrease lone pair stabilization of the radical center resulting from resonance between the nitro group and the amino lone pair.

It is difficult to evaluate the likelihood of electron transfer among products, intermediates and HMX or RDX molecules.

Another possible type of bimolecular follow-up step that may be unlikely but should be kept in mind consists of attack by free radicals formed in the reaction, on the double bond of the imine resulting from HONO elimination of starting HMX or RDX.

Furthermore, it is difficult to evaluate the possible importance of aqueous hydrolysis of the nitramine group by water formed in the reaction, at the temperatures (ca 200-300°C) at which most decomposition experiments are performed. RDX and related compounds have been reported[111-114] to decompose at or near room temperature in acid or basic aqueous solution, or in neutral aqueous solution, including sea water. (See for example References 111-114.) It also seems worth noting at this point that hydrolysis, or a combination of hydrolysis and oxidation by HNO_3 or nitrogen oxides, has been suggested as a possible explanation for apparent autocatalysis in decomposition of compounds such as nitroglycerin and $(O_2N)OCH_2CH_2N(NO_2)CH_2CH_2O(NO_2)$. (See for example References 115 and 116.)

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[111] J. Simecek, "Decomposition of Nitrosoamines and Nitroamines in Protogenic Solvents. I. Decomposition of Cyclotrimethylenetri-Nitrosoamine by Concentrated Sulfuric Acid," Chem. Listy, Vol. 51, p. 1323, 1957. (Chem. Abstr. Vol. 51, 17942C)

[112] C. Holstead and A.H. Lamberton, "Nitramines and Nitramides. III. The Formation of Nitric Acid by the Action of Sulfuric Acid," J. Chem. Soc., p. 1886, 1952.

[113] J.C. Hoffsommer and J.C. Rosen, "Hydrolysis of Explosives in Sea Water," Bull. Environ. Contam. Toxicol. Vol. 10, p. 78, 1973.

[114] J.C. Hoffsommer, J.C. Kubose, and D.J. Glover, "Kinetic Isotope Effects and Intermediate Formation in the Aqueous Alkaline Homogeneous Hydrolysis of 1,3,5-Triaza-1,3,5-Trinitrocyclohexane (RDX)," J. Phys Chem., Vol. 81, p. 380, 1977.

IV. FINAL COMMENT ON RELATION OF THERMAL DECOMPOSITION STUDIES TO COMBUSTION AND EXPLOSIVE BEHAVIOR

Since combustion takes place at much higher temperatures and pressures than encountered in the low-temperature decomposition studies encountered here, it seems appropriate to discuss the possible effect of high temperature, pressure and heating rate. These have been discussed in our previous reports and presentations.[2,3] Some further discussion follows.

First, when the decomposition takes place at increased pressure, there might be an increase in the importance of bimolecular processes relative to unimolecular processes; this might have an important effect on combustion behavior, as discussed previously.[2] Another possible effect of pressure might be that at sufficiently high pressures, the vapor phase might become so compressed that the environment "seen" by a single molecule might resemble a liquid more than a low pressure vapor or gas; if this were the case the decomposition mechanism might well resemble the liquid decomposition rather than a low-pressure gas-phase decomposition, and activation energies and frequency factors should be modified accordingly.

The effect of temperature on reaction mechanisms and products could also be important; as temperature rises, reactions with high activation energy would be expected to accelerate relative to those with lower activation energies, since the activation energy is simply the slope of a plot of rate constant vs reciprocal temperature. Two examples of this have appeared earlier[2,3] in the present review; these are the apparent temperature dependence of the relative rate of $N\text{-}NO_2$ cleavage and of HONO elimination in the gas-phase decomposition,[86] and the possible tendency for cleavage of $H_2C{=}NNO_2$ to H_2CN and NO_2 to become more important relative to formation of N_2O and H_2CO, as temperature rises.[2,3] Such changes in relative importance of various chemical mechanism could give rise to temperature- and heating-rate-dependent changes in decomposition product distribution and chemistry; as with the pressure effects, these might well be very important in modeling and understanding combustion and explosive behavior.

Another possible effect of high heating rate or high temperature might be to cause the first steps to become faster relative to bimolecular follow-up steps because of the higher activation energy characteristic of unimolecular

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[115] C.E. Waring and G. Krastins, "The Kinetics and Mechanism of the Thermal Decomposition of Nitroglycerin," J. Phys. Chem., Vol. 74, p. 999, 1970.

[116] N.G. Samoilenko, A.A. Vinokurov, V.G. Abramov, and A.G. Merzhanov, "Kinetics of the Thermal Decomposition of Dinitroxydiethylnitramine with No Removal of Gas from the Reaction Zone," Zh. Fiz. Khim. (English Translation), Vol. 44, p. 22, 1970.

reactions, and since more unimolecular decomposition might be expected to take place immediately, with corresponding decrease in opportunity for bimolecular follow-up steps involving starting HMX or RDX molecules or early intermediates. This effect might also cause important changes in product distribution or chemistry with increasing temperature of heating rate. The temperature and pressure effects on the unimolecular/bimolecular ratio apparently work in opposite direction, but complete compensation is not assured.

In view of the preceding paragraphs, possibly the most useful aspect of thermal decomposition studies at low temperatures and pressures is not to provide product distributions and kinetic parameters that can be applied directly to combustion conditions, but rather to elucidate the types of chemical decomposition processes involved, including minor (at low temperatures and pressures) pathways in addition to the principle ones. Informed extension of this body of knowledge to combustion conditions could then provide the basis for improved understanding such as stability, sensitivity, and burning rate behavior.

V. SUGGESTIONS FOR FUTURE WORK

More work is needed on all aspects of HMX and RDX decomposition mechanisms. While the mechanisms discussed above seem reasonable and consistent to the present writer, it should be kept carefully in mind that they are not firmly established. In fact, at present they are best considered only as a basis for further discussion.

Previous writeups in connection with the present review have included a number of suggestions for future work that seemed to be needed in the area of nitramine decomposition; these types of work included, among others, isotope labeling studies, spectroscopic studies of various types including fast-pyrolysis and time-resolved laser spectroscopic techniques, and work aimed at improving our understanding of such topics as the gas-phase and the true solid-phase decomposition, the first step of the decomposition of HMX and RDX, and autocatalysis behavior in HMX and RDX decomposition. In the present discussion, we will suggest a variety of chemical studies, many of which are related to the effect of pressure, temperature and heating rate on HMX, RDX and nitramine decomposition.

There is a need for more research into the effect of pressure on HMX and RDX decomposition, with regard to both kinetics and product distributions. One study,[50] carried out at pressures up to 1000 psi (0.067 kbar), resulted in activation energies for HMX decomposition which decreased from 55.9 kcal/mole at atmospheric pressure to 41.8 kcal/mole at 1000 psi (0.067 kbar) of argon, although the activation energy for RDX decomposition was reported to be independent of pressure from atmospheric pressure to 500 psi (0.03 kbar). In a study of time-to-explosion versus temperature for a number of explosives including HMX,[117] it was found that activation energy appeared constant from <1 kbar to 50 kbar; it was suggested that the decomposition mechanism was independent of pressure. There has also been a report[118] that the activation energy for decomposition of RDX was much lower when measured by closed-pan higher pressure due to confinement than by open-pan DSC. With regard to product distributions, there has been a report[119] that when RDX was decomposed at about 5 kbar, N_2O and CO_2 were by far the major products; no H_2O, H_2CO, or CO were observed, although some H_2CO, H_2O CO and HCN were found in the decomposition gases from a much larger sample volume. The method of analysis (infrared) used would not have detected H_2, O_2, or N_2. Finally, in a study of closed-bomb combustion of explosives[120] at pressures up to 1780 psi, (0.12 kbar) it was found that, in some of the low-pressure experiments (15-20 psi, 0.001 kbar), product distributions were obtained which differed from the high-pressure combustion in that they gave product distributions paralleling the thermal decomposition products from low-pressure-low-temperature studies (larger amounts of formaldehyde, N_2O NO, HCN, etc., rather than just N_2, carbon oxides and H_2). One possible tendency which emerges from these higher-pressure product studies is that more formaldehyde seems to be observed when time from reaction to analysis is short and pressure is low; maybe this due to further reaction (possibly with NO_2) at higher pressures or in some cases to polymerization. In view of the differences between experimental conditions and results reported in these studies[50,117-20] it is clear that pressure effects on HMX and RDX are far from well understood, and much more work in this area is required.

There is also a need for further studies of temperature and heating rate effects on HMX and RDX decomposition; Section II B attempts to summarize all existing studies in this area. Together with Tables 1 and 2, the material in this section suggests that at higher temperatures and heating rates, there may be a tendency for detection of more HCN and NO_2 and less products such as H_2CO and N_2O, but the data are often qualitative; furthermore it is difficult to be sure whether the effect is due to actual chemical effects, or to "freezing out" of NO_2 and HCN before they have a chance to react further. This is a very important point, because a shift in product distribution away from H_2CO and N_2O at lower temperatures to more HCN and NO_2 at higher temperatures could

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[117] E.R. Lee, R.H. Sanborn, and H.D. Stromberg, "Thermal Decomposition of High Explosives at Static Pressures 10-50 Kilobars," Proceedings of 5th Symposium (International) on Detonation, p. 331, 1970.

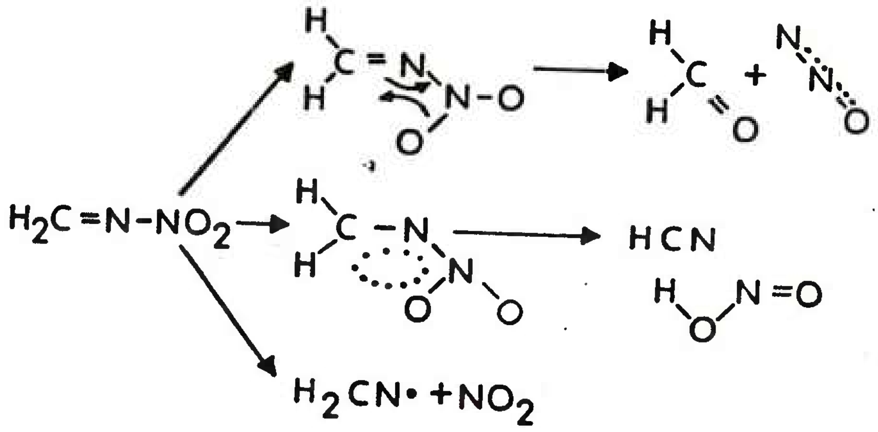
[118] K. Kishore, "Thermal Decomposition Studies on Hexahydro-1,3,5-Trinitro-s-Triaxine (RDX) by Differential Scanning Calorimetry," Propellants and Explosives, Vol. 2, p. 78, 1977.

[119] P.J. Miller, G.W. Nauflett, D.W. Carlson, and J.W. Brasch, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triaxine (RDX) and RDX at High Pressures," Proceedings of 17th JANNAF Combustion Meeting, CPIA Publication No. 329, p. 479, September 1980.

[120] R.R. Bernecker and L.C. Smith, "On the Products Formed in the Combustion of Explosives. Freeze-Out of the Water-Gas Reaction," J. Phys. Chem., Vol. 71, p. 2381, 1967.

have a profound effect on the chemical reactions taking place during combustion, and hence on the combustion behavior of HMX, RDX, nitramines and of propellants containing them. More work is needed on the verification and further study of this possible shift in product distribution.

Some possible lines of approach may be suggested by the following discussion of a possible chemical explanation for the above shift with temperature in product distribution. As mentioned in Section III of the present report, there appears to be a fair amount of evidence consistent with the occurrence of N-Nitroformimine, $H_2C=N-NO_2$, as an intermediate in HMX and RDX decomposition. This molecule could break down in three possible ways, illustrated in Scheme 31.



(31a)

(31b)

(31c)

Activation parameters for these three steps were estimated approximately in Reference 2; the cyclic elimination reaction giving H_2CO and N_2O was estimated to have the lowest activation energy (27 kcal/mole), based on combining approximate frequency factor and a single, **crude estimate** (based on **information** concerning $(CH_3)_2C=N-NO_2$, given in Reference 76 of the present report). The HONO elimination and $N-NO_2$ cleavage pathways were estimated to have activation energies of at least 38 and 46 kcal/mole respectively, based on the estimates of Shaw and Walker[87] for the sp^3 nitrogen in dimethylnitramine and the expectation that similar reactions involving sp^2 nitrogens in nitro- and nitrosoimines would have higher activation energies. (See the values given for dissociation energies of bonds involving sp^2 and sp^3 carbon atoms, Reference 89, page 309.) Crude estimates using these activation parameters suggested that formation of N_2O and H_2CO would predominate at most temperatures, with N-Nitro cleavage becoming comparable at 1100°K. In any case, the cyclic elimination to H_2CO and N_2O is expected to have a lower activation energy than the two N-N cleavage pathways 31b and 31c, with the result that there may be a tendency for a shift in decomposition pathway of $H_2C=N-NO_2$ from formation of N_2O and H_2CO at low temperatures, to formation of HCN, NO_2, HONO, NO etc. at higher temperatures. This possibility should be checked out, paying careful attention to the possibility that the apparent shift may in fact be an artifact due to "freezing out" of the more reactive

NO_2 and HCN under the conditions of the higher-temperature experiments before they have a chance to react further, as they do at lower temperatures without quenching (see for example References 16 and 17).

N-Nitro- and N-Nitrosoformimines generally decompose to yield carbonyl compounds and N_2O or N_2 respectively,[76,78,79] although N-nitro cleavage is also a known reaction of these compounds, products characteristic of it having been reported for both the N-nitro[80] and the N-nitrosoimines.[77] It has been suggested[77] that N-N cleavage appears to be facilitated (or cyclic cleavage retarded) when the groups attached to the nitrosoimine carbon are bulky. The point here is that although the decomposition to N_2O and carbonyl compounds seems to predominate[76,78,79] at low temperatures, the N-N cleavage is also a respectable reaction for these compounds.

Although as mentioned above (pp. 65-68) a reasonable amount of evidence seems consistent with the intermediacy of N-nitroformimine in the decomposition of HMX and RDX, it would still be helpful to have more evidence and, if possible, to actually detect it in situ, possibly by a spectroscopic technique. Another thing that might be of interest might be studies on the chemistry of organic nitrosoimines such as $(CH_3)_2C{=}N{-}NO_2$; of particular interest would be studies of the temperature-dependence of the partitioning between formation of formaldehyde and N_2O (scheme 31a) and the two forms of N-N cleavage (schemes 31b and 31c). Possibly this partitioning could be studied as a function of structure and the results extrapolated back to get the degree of partitioning for $H_2C{=}N{-}NO_2$, at various temperatures. It seems of considerable interest to study the thermal decomposition behavior of organic nitro- and nitrosoimines under conditions duplicating those of as many as possible of the existing (Section II of the present report) studies of HMX and RDX decomposition.

There are a number of other types of chemical studies which are of interest. For example in Reference 2 and in Section III of the present report, there was discussion of attack on nitro oxygens by free radical species formed in the decomposition. This seems like a reasonable reaction to suggest, on the basis of the References quoted in Reference 2 on the behavior of nitroaromatic and nitroaliphatic compounds; but the present writer is aware of no case in which a similar reaction of HMX involving a nitroamine has been reported or even knowingly attempted; studies of this type would be of considerable interest, especially for radicals (H_2CN, HCO, NO, NO_2, denitro HMX or RDX, etc.) that are known or suspected to be intermediates in HMX, RDX and nitramine decomposition.

Shaw and Walker[87] mentioned a number of unanswered questions in HMX decomposition; answers to some of these could be least suggested on the basis of the discussion in section III of the present report, but others remain obscure, for example the one about the relative strengths of the N-NO and the $N{-}NO_2$ bonds. With regard to others, more than one answer can be suggested; for example the radical left when NO_2 is removed from HMX might reasonably be expected to (a) undergo β-cleavage of a C-N bond (as illustrated in scheme 15 for RDX); or to (b) undergo β-cleavage or abstraction of a hydrogen atom to give the corresponding imine; or to (c) undergo rearrangement of a hydrogen atom from carbon to nitrogen (as illustrated in Scheme 26). Possibly further thermochemical estimates or other theoretical studies would be helpful in elucidating these points.

In a very recent (as these closing paragraphs of the present report are being written) review,[5b] Dubovitskii and Korsunskii have listed a number of unsolved problems and future-work needs in nitramine decomposition.

Possibly the most interesting experiment, however, would be isotope labeling experiments; a number of types of such experiments have been discussed in our previous writeups.[3c,110] The most interesting of these involve labeling of the nitrogen atom. This could be done in two possible ways; these complement each other and both are needed for complete understanding of the decomposition under any set of conditions. These are: (a) labeling a single nitrogen[54-56] in all molecules in the sample, as was done for the studies described in References 54 and 55; and (b) carrying out the decomposition on a mixture[56] of unlabeled and fully (all nitrogen, both nitro and amine) labeled HMX or RDX (as in Reference 56). Type (a) studies provide a check for the integrity of the N-N bond in the later stages of the decomposition, while type (b) studies provide a check for the effects of an N-NO_2 cleavage equilibrium (e.g., Scheme 9). When carrying out type (b) studies, type (a) studies should be done under the same conditions, so as to be sure that any scrambling occurs in the decomposition itself, and not as a result of later reaction between products or during analysis. The degree of scrambling of as many products (nitrosoamines, N-nitro and N-nitrosoformimine, N_2O, N_2, etc.) as possible should be evaluated, since at present it is difficult to evaluate the importance of equilibria such as those in Schemes (5) and (9).

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REFERENCES

1. K.P. McCarty, "HMX Propellant Combustion Studies," AFRPL-TR-76-59 (AD-B017 527L).

2. M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Results: Some Comments on Chemical Mechanisms," Proceedings of 16th JANNAF Combustion Meeting, CPIA Publication No. 308, Volume II, P. 17, September 1979.

3a. M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Results: Activation Energies and Frequency Factors," BRL Report being typed.

3b. A short summary of this work is given in the Proceedings of 17th JANNAF Combustion Meeting, CPIA Publication No. 329, Vol. II, p. 493, September 1980.

3c. A short summary of the material covered in the present report is given in the Proceedings of 18th JANNAF Combustion Meeting, CPIA Publication No. 347, Volume II, p. 395, October 1981.

4. F.C. Rauch and R.B. Wainwright, "Studies of Composition B," Final Report, Contract No. DAAA21-68-C-0334, American Cyanamid Company, AD-850 928, February 1969.

5. (a) K.K. Andreyev, "Thermal Decomposition and Combustion of Explosives," FTD-HT-23-1329-68, AD-693 600, pp. 87-92 and 129-30.
(b) F.I. Dubovitskii and B.L. Korsundkii, "Kinetics of the Thermal Decomposition of N-Nitro Compounds," Russian Chemical Reviews, Vol. 50, p. 1828, 1981.

6. M. BenReuven and L.H. Caveny, "Nitramine Monopropellant Deflagration and General Nonsteady Reacting Rocket Chambers," Princeton University Department of Mechanical and Aerospace Engineering, MAE Report No. 1455, Chapter II, January 1980.

7. A.J.B. Robertson, "The Thermal Decomposition of Explosives. Part II. Cyclotrimethlenetrinitramine and Cyclotetramethylenetetranitramine," Trans. Faraday Soc., Vol. 45, p. 85, 1949.

8. A.J.B. Robertson, "The Thermal Decomposition of Explosives. Part I. Ethylenedinitramine and Tetryl," Trans. Faraday Soc., Vol. 44, p. 677, 1948.

9. G.K. Adams, "The Thermal Decomposition of RDX," S.A.C. 5766, Feb 44.

10. G.K. Adams and L.A. Wiseman, "The Thermal Decomposition of PETN Alone and in the Presence of Metallic Oxides," S.A.C. 4258, Jun 43.

11. P.R. Rowland and L.A. Wiseman, "A Study of Possible Catalysts for the Thermal Decomposition of Ammonium Nitrate," S.A.C. 4257, Jun 43.

12. Bristol Research Report No. 6 (A.C. 242). No further information available; we were unable to obtain a copy of this document.

13. G.K. Adams and L.A. Wiseman, "The Thermal Decomposistion of HMX in the Solid State (U)," S.A.C. No. 5149, Nov 1943, Secret, AD-057 605.

14. C.E.H. Bawn, J.K. Hays, and F.H. Pollard, "The Thermal Decomposition of Tetryl and RDX," S.A.C. No. 2025, 25 Apr 42.

15. R.C. Weast, ed., "Handbook of Chemistry and Physics," 49th Edition, The Chemical Rubber Company, Cleveland, OH 44128, No. 1086-9, p. B-224.

16. F.C. Rauch and A.J. Fanelli, "The Thermal Decompostion Kinetics of Hexahydro-1,3,5-Trinitro-s-Triazine Above the Melting Point: Evidence for Both a Gas and Liquid Phase Decomposition," *J. Phys. Chem.*, Vol. 73, p. 1604-8, 1969.

17. F.C. Rauch and R.B. Wainwright, "Studies on Composition B," Final Report, Contract No. DAAA21-68-C-0334, American Cyanamid Company, AD-850 928, Feb 69.

18. F.C. Rauch and W.P. Colman, "Studies on Composition B," Final Report, Contract No. DAAA21-70-0334, American Cyanamid Company, AD-869 226, Mar 70.

19. W.P. Colman and F.C. Rauch, "Studies on Composition B," Final Report, Contract No. DAAA21-70-0531, American Cyanamid Company, AD-881 190, Feb 71.

20. J.D. Cosgrove and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX)," *Chemical Communications*, p. 286, 1968.

21. J.D. Cosgrove and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro 1,3,5-Triazine (RDX). Part I: The Products and Physical Parameters," *Combustion and Flame*, Vol. 22, p. 13, 1974.

22. J.D. Cosgrove and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX). Part II. The Effects of the Products," *Combustion and Flame*, Vol. 22, p. 19, 1974.

23. J.J. Batten and D.C. Murdie, "The Thermal Decomposition of RDX at Temperatures Below the Melting Point. I. Comments on the Mechanism," *Aust. J. Chem.*, Vol. 23, p. 737, 1970.

24. J.J. Batten and D.C. Murdie, "The Thermal Decomposition of RDX at Temperatures Below the Melting Point. II. Activation Energy," *Aust. J. Chem.*, Vol. 23, p. 749, 1970.

25. J.J. Batten, "The Thermal Decomposition of RDX at Temperatures Below the Melting Point. III. Towards the Elucidation of the Mechanism," *Aust. J. Chem.*, Vol. 24, p. 945, 1971.

26. J.J. Batten, "The Thermal Decomposition of RDX at Temperatures Below the Melting Point. IV. Catalysis of the Decomposition by Formaldehyde," Aust. J. Chem., Vol. 24, p. 2025, 1971.

27. B.B. Goshgarian, "The Thermal Decomposition of Cyclotrimethylenetrinitramine (RDX) and Cyclotetramethylenetetranitramine (HMX)," AFRPL-TR-78-76, AD-B032 275L, October 1978.

28. D.F. Debenham and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX) in 1,3,5-Trinitrobenzene," Proceedings of Symposium on Chemical Problems Connected with Stability of Explosives, No. 4, p. 201, 1977.

29. B. Suryanarayana and R.J. Graybush, "Thermal Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane (HMX): A Mass Spectrometric Study of the Products from β-HMX," Proceedings of 39th Congress on Ind. Chem., Gr. X-S.24-591, 1966.

30. A.E. Fogel'zang, B.S. Svetlov, V. Ya. Adzhemyan, S.M. Kolyasov, O.A. Sergienko, and S.M. Petrov, "Combustion of Explosive Compounds with Nitrogen-Nitrogen Bonds", Fizika Goremya I. Vzryvava, Vol. 12, No.6, p. 827, 1974. English translation, page 732.

31. Yu. Ya. Maksimov, "Thermal Decompositions of Hexogen and Octogen," Tr. Mosk. Khim-Tekhnol., Inst. No. 53, pp. 73-84, 1967 (Chem. Abstracts., Vol. 68, p. 4174r). A translation is available: LA-TR-68-30, Los Alamos Scientific Laboratory, July 1968, translated by Helen J. Dahlby.

32. K.K. Andreyev, "Thermal Decomposition and Combustion of Explosives," FTD-HT-23-1329-68, pp. 87-92 and 129, AD-693 600, 14 July 1969. References are given in a second volume, FTD-MT-24-147-70.

33. A.E. Axworthy, J.E. Flanagan, and D.O. Woolery, "High Temperature Pyrolysis Studies of HMX, RDX, and TAGN," Proceedings of 15th JANNAF Combustion Meeting, Vol. I, p. 253, September 1978.

34a. A.E. Axworthy, J.E. Flanagan, D.O. Woolery, and J.C. Gray, "Kinetic-Combustion Interactions of Nitramines," Proceedings of 16th JANNAF Combustion Meeting, Vol. III, p. 289, December 1978, CPIA Publication No. 308.

34b. A.E. Axworthy, J.E. Flanagan, and J.C. Gray, "Interaction of Reaction Kinetics and Nitramine Combustion," AFATL-TR-80-58, AD-B052 861L, May 1980.

35. A.A. Juhasz and J.J. Rocchio, "Determination of the Gasification Products from Developmental Propellants Which Are Self-Extinguishing at Atmospheric Pressure," Proceedings of 10th JANNAF Combustion Meeting, p. 341, August 1973.

36. A.A. Juhasz and J.J. Rocchio, "Pyrolytic Fragmentation Studies," in "Army Materiel Command Program, The Fundamentals of Ignition and Combustion. Volume II: Combustion," I.W. May and A.W. Barrows, eds., BRL Report 1708, p. 179, April 1974. (AD-919 316L)

37. J.J. Rocchio, "The Effect of Heating Rate on the Thermal Decomposition of Propellants," in "Army Materiel Command Program, The Fundamentals of Ignition and Combustion. Volume I: Ignition," I.W. May and A.W. Barrows, eds., BRL Report 1707, p. 327, April 1974. (AD-919 315L)

38. J.J. Rocchio and A.A. Juhasz, "HMX Thermal Decomposition Chemistry and Its Relation to HMX-Composite Propellant Combustion," Proceedings of 11th JANNAF Combustion Meeting, p. 247, September 1974.

39. A.A. Juhasz, "Nitramine Pyrolysis Mechanisms," in "1975 Annual Review of the ARMCOM Program, The Fundamentals of Ignition and Combustion," E. Freedman and K.J. White, eds., BRL Report 1883, AD-B011 644L, May 1976.

40. J.J. Rocchio and R.A. Wires, "The Effect of Heating Rate on the Thermal Decomposition of Propellant Ingredients," in "1975 Annual Review of the ARMCOM Program, The Fundamentals of Ignition and Combustion," E. Freedman and K.J. White, eds., BRL Report 1883, AD-B011 644L, May 1976.

41. J.P. Pfau, J.J. Rocchio, and R.A. Wires, "New Aspects of HMX Thermal Decomposition as Studied by Pyrolysis/Mass Spectroscopy," Proceedings of 15th JANNAF Combustion Meeting, p. 267, September 1978.

42. B.B. Goshgarian, "The Thermal Decomposition of Cyclotrimethylenetrinitramine (RDX) and Cyclotetramethylenetetranitramine (HMX)," AFRPL-TR-78-76, AD-B032 275L, October 1978.

43. W.W. Wendlandt, "Thermal Methods of Analysis," 2nd ed., John Wiley & Sons, New York, NY, p. 187, 1974.

44. J.H. Sharp, Differential Thermal Analysis, R.C. Mackenzie, ed., Academic Press, Vol. 2. Chapter 28. See especially page 55.

45. R.N. Rogers and L.C. Smith, "Application of Scanning Calorimetry to the Study of Chemical Kinetics," Thermochimica Acta, Vol. 1, No. 1, 1970.

46. R.A. Beyer, "Molecular Beam Sampling Mass Spectroscopy of Fast Thermal Decomposition of HMX, Polyurethane and Nitrocellulose," Abstract of paper for presentation at the Fall Technical Meeting of the Eastern Section, The Combustion Institute, 10-11 November 1977.

47. R.A. Beyer, "Molecular Beam Sampling Mass Spectrometry of High Heating Rate Pyrolysis: Description of Data Acquisition System and Pyrolysis of HMX in a Polyurethane Binder," ARBRL-MR-02816, AD-A054 328, March 1978.

48. C.U. Morgan and R.A. Beyer, "ESR and IR Spectroscopic Studies of HMX and RDX Thermal Decomposition," Proceedings of 15th JANNAF Combustion Meeting, pp. 359-366, September 1978.

49. R.A. Beyer, Ballistic Research Laboratory, private communication, 1980.

50. D.A. Flanigan and B.B. Stokes, "HMX Deflagration and Flame Characterization. Volume I: Phase II Nitramine Decomposition and Deflagration Characterization," Thiokol/Huntsville, AFRPL-TR-79-94, AD-B053 058L, October 1980.

51. C.U. Morgan and R.A. Beyer, "Electron-Spin Resonance Studies of HMX Pyrolysis Products," Combustion and Flame, Vol. 36, p. 99, 1979.

52. R.A. Beyer and C.U. Morgan, "ESR Studies of HMX Pyrolysis Products," ARBRL-MR-02921, May 1979.

53. R.A. Beyer and C.U. Morgan, "Electron Spin Resonance Studies of HMX and RDX Thermal Decomposition," Proceedings of 16th JANNAF Combustion Meeting, CPIA Publication No. 308, Vol. II, p. 51, December 1979.

54. B. Suryanarayana, R.J. Graybush, and J.R. Autera, "Thermal Degradation of Secondary Nitramines: A Nitrogen-15 Tracer Study of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetracyclooctane)," Chem. Ind., London, p. 2177, 1967.

55. B. Suryanarayana, J.R. Autera, and R.J. Graybush, "Mechanism of Thermal Decomposition of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane)," DDC, AD-837 173, 9 August 1968.

56. R.J. Powers, AFATL, Eglin AFB, private communication, June 1980.

57. S. Bulusu and T. Axenrod, "Electron Impact Fragmentation Mechanisms of 2,4,6-Trinitrotoluene Derived from Metastable Transitions and Isotope Labeling," Organic Mass Spectrometry, Vol. 14, p. 585, 1979.

58. B.H. Rockney and E.R. Grant, "Resonant Multiphoton Ionization Detection of the NO_2 Fragment from Infrared Multiphoton Dissociation of CH_3NO_2," Chem. Phys. Lett., Vol. 79, p. 15, 1981.

59. R.C. Dougherty, "The Relationship Between Mass Spectrometric, Thermolytic, and Photolytic Reactivity," Topics in Current Chemistry (Fortschritte der Chemischen Forschung), Vol. 45, p. 93, 1974.

60. R.R. Miller, A.F. Grigor, R.C. Musso, and R.A. Yount, "Combustion Mechanism of Low Burning Rate Propellant," Hercules Incorporated, AFRPL-TR-69-130, AD-502 957, May 1969.

61. R.R. Bernecker and L.C. Smith, "On the Products Formed in the Combustion of Explosives. Freeze-Out of the Water-Gas Reaction," J. Phys. Chem., Vol. 71, p. 2381, 1967.

62. S. Bulusu, "Electron-Impact Fragmentation of Some Secondary Aliphatic Nitramines. Migration of the Nitro Group in Heterocyclic Nitramines," Organic Mass Spectrometry, Vol. 3, p. 13, 1970.

63. J. Stals, "Chemistry of Aliphatic Unconjugated Nitramines. Part 7. Interrelations Between the Thermal, Photochemical, and Mass Spectral Fragmentation of RDX," Trans. Faraday Soc., Vol. 67, p. 1768, 1971.

64. M. Farber and R.D. Srivastava, "Mass Spectrometric Investigation of the Thermal Decomposition of RDX," Chem. Phys. Lett., Vol. 64, p. 307, 1979.

65. M. Farber, "A Mass Spectrometric Investigation of the Decomposition Products of Advanced Propellants and Explosives," Space Sciences, Inc., Annual Summary Report on Contract N00014-75-C-0986, AD-A074 963, August 1979.

66. M. Farber and R.D. Srivastava, "Thermal Decomposition of HMX," Proceedings of 16th JANNAF Combustion Meeting, p. 59, September 1979.

67. M. Farber and R.D. Srivastava, "A Mass Spectrometric Investigation of the Chemistry of Advanced Composite and Double Base Propellants," Proceedings of 15th JANNAF Combustion Meeting, September 1978.

68. J.N. Bradley, A.K. Butler, W.D. Capey, and J.R. Gilbert, "Mass Spectrometric Study of the Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX)," J. Chem. Soc., Faraday Trans. Pt. 1, Vol. 73, p. 1789, 1977.

69. R.R. Miller, A.F. Grigor, R.C. Musso and R.A. Yount, "Combustion Mechanism of Low Burning Rate Propellant," Hercules Inc., AFRPL-TR-69-130, AD-502 957, May 1969.

70. K.P. McCarty, "HMX Propellant Combustion Studies. Phase II. Ballistic Modeling and Phase III. Nitramine Propellant Combustion Investigation," AFRPL-TR-78-73, AD-B034 774, November 1978.

71. D.F. Debenham and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX) in 1,3,5-Trinitrobenzene," Proceedings of Symposium on Chemical Problems Connected Stability Explosives, Vol. 4, p. 201, 1977.

72. J. Kimura and N. Kubota, "Thermal Decomposition Process of HMX," Propellants and Explosives, Vol. 5, p. 1, 1980.

73. J.C. Dechaux, "Nitration of Alkanes in the Gas Phase," Oxidation and Combustion Reviews, Vol. 6, 1973.

74. B.L. Korsunskii and F.I. Dubovitskii, "Thermal Decomposition Kinetics of N,N-Dimethylnitroamine," Dokl. Akad. Nauk. SSSR, Vol. 115, p. 266, 1964.

75. B.L. Korsunskii, F.I. Dubovitskii, and E.A. Shurygin, "Kinetics of the Thermal Decomposition of N,N-Diethylnitroamine and N-Nitropiperidine," Izv. Akad. Nauk. SSSR, Ser. Khim., p. 1452, 1967.

76. J. Burdon and A. Ramirez, "Reaction of Gem-Nitronitroso Compounds with Triethyl Phosphite," Tetrahedron, Vol. 29, p. 4195, 1973.

77. J. Jappy and P.N. Preston, "Reaction of Group IV Organometallic Ketimines with Nitrosyl Chloride. Comment on the Thermolysis of the Product N-Nitrosoketimines," Tetrahedron Letters, p. 1157, 1970.

78. K. Akiba and N. Inamoto, "Chemistry of N-Nitrosoimines," Heterocycles, Vol. 7, p. 1131, 1977.

79. C.L. Coon, Lawrence Livermore Laboratories, private communication, 1980.

80. G. Buchi and H. Wuest, "Transformation of Nitramines to Acetylenes and Allenes. 1,3 Rearrangement of N-Nitroenamines to C-Nitro Compounds," J. Org. Chem., Vol. 41, p. 4116, 1979.

81. B.G. Gowenlock and K.E. Thomas, "The Gaseous Equilibrium of 1,3,5-Trimetrylhexahydo-1,3,5-Triazine and N-Methylenemethylamine," J. Chem. Soc., Vol. B, p. 409, 1966.

82. J. Wilby, "The Thermal Decomposition of RDX/TNT Mixtures. Part 2," RARDE Report (X)7/63, June 1963.

83. J. Wilby, "Thermal Decomposition of RDX/TNT Mixtures. Part 1," A.R.D.E. Report (MX)16/59, AD-225 991, August 1959.

84. J. Wilby, "Thermal Stability of RDX and HMX Compositions, Particularly Their Mixtures with TNT," Proceedings of Symposium on Chemical Problems Connected Stability of Explosives, p.51-65, 1968.

85. D. Barton, "Deuterium Isotope Effects in the Gas Phase Oxidation of Formaldehyde by Nitrogen Dioxide," J. Phys. Chem., Vol. 65, p. 1831, 1961.

86. D.F. McMillen, J.R. Barker, K.E. Lewis, P.L. Trevor, and D.M. Golden, "Mechanisms of Nitramine Decomposition: Very Low-Pressure Pyrolysis of HMX and Dimethylnitramine," Final Report on SRI Project PYU 5787, June 1979. (AD-A039 019)

87. R. Shaw and F.E. Walker, "Estimated Kinetics and Thermochemistry of Some Initial Unimolecular Reactions in the Thermal Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetraazacycloctane in the Gas Phase, J. Phys. Chem., Vol. 81, p. 2572, 1977.

88. M.T. Reetz, "Anchimerically Accelerated Bond Homolyses," Angew. Chem. Int. Ed. Engl., Vol. 18, p. 173, 1979.

89. S.W. Benson, Thermochemical Kinetics, John Wiley & Sons, Chapter IV, 1976.

90. S.W. Benson, Thermochemical Kinetics, John Wiley & Sons, p. 3, 1976.

91. E.H. White and D.J. Woodcock, "The Chemistry of the Amino Group," S. Pataz, ed., Interscience, Chapter 8, 1968.

92. J.M. Fluornoy, "Thermal Decomposition of Gaseous Dimethylnitramine", J. Chem. Phys., Vol. 36, p. 1106, 1962.

93. E.W. Kaiser and C.H. Wu, "A Kinetic Study of the Gas Phase Formation and Decomposition Reactions of Nitrous Acid," J. Phys. Chem., Vol. 81, p. 1701, 1977.

94. S.W. Benson, Thermochemical Kinetics, John Wiley & Sons, Eq. (4.17), p. 163, 1976.

95. P.J. Robinson and K.A. Holbrook, "Unimolecular Reactions," Wiley-Interscience, 1972.

96. R.A. Fifer, "Cage Effects in the Thermal Decomposition of Nitramines and other Energetic Materials," Proceedings, 19th JANNAF Combustion Meeting, Greenbelt, Maryland; October 1982, Vol. I, CPIA Publication 366, p. 311-319.

97. W.A. Pryor, Free Radicals, McGraw-Hill, New York, 1966. See for example Tables 12-3 and 12-6 and accompanying discussion.

98. J.C. Martin, "Solvation and Association", Free Radicals, Vol. II, Chapter 20, 1973.

99. B.G. Gowenlock and K.E. Thomas, "The Gaseous Equilibrium of 1,3,5-Trimethylhexahydro-1,3,5-Triazine and N-Methylenemethylamine," J. Chem. Soc. B., p. 409, 1966.

100. W.K. Busfield and D. Merigold, "Gas-Phase Equilibrium Between Trioxane and Formaldehyde: The Standard Enthalpy and Entropy of the Trimerization of Formaldehyde," J. Chem. Soc. A., p. 2975, 1969.

101. S.W. Benson and H.E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS 21, United States Department of Commerce, Washington, pp. 314-317, 1970. We thank Dr. D.F. McMillen for calling this Reference to our attention.

102. W. Hogg, "The Pyrolysis of 1,3,5-Trioxan," J. Chem. Soc., p. 1403, 1961.

103. R. le G. Burnett and R.P. Belt, "The Decomposition of Gaseous Trioxymethylene and Paraldehyde," Trans. Faraday Soc., Vol. 34, p. 420, 1938.

104. C.C. Coffin, "Studies on Homogeneous First Order Gas Reactions," Can. J. Res., Vol. 7, p. 75, 1932.

105. C.C. Coffin, "Studies on Homogeneous First Order Gas Reaction. IV. The Decomposition of Para-n-Butyraldehyde and Para-Isobutyraldehyde," Can. J. Res., Vol. 9, p. 603, 1933.

106. H.L. Pugh, L.P. Davis, J.S. Wilkes, W.R. Carper, and R.C. Dorey, "Thermal Decomposition of RDX Below the Melting Point," Proceedings of 7th Symposium on Detonation, Preprints, Vol. I, p. 45, June 1981.

107. S.W. Benson, Thermochemical Kinetics, John Wiley and Sons, NY, 1976.

108. R.C. Weast and M.C. Astle, CRC Handbook of Chemistry and Physics, 62nd Edition, Chemical Rubber Publishing Company, p. F-191, 1981.

109. L. Lunazzi, F. Placucci, and N. Ronchi, "Alkoxy Nitroxide Radicals from Photolysis of Nitropyridines: A Kinetic Investigation by Electron Spin Resonance Spectroscopy," J. Chem. Soc., Perkin Trans., Part II, p. 1132, 1977.

110. M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Some Suggestions for Needed Research Work," ARBRL-MR-03181, June 1982.

111. J. Simecek, "Decomposition of Nitrosoamines and Nitroamines in Protogenic Solvents. I. Decomposition of Cyclotrimethylenetri-Nitrosoamine by Concentrated Sulfuric Acid," Chem. Listy, Vol. 51, p. 1323, 1957. (Chem. Abstr., Vol. 51, 17942C)

112. C. Holstead and A.H. Lamberton, "Nitramines and Nitramides. III. The Formation of Nitric Acid by the Action of Sulfuric Acid," J. Chem. Soc., p. 1886, 1952.

113. J.C. Hoffsommer and J.C. Rosen, "Hydrolysis of Explosives in Sea Water," Bull. Environ. Contam. Toxicol, Vol. 10, p. 78, 1973.

114. J.C. Hoffsommer, J.C. Kubose, and D.J. Glover, "Kinetic Isotope Effects and Intermediate Formation in the Aqueous Alkaline Homogeneous Hydrolysis of 1,3,5-Triaza-1,3,5-Trinitrocyclohexane (RDX)," J. Phys. Chem., Vol. 81, p. 380, 1977.

115. C.E. Waring and G. Krastins, "The Kinetics and Mechanism of the Thermal Decomposition of Nitroglycerin," J. Phys. Chem., Vol. 74, p. 999, 1970.

116. N.G. Samoilenko, A.A. Vinokurov, V.G. Abramov, and A.G. Merzhanov, "Kinetics of the Thermal Decomposition of Dinitroxydiethylnitramine with No Removal of Gas from the Reaction Zone," Zh. Fix. Khim. (English translation), Vol. 44, p. 22, 1970.

117. E.R. Lee, R.H. Sanborn, and H.D. Stromberg, "Thermal Decomposition of High Explosives at Static Pressures 10 50 Kilobars," Proceedings of 5th Symposium (International) on Detonation, p. 331, 1970.

118. K. Kishore, "Thermal Decomposition Studies on Hexahydro-1,3,5-Trinitro-s-Triaxine (RDX) by Differential Scanning Calorimetry," Propellants and Explosives, Vol. 2, p. 78, 1977.

119. P.J. Miller, G.W. Nauflett, D.W. Carlson, and J.W. Brasch, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triaxine (RDX) and RDX at High Pressures," Proceedings of 17th JANNAF Combustion Meeting, CPIA Publication No. 329, p. 479, September 1980.

120. R.R. Bernecker and L.C. Smith, "On the Products Formed in the Combustion of Explosives. Freeze-Out of the Water-Gas Reaction," J. Phys. Chem., Vol. 71, p. 2381, 1967.

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