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CRITICAL ANALYSIS OF NITRAMINE
DECOMPOSITION DATA: PRELIMINARY
COMMENTS ON AUTOACCELERATION AND
AUTOINHIBITION IN HMX AND RDX
DECOMPOSITION

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Abstract (Cont'd):

residue that is formed in HMX and RDX decomposition; and (b) autocatalysis due to more volatile reaction products such as $\text{HOCH}_2\text{NHCOH}$, H_2CO and nitrogen oxides. There does seem to be evidence indicating the existence of homogeneous chemical autocatalysis by the decomposition residue. With regard to true chemical autocatalysis by more volatile reaction products, a number of pieces of information seem to suggest that such autocatalysis operates, but there are also a few confusing notes. Some possible chemical mechanisms that might be involved are presented and discussed, and it is pointed out that even if such reactions are unimportant under low-pressure conditions, they may become more important under the higher pressures characteristic of combustion and explosion. Suggestions for future work are made, with emphasis on studies allowing unambiguous interpretation in terms of true chemical effects, uncomplicated by physical factors such as liquefaction and thermal effects.

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TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION.....	5
II. RELEVANT EXPERIMENTAL RESULTS	7
A. Need to Distinguish Between Chemical and Physical Effects.....	7
B. Evidence Consistent with Autoacceleration of HMX and RDX Decomposition.....	8
C. Autocatalytic Effect of Decomposition Residue.....	10
D. Autocatalysis Due to Gaseous and Liquid Products.....	10
III. CHEMICAL MECHANISMS.....	12
A. Chemical Mechanisms: Autocatalysis and Autoinhibition by Gaseous Products.....	12
B. Chemical Mechanisms: Autocatalysis by the Nonvolatile Residue.....	16
IV. CONCLUSIONS.....	16
V. WORK NEEDED.....	18
VI. FINAL COMMENT ON RELATION OF THERMAL DECOMPOSITION STUDIES TO COMBUSTION AND EXPLOSIVE BEHAVIOR.....	19
ACKNOWLEDGEMENTS.....	21
REFERENCES.....	22
DISTRIBUTION LIST.....	26



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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 existing reviews,¹⁻⁵ most of which tend to emphasize 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 pressure < 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 report containing some suggestions for needed research work⁶ has appeared. Also, a brief discussion of some possible chemical mechanisms has already been

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

²M. Benreuen and L.H. Caveny, "Nitramine Monopropellant Deflagration and General Nonsteady Reacting Rocket Chambers," Chapter II, Princeton University Department of Mechanical and Aerospace Engineering, MAE Report No. 1455, January 1980, AD-A085 650.

³Ye. Yu. Orlova, N.A. Orlova, et al, "Octogen-Thermoresistant Explosive," Publishing House "Nedra," Moscow, 1975; FTD-ID(RS)T-0667-80, 2 May 1980, AD-B047 181.

⁴A.E. Axworthy, J.E. Flanagan, and J.C. Gray, "Interaction of Reaction Kinetics and Nitramine Combustion," AFATL-TR-80-58, May 1980, AD-B052-861L.

⁵F.I. Dubovitskii and B.L. Korsunskii, "Kinetics of the Thermal Decomposition of N-Nitro Compounds," Russian Chemical Reviews, Vol. 50, p. 958, 1981 (Russian Original, p. 1828).

⁶M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Some Suggestions for Needed Research Work," BRL Memorandum Report ARBRL-MR-3181, June 1982, AD-A116 194.

prepared⁷ as well as a report^{8,9} summarizing activation energies, frequency factors and other features of HMX and RDX decomposition kinetics. Product distributions have been presented in the same way.^{10,11} The author would greatly appreciate receiving any comments on any of these writeups that anyone may care to send.

The present phase is a continuation of this pattern of reviewing selected topics in nitramine, HMX and RDX decomposition chemistry; it consists of a preliminary discussion of the question of bimolecular followup reactions, autocatalytic, autoacceleratory and autoinhibitory behavior in the slow, low temperature thermal decomposition of HMX and RDX. This will be helpful in understanding deviations from first-order kinetics, and in understanding product distributions and chemical mechanisms, since the product distributions may be influenced by the bimolecular followup steps as well as the first order steps.

However, 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 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.

⁷M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Some Comments on Chemical Mechanisms," *Proceedings of 16th JANNAF Combustion Meeting, Vol. II, pp. 17-34, September 1979.*

⁸M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Activation Energies and Frequency Factors for HMX and RDX Decomposition," *Proceedings of 17th JANNAF Combustion Meeting, CPIA Publication 329, Vol. II, pp. 493-508, September 1980.*

⁹M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Activation Energies and Frequency Factors for HMX and RDX Decomposition," BRL Report being typed; this represents an attempt to include all data, while Reference 8 is just a brief review of some of the most important observations.

¹⁰M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Product Distributions for HMX and RDX Decomposition," BRL Report being typed; this represents an attempt to include all data, while Reference 11 is just a brief review of some of the most important observations.

¹¹M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Product Distributions from HMX and RDX Decomposition," *Proceedings of 18th JANNAF Combustion Meeting, CPIA Publication 347, Vol. II, pp. 395-413, October, 1981.*

II. RELEVANT EXPERIMENTAL RESULTS

In this section we attempt to summarize experimental evidence favoring or contradicting the operation of true homogeneous chemical autoacceleration or autoinhibition; some discussion is first given of the manner in which physical mechanisms can produce effects which may mimic those of true homogeneous chemical autoacceleration. It is concluded that the evidence is consistent with some degree of autoacceleratory behavior. In the following section (Section III), we discuss some possible chemical mechanisms which might be responsible for this apparent true chemical autocatalysis.

A. Need to Distinguish Between Chemical and Physical Effects

In discussing autocatalysis and related topics in HMX and RDX decomposition, some care is needed in distinguishing true chemical autoacceleratory behavior from physical effects, since otherwise confusion may result due to application of chemical interpretations to what are in fact physical phenomena.

One example of a rate acceleration due to mimicking of a chemical effect by a physical one is provided by self-heating behavior, in which the rate is accelerated by a temperature rise due to heat generated in the reaction.

Another example is provided by rate acceleration due to liquefaction, with faster decomposition of the liquid than the solid or gas phases. For example, Batten¹²⁻¹⁵ has explained the kinetic behavior (S-shaped curve) of RDX when it is decomposed below its melting point, in terms of initial (presumably solid-phase) decomposition followed by autocatalytic and

¹²J.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.

¹³J.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.

¹⁴J.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.

¹⁵J.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.

autoinhibitory steps; however, Cosgrove and Owen¹⁶⁻¹⁸ obtained results (decomposition rate increases with increasing container volume but is independent of sample size) which they explained in terms of initial vaporization followed by gas-phase decomposition and acceleration of the decomposition due to liquefaction resulting from condensation of nonvolatile products of the gas-phase decomposition onto the solid RDX.

The present writer^{8,9} tentatively accepts the latter interpretation, at least for RDX, although more work on this subject is clearly needed. In addition to the arguments of Cosgrove and Owen,¹⁷ this interpretation is consistent with Batten's¹² observation that "with 0.4 g RDX in a standard sample tube, the induction rate ($\% \text{ min}^{-1}$) is one-half that obtained with 0.2 g RDX in the sample tube." This corresponds to the same rate of decomposition for the two samples in grams per minute; this is consistent with the idea that RDX decomposes in the vapor phase after vaporizing off the top of the sample, the vaporization rate in grams per minute being the same for the two samples due to constant diameter of the sample tube (vaporization of the RDX at the bottom of the sample tube being suppressed by the RDX above it). For HMX the same interpretation also seems to hold to some extent, although there are indications that true solid-state decomposition may be more important.⁸⁻¹¹

One type of experiment that might shed further light on this would involve studies of the rate of decomposition in sample tubes of identical construction but with different sample sizes and in reaction vessels of differing volumes.

There are many similar instances in the literature in which apparent autocatalysis turns out on closer examination to be explainable in terms of physical effects. Care should be exercised, since otherwise chemical and physical effects may be confused. In the following discussion, an attempt has been made to consider only results which allow an unambiguous chemical interpretation.

3. Evidence Consistent with Autoacceleration of HMX and RDX Decomposition

At small m/V ratios, homogeneous gas- and liquid phase HMX and RDX decomposition generally seem to fit first order kinetics, but signs of

¹⁶J.D. Cosgrove and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX)," J. Chem. Soc., Chem. Commun., p. 286, 1968.

¹⁷J.D. Cosgrove and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine. Part I: The Products and Physical Parameters," Combustion and Flame, Vol. 22, p. 13, 1974.

¹⁸J.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.

autocatalytic behavior are sometimes observed.^{5,8,9,19,20} In particular, for decomposition of RDX in dicyclohexylphthalate below 250C,^{20a} autocatalysis was evident from an initial linear portion of the pressure-time curve; the effect became more noticeable at lower temperatures. After this initial portion, first order kinetics was followed. Possibly the initial linearity was the result of compensation between decrease in rate due to decrease in RDX concentration and increase in rate to a steady-state value due to increase in autocatalyst concentration, the final first-order rate including an autocatalytic component in addition to the primary first-order reaction. Decomposition of RDX in TNT followed a similar pattern.^{20a} Decomposition of HMX and of RDX in *m*-dinitrobenzene,^{20b} was examined^{20b} in some detail. Some initial acceleration was reported, followed by a decrease in rate according to the first-order law. The initial uncatalyzed rate constant appeared independent of concentration, confirming the first-order nature of the initial decomposition step. The degree of conversion at maximum rate was practically the same for both substances and increased with temperature, going from 16 percent at 171°C to 55 percent at 215°C. No dependence of acceleration on concentration between 0.5 and 15 percent was noted, although the final, first-order rate increased slightly with increasing concentration.^{20b} From studies on neat RDX and on RDX in solution in TNT^{8,9,20a} and in dicyclohexylphthalate,^{20a} it appears that there is some increase in first-order rate with increasing concentration. Maksimov^{20b} interpreted the then available results in terms of consecutive reactions, but the present writer tends to prefer something like Robertson's original explanation,^{20a} involving at least a slight chain or autocatalytic or other true homogeneous chemical autoacceleratory component to the decomposition; the only evidence which might argue against autocatalysis is the concentration-independence of the acceleration; but the present writer feels that this is outweighed by the concentration-dependence of the final first-order rate.

Note that one possible form of autoacceleration might involve short, fast chain reactions between products or intermediates and starting HMX or RDX; the effect of these reactions would be that each decomposing molecule of HMX and RDX would take a number of others with it. The final result might still be first order kinetics^{8,9}, but with a higher frequency factor. The observed frequency factors^{8,9} are in fact unexpectedly high ($\log A (\text{sec}^{-1}) = 18-20$) for a first order reaction; but other explanations cannot be ruled out until more is understood about such factors as cage effects, the nature of energy transfer in liquid HMX or RDX, etc. Note also the discussion below of Robertson's treatment^{20a} of chain reactions in RDX decomposition.

¹⁹K. Kishore, "Thermal Decomposition Studies on Hexahydro-1,3,5-Trinitro-s-Triazine (RDX) by Differential Scanning Calorimetry," Propellants and Explosives, Vol. 2, p. 78, 1977.

²⁰a A.J.B. Robertson, "The Thermal Decomposition of Explosives. Part II. Cyclotrimethylenetrinitramine and Cyclotrimethylene-tetranitramine," Trans. Faraday Soc., Vol. 45, p. 85, 1949.

b Yu. Ya. Maksimov, "Thermal Decomposition of Hexogen and Octogen," Tr. Mosk. Khim.-Tekhnol. Inst., Vol. 53, p. 73, 1967, translated by H.J. Dahlby, Los Alamos Report LA-TR-68-30, Los Alamos, New Mexico, 1968; See also Chem. Abstr., Vol. 68, p. 41742r.

C. Autocatalytic Effect of Decomposition Residue

Thermal decomposition of HMX and RDX above or below the melting point leaves a small amount (ca 3-5 percent) of nonvolatile residue.^{10,11} Prior heating of the sample or addition of residue to the decomposition sample leads to acceleration of rate;^{14,20a,21,22} this is apparently a true chemical effect rather than a physical effect due to lowered melting point, since (a) it was reported^{20a} that use of spent solvent from a decomposition of RDX in dicyclohexylphthalate gave a faster rate than when fresh solvent was used; and (b) decomposition of RDX¹⁴ or HMX²¹ over the decomposition residue from a previous experiment resulted in an accelerated (by a factor of about 3) rate even when comparison was limited to that portion of the reaction during which the sample was completely liquid,¹⁴ or in a lower decomposition temperature without lowering of melting point.²¹

D. Autocatalysis Due to Gaseous and Liquid Products

Added gaseous products and hydroxymethylformamide also have an effect on the rate of the decomposition,^{14,15,18,23,24,25} although in many cases it is difficult to interpret the data. Since the additives are often gaseous (e.g., H₂CO, NO₂, NO) and the systems under study heterogeneous systems of low m/V ratio, the reaction may well (see above) involve a complex combination of vaporization, vapor-phase decomposition, condensation of products, liquefaction and liquid (or solution in decomposition products) decomposition, as well as true solid-state decomposition, at least in the case of HMX. Furthermore, the reports are sometimes conflicting. For example, it is variously reported that added NO₂ accelerates^{20b} or decelerates^{14,25} the decomposition. Addition of O₂ has been reported to decelerate the

²¹B. Suryanarayana and R.J. Graybush, "Thermal Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetraazacyclooctane (HMX): A Mass Spectrometric Study of the Products from -HMX," Gr. X-S.24-591, Proceedings of 39th Congress on Ind. Chem., Brussels, Belgium, 1966.

²²B.B. Goshgarian, "The Thermal Decomposition of Cyclotrimethylene-trinitramine (RDX) and Cyclotetramethylenetetranitramine (HMX)," AFRPL-TR-78-76, October 1978, AD-B032 275L.

²³D.F. Debenham and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX) in 1,3,5-Trinitrobenzene," Symp. Chem. Probl. Connected Stab. Explos. (Proc.), Vol. 4, p. 201, 1977.

²⁴Yu. M. Burov and G. M. Nazin, "Influence of Structure on Rate of Decomposition of Secondary Nitramines in the Gas Phase," *Kinetica i Kataliz*, 23, 12 (1982), (English trans., p.5).

²⁵A. Cohen and L.J. Decker, "Shock Tube Propellant Reactions: Ignition of M-9 and Catalysis of RDX," Proceedings of 17th JANNAF Combustion Meeting, CPIA Publication 329, Vol. II, pp. 469-479, September 1990.

reaction;^{14,26,27} this was attributed^{26,27} to formation of NO₂ by reaction between NO and O₂, followed by reversal of a preliminary equilibrium involving N-NO₂ cleavage. Similarly, formaldehyde has been variously reported to raise^{14,15,18} and to lower²³ decomposition rate. Hydroxymethyl formamide, a known product,^{10,11,17,18,28} has been reported to accelerate the decomposition. It may be worth mentioning that ammonia and amines have been found to accelerate the decomposition.^{21,26,27} Some products such as N₂, N₂O, CO, CO₂, do not affect the decomposition except by retarding vaporization.^{14,18}

In connection with autocatalysis by added gaseous products, it seems worthwhile to mention some Russian work on thermal decomposition of some nitramines other than HMX and RDX, in the presence of H₂CO and of NO₂. It has been reported²⁹ that the decomposition of dimethylnitramine in the homogeneous gaseous phase is accelerated by added NO₂, although at low NO₂ concentrations in the early stages of decomposition, retardation might be expected due to reversal of the preliminary equilibrium involving N-NO₂ cleavage (see below, Scheme 3). Addition of formaldehyde³⁰ affects the decomposition of gaseous dimethylnitramine, causing the rate curve to become less S-shaped and more first-order. Above a certain limiting concentration of formaldehyde, the S-shape disappears altogether and the kinetics are apparently first-order to the end; further addition of formaldehyde has no effect on the course of the reaction. All of this behavior was interpreted in terms of autocatalysis by NO₂, and removal of NO₂ by reaction with formaldehyde. Similar results and conclusions were reported for diethylnitramine and for N-nitropiperidine. It does not seem unreasonable to suppose HMX and RDX might behave similarly. However, one should consider the possibility that some of the reactions

²⁶K.J. Kraeutle, "A Contribution to the Knowledge of HMX Decomposition and Application of Results," *Proceedings of 17th JANNAF Combustion Meeting, CPIA Publication 329, Vol. II, pp. 509-527, September 1980.*

²⁷K.J. Kraeutle, "The Thermal Decomposition of HMX: Effect of Experimental Conditions and of Additives," *Proceedings of 18th JANNAF Combustion Meeting, CPIA Publication 347, Vol. II, p. 383, October 1981.*

²⁸J. Kimura and N. Kubota, "Thermal Decomposition Process of HMX," *Propellants and Explosives, Vol. 5, p. 1, 1980.*

²⁹B.L. Korsunskii and F.I. Dubovitski, "Thermal Decomposition Kinetics of N,N-Dimethylnitroamine," *Dokl. Akad. Nauk. SSSR, Vol. 155, p. 402, 1964, (English trans., p. 266).*

³⁰B.L. Korsunskii, F.I. Dubovitskii, and G.V. Sitonina, "Kinetics of the Thermal Decomposition of N,N-Dimethylnitroamine in the Presence of Formaldehyde," *Dokl. Akad. Nauk. SSSR, Vol. 174, p. 1126, 1967, (English trans., p. 436).*

involved may take place not in the gas phase, but on the surface of the container. There seems to be some discrepancy here, since the Russians³¹ reported that the kinetics of diethylnitramine decomposition were not particularly affected when the reaction vessel was filled with glass packing (suggesting that wall effects are unimportant), while the group at SRI³² reported that the rate of dimethylnitramine decomposition was dependent on the nature of the container surface, although the surface-material dependence was much less for HMX decomposition (except when the surface was made of gold). These results would be much easier to interpret if the source of this discrepancy were understood. One possible explanation might involve differences in the pressures at which the experiments were carried out, since the SRI studies³² were carried out under VLPP conditions while the Russian studies²⁹⁻³¹ were carried out under moderate pressures (hundreds of mm) where wall reactions might be less important.

A further indication of the possible importance of autocatalysis from gaseous decomposition products is provided by the report²⁴ that addition of NO retards the gas-phase decomposition of RDX, N,N'-dinitropiperidine and 1,3-dinitro-1,3-diazacyclopentane ("pentogen"). This at first seems consistent with the idea that it may be acting as a terminator with respect to chain or other bimolecular followup steps; but note that the only compound whose frequency factor was lowered by addition of NO was N,N'-dinitropiperazine; the frequency factors for decomposition of pentogen and RDX were actually raised by addition of NO.

III. CHEMICAL MECHANISMS

A. Chemical Mechanisms: Autocatalysis and Autoinhibition by Gaseous Products

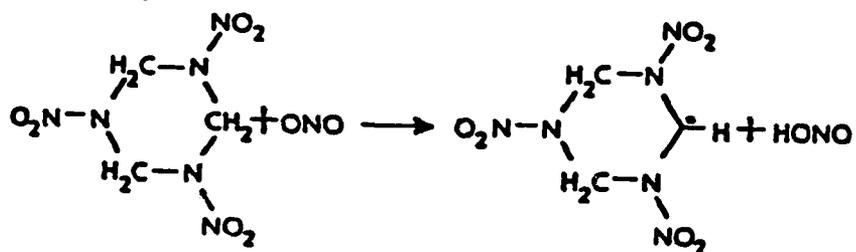
The interpretation of existing data on the effects of gaseous products (NO₂, formaldehyde, etc.) on the rates of HMX and RDX decomposition is complicated by the fact that much of the data (References 12-28) was obtained under conditions such that it is difficult to rule out the possibility that apparent acceleration or retardation of the rate may be due to physical rather than to chemical effects. For example, Batten¹⁴ reports that NO₂ and oxygen retard the decomposition of RDX, but also notes that these gases tended to eliminate residue formation and to prevent liquefaction of the sample. This raises the possibility that the observed rate retardation may have been due to a physical effect, since elimination of the liquid phase, which would decompose faster than the solid,^{8,9} would be expected to slow the

³¹B.L. Korsunskii, F.I. Dubovitskii, and E.A. Shurygin, "Kinetics of the Thermal Decomposition of N,N-Diethylnitroamine and N-Nitropiperidine," *Izvest. Akad. Nauk SSSR, Ser. Khim.*, p. 1452, 1967, (English trans., p. 1405).

³²D.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.*

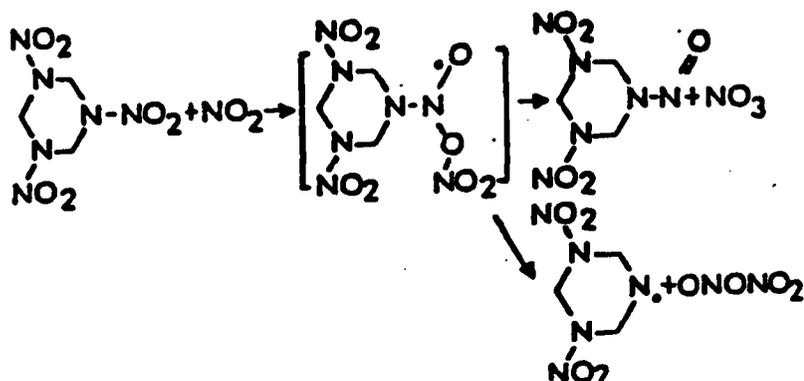
decomposition. Therefore, it should be remembered that the following discussion of possible chemical mechanisms applies more directly to homogeneous, single-phase decomposition of HMX, RDX and other nitramines, than to many of the studies carried out below the melting point^{12-18,20b,25-28} on heterogeneous systems which may involve physical complications of the types mentioned above.

Among the gaseous products, probably the most important potential catalysts are formaldehyde and nitrogen oxides, especially NO₂. NO₂ could accelerate decomposition by bimolecular reactions with unreacted starting material, such as



SCHEME 1

or by reaction with nitro oxygen, as in Scheme 2.



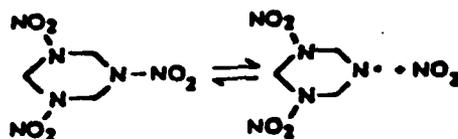
SCHEME 2

Kamlet³³ has discussed nitramine autocatalysis and suggested^{33a} that reaction of RDX with NO₂ to give N₂O₄ (in equilibrium with 2NO₂), as in Scheme 2, might be an important autocatalytic step, since it involves formation of two moles of NO₂ after starting with only one, in addition to initiating the decomposition of a molecule of starting material. This seems consistent with the observation³⁴ of an orange-brown color in decomposition of liquid HMX and RDX; when the concentration of orange-brown material in the melt exceeded a certain concentration, the authors apparently felt that very rapid catalytic decomposition of the melt occurred. Furthermore, these authors noted that thermocouple studies showed a temperature rise of about 30°C of the sample over the program temperature, although it is difficult to evaluate the role of self-heating effects here. Other possible mechanisms of interaction might involve reaction with the amine nitrogen as suggested by Dubovitskii and Korsunskii;⁵ they suggest attack by an oxygen atom of the NO₂, although an electron transfer mechanism, possibly involving the amino lone pair, might be another possibility.

The situation with regard to NO₂ is complicated by the possibility of retardation due to the equilibrium of Scheme 3. Nitric oxide (NO) could conceivably react by pathways analogous to many of the above.

^{33a} M.J. Kamlet, Research Brief, "Changes in Chemical Reaction Mechanisms with Increasing Pressure as Possible Causes of Deflagration to Detonation Transitions (DDT) in HMX-Based Propellants," July 1977. b M.J. Kamlet, "The Relationship of Impact Sensitivity with Structure of Organic High Explosives. I. Polynitroaliphatic Explosives," Proceedings 6th Symposium (Int.) on Detonation, August 1976, p. 312.

³⁴ D.A. Flanigan and B.B. Stokes, "HMX Deflagration and Flame Characterization. Volume I. Phase II. Nitramine Decomposition and Deflagration Characterization," AFRL-TR-79-94, Thiokol Corporation, October 1980, AD-B053 058L.



SCHEME 3

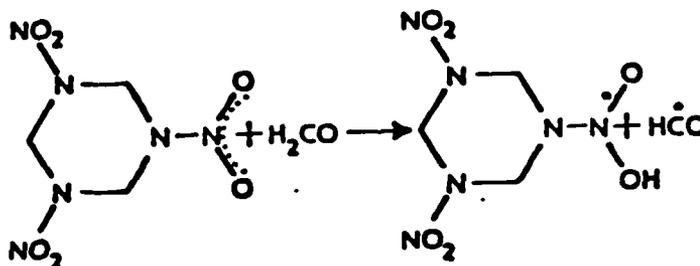
In view of the low (40 kcal/mole) dissociation energy given for the N-O bond in N_2O ,³⁵ it seems worth discussing the possibility of autocatalysis by the reaction of Scheme 4



SCHEME 4

followed by oxidation by O or by O_2 . When N_2 and N_2O yields and ratios are calculated from available data on changes in product distribution with reaction time, for the decomposition of liquid RDX at $212^\circ C$,³⁶ and for RDX below its melting point at $195^\circ C$,¹⁷ they show no striking evidence that this is very important. However, the scatter in the data is such that it is sometimes hard to be sure. Also, the data for the below-melting-point decomposition data show a slight drift especially at the beginning of the reaction, that might be explainable in terms of a decrease in the relative importance of gas- and increase in liquid-phase decompositions, as the reaction proceeds. Note also that N_2O apparently has little if any catalytic effect on the decomposition of RDX below its melting point.^{14,18}

Formaldehyde might possibly react with a nitro group of unreacted HMX or RDX, as shown below



SCHEME 5

³⁵R.C. Weast and M.J. Astle, Eds., "CRC Handbook of Chemistry and Physics," CRC Press, Inc., Boca Raton Florida, 62nd Edition, p. F-195, 1981-1982.

³⁶F.C. Rauch and R.B. Wainright, "Studies on Composition B," Final Report, Contract No., DAAA21-68-C-0334, American Cyanamid Company, February 1969, AD-850 928.

However, this might well prove to be too high-energy a process to be readily accessible. Another possibility might be simple reaction of radicals such as OH or HCO, possibly formed by reaction between formaldehyde and NO₂ formed in the decomposition, with starting materials, by pathways analogous to those discussed above for reaction of NO₂ with starting materials. Any radical intermediate formed in the decomposition could also conceivably react with unreacted starting material by a similar mechanism.

Another possibility might be hydrolytic reactions due to water^{10,11} formed in the reaction, or a combination of hydrolysis and oxidation reactions, as suggested in the case of di(nitroxyethyl)nitramine.³⁷

Note that even if any of these reactions individually, or autocatalysis generally, should be shown to be unimportant at low pressures, it should still be remembered that they are bimolecular reactions and hence would be expected to proceed more readily at higher pressures; thus they may become more important under the higher pressures typical of explosion and propellant combustion conditions.

B. Chemical Mechanisms: Autocatalysis by the Nonvolatile Residue

The chemical mechanisms involved in autocatalysis by the nonvolatile residue are obscure. Before they can be understood it will be necessary to know something of the nature of the residue. The present writer is now examining the literature for information on the residue that can be used to infer the nature of the residue; the subject will be reviewed more fully at a later date.

It has been reported¹⁴ that added NO₂ results in suppression of residue formation; consequently, it seems possible that, at least at relatively low NO₂ concentrations, residue autocatalysis may result* from removal of NO₂ by residue or precursor, thereby driving the equilibrium of Scheme 3 to the right. Note, however, that the systems are undoubtedly complex and it is possible to envisage mechanisms involving such processes as acceleration or retardation of chain reactions due to radicals formed in reaction between residue or its precursor and other products such as nitrogen oxides.

IV. CONCLUSIONS

The most convincing evidence for autocatalysis in HMX and RDX decomposition seems to involve the nonvolatile residue; the results from References 14, 20a and 21, summarized and discussed in section II C above would appear to indicate that this occurs and is an example of a true chemical effect, not just a physical effect. However, the detailed mechanisms remain obscure; a better understanding of the nature of the residue itself would help here.

³⁷B.S. Svetlov and B.A. Lur'e, "Thermal Decomposition of Di(nitroxyethyl) Nitramine," Russian Journal of Physical Chemistry, Vol. 37, p. 1073, 1963.

*The author thanks Sean Wise for this suggestion.

With regard to true chemical autocatalysis by gaseous products, a number of items suggest that it occurs. However, there is a need for more conclusive evidence for or against the acceleration or inhibition of decomposition of HMX and RDX themselves by gaseous products such as nitrogen oxides, formaldehyde, etc. It does appear^{14,15,18,20a,23,24,25} that these materials have effects on the rate of decomposition, but the results are often obtained from heterogenous, complicated systems, such that it is difficult to tell whether the effects correspond to true chemical autocatalysis or to physical effects related to residue formation, liquefaction, heat effects, etc.

Analogies consistent with occurrence of true chemical autocatalysis in HMX and RDX decomposition include the Russian work²⁹⁻³¹ on the effect of NO₂ and H₂CO on gas-phase decomposition of nitramines other than HMX and RDX; it was suggested that NO₂ acted as an autocatalyst but was removed by added formaldehyde, causing reversion to a first-order process. Although the checks performed on the effect of increasing surface area by filling the reaction vessel with glass packing suggest that wall reactions are not important, it would help to have more information on this point. Furthermore, before extrapolating these result to HMX and RDX it should be remembered that the additional nitro groups in HMX and RDX may exert a substituent effect on the reactivity of the reacting nitro group, possibly affecting the relative rates of the initial and followup steps in such a way as to affect the occurrence of autocatalysis. Nevertheless, it seems reasonable to suggest that the formaldehyde formed^{10,11,17,18,21,23} in HMX and RDX decomposition acts in the same manner as that added in the experiments of References 29-31, thereby reducing or eliminating autocatalytic behavior by the NO₂. This would be in agreement with the observation²³ that, in contrast to its behavior with pure RDX below the melting point,^{14,15,18} formaldehyde retards the decomposition of RDX in solution in TNB, with an increase in formation of 2,4,6,3',5'-pentanitrodiphenyl; possibly the pentanitrodiphenyl arises after attack on the nitro oxygens by free radicals formed, for example in the reaction between NO₂ and formaldehyde.

Also, there are reports of increased reaction rates when RDX was decomposed in a sealed instead of an open DSC pan,¹⁹ although the possibility of failure, in spite of precautions, to maintain absolutely isothermal conditions in the face of reactions of the products (such as NO₂ and H₂CO) with each other, should be carefully considered here. Also of interest are reports^{20b,26,27} that when HMX is decomposed below its melting point, liquefaction occurs faster for larger samples and particle sizes; although the possibility of self-heating or simple lowering of the melting point by decomposition products entrapped in the crystal should be considered here.

On the other hand, long-term, low temperature studies on stability of PBX-9404 (an explosive having the nominal composition 94% HMX, 3% nitrocellulose binder, 3% chloroethylphosphate plasticizer and 0.1% diphenylamine stabilizer) can be interpreted in a way indicating that decomposition of the nitrocellulose binder is responsible for the observed

changes.^{38,39} However, studies of the NO₂-reducing ability of pure HMX and pure RDX were not reported; these would probably be more applicable to the question of the role of NO₂ autoacceleration in HMX and RDX decomposition.

Furthermore, Robertson^{20a} presents a treatment of chain reactions which suggests the existence of short chains at least in RDX decomposition. However, the expected ^{5,20a} (ca 1.2-3.0) chain lengths seem very short, in fact possibly too short to allow for very much acceleration by molecular followup reactions, especially when it is remembered that the residue apparently accounts for a sizeable portion of the effect as discussed above.

It also seems worth mentioning that Kamlet³³ has discussed nitramine autocatalysis and has suggested that the greater impact sensitivity of nitramines relative to the corresponding nitroalkanes is due to acceleration of decomposition in the case of the nitramines due to autocatalysis. In the case of the nitroalkanes, where autocatalysis is not observed (references summarized in reference 33b), decomposition under the impact hammer is presumably slower and hence the compounds less sensitive.

V. WORK NEEDED

There is clearly a need for better understanding of the chemical interaction between unreacted HMX and RDX, and products of the decomposition. Many of the additive studies reported to date involve studies on HMX and RDX decomposition below their melting points, in systems that probably involve physical complexities due to presence of and simultaneous decomposition in vapor and condensed phases. There is therefore a need for more studies constructed in such a way as to be as specific as possible to the question of the effect of these products on the decomposition in homogeneous gaseous and liquid states; such studies would be much easier to interpret in terms of the operation or non-operation of true chemical autocatalysis. Possibly these studies could be carried out in a manner similar to the Russian studies on the effect of NO₂ and formaldehyde on gas-phase decomposition of nitramines other than HMX and RDX.^{5,29-31} Another possibility might be to study the effect of the added products on solution-phase decomposition, as was done for RDX decomposition in TNB by Debenham and Owen.²³

Another way of studying interactions of HMX and RDX with product gases might involve passing product gases over samples of pure HMX and RDX in an apparatus such as that used in the long-term, low-temperature studies on nitrocellulose and PBX-9404.³⁹ In particular, studies of the NO₂-reducing ability of pure HMX and RDX might lead to much-improved understanding of the role of NO₂ in bimolecular followup steps in HMX and RDX decomposition.

³⁸H.N. Volltrauer and A. Fontijn, "Low-Temperature Pyrolysis Studies by Chemiluminescence Techniques. Real-time Nitrocellulose and PBX 9404 Decomposition," *Combustion and Flame*, Vol. 41, p. 313, 1981.

³⁹H.R. Leider and D.L. Seaton, "Gas Evolution and Weight Loss from Thermal Decomposition of PBX-9404 Below 100°C," UCRL-52692, Lawrence Livermore Laboratory, March 1979.

Another way to evaluate the importance of bimolecular follow-up steps might involve carrying out studies aimed at comparing vapor and liquid-phase decomposition, especially with regard to product distribution.

In addition, many work-needed suggestions are included in earlier reports⁶⁻¹¹ on the present literature review; a number of these have obvious application to the questions of autocatalysis, autoinhibition and bimolecular follow-up reactions.

VI. 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 presentations.⁷⁻¹¹ 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.⁷ 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; for modeling purposes, possibly assumed 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 earlier⁷⁻¹¹ in the present review; these are the apparent temperature dependence of the relative rate of N-NO₂ cleavage and of HONO elimination in the gas-phase decomposition,³² and the possible tendency for cleavage of H₂C=NNO₂ to H₂CN and NO₂ to become more important relative to formation of N₂O and H₂CO, as temperature rises.^{7,8} Such changes in relative importance of various chemical mechanisms 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 step of the decomposition and unimolecular follow-up steps to become faster relative to bimolecular follow-up steps because of the higher activation energy characteristic of unimolecular 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 principal ones. Informed extension of this body of knowledge to storage, explosion and combustion conditions could then provide the basis for improved understanding of such topics as stability, sensitivity, and burning rate behavior.

Possibly the use of information and estimates on the nature and temperature-variation of the reactions involved, together with experimental data on solid-, liquid-, and vapor-phase temperatures under combustion conditions, would make it possible to obtain information as to the location of the primary heat release under combustion conditions. The approach would be to use measured temperatures in the gas, liquid, and solid phases under combustion conditions, together with information on the nature, temperature-variation, and thermochemistry of the reactions involved, to get an idea of how heat release varies with phase and location.

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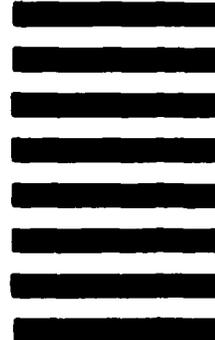
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