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MEMORANDUM REPORT ARBRL-MR-⁹3181

CRITICAL ANALYSIS OF NITRAMINE
DECOMPOSITION DATA: SOME SUGGESTIONS
FOR NEEDED RESEARCH WORK

Michael A. Schroeder

June 1982

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

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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 such as that of McCarty (AFRPL-TR-76-59 (AD-B017 527)), which emphasize combustion behavior from the point of view of a physical chemist or combustion engineer.

In the original proposal for the present literature review, it was stated that one of the principal objectives of the work would be to identify needed data and to suggest work needed to elucidate the physical and chemical mechanisms involved in decomposition of nitramines, HMX, RDX, and other nitramines. Other publications on this review have appeared or are still being prepared for publication¹⁻⁴; these describe summaries of possible chemical mechanisms, and of kinetic parameters and of product distributions for HMX and RDX decomposition. It also seemed appropriate to present a brief discussion of work that seems to be needed; such a discussion is presented in the present report. Note that it is not claimed that this is a definitive enumeration of everything that needs to be done; rather it is just a list of some things that impressed the present writer as being particularly necessary or at least worthwhile. Other people will probably look at the same information,¹⁻⁴ and think of other things that may seem more important than some of the things that are included here. Note also that no effort has been made to cite all possible references on the various subjects. Such an attempt has been made in references 3 and 4.

¹M. A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Some Comments on Chemical Mechanisms," *Proceedings, 16th JANNAF Combustion Meeting, Monterey, California, September 1979, Volume II*, pp. 17-34.

²M. A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Activation Energies and Frequency Factors for HMX and RDX Decomposition," *Proceedings of the 17th JANNAF Combustion Meeting, Hampton, Virginia, September 1980, Volume II*, pp. 493-508.

³M. 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 2 is just a brief summary of the most important references.

⁴M. A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Product Distributions from HMX and RDX decomposition," BRL Report being typed.

II. DISCUSSION

Some possible areas for future work will now be mentioned, and then discussed at varying degrees of length.

A. Work Needed: First Step of Nitramine Decomposition

The first step of the decomposition of nitramines, HMX and RDX is still not well understood. In addition to an improved understanding of the nature of the first step itself (for example, is it HONO elimination, N-NO₂ cleavage, C-N cleavage, or something else?) there is a need for a better understanding of the effect of temperature, pressure and state of aggregation (solid, liquid, vapor, as well as solvent effects). Time-resolved laser spectroscopic techniques may be helpful here (see for example reference 5) at least for the vapor-phase decomposition.

B. Work Needed: Studies on Gas-phase Decomposition of Nitramines, HMX and RDX

There is a great need for more work on the vapor-phase decomposition of nitramines, HMX and RDX, especially since the gas-phase decomposition would best reflect the intrinsic behavior of molecules themselves; behavior in the liquid and solid phases could then be regarded as variations on the vapor phase behavior, induced by the environment set up by neighboring molecules.

There seems to be little, if any, information on product distributions that can be unambiguously traced to gas-phase decomposition, although (see next section) it seems possible that decomposition below the melting point may be a gas phase process, at least in the early stages; if this is so, it is possible that the product distributions from the early stages of such studies might give some hint of what the true gas-phase product distributions might look like. There have been some reports^{6,7} in which it was suggested that the container-volume dependence of NO₂ formation indicated that NO₂ was a product of the gas-phase reaction; but it seems to the present writer as if there is at least a good possibility that at least some of the NO₂ may have originated in the liquid phase; the shapes of the yield-time curves may be a result of NO₂ formation in, and escape from, the liquid

⁵B.H. Rockney and E.R. Grant, "Resonant Multiphoton Ionization Detection of the NO₂ Fragment from Infrared Multiphoton Dissociation of CH₃NO₂," *Chem. Phys. Lett.*, 79, 15 (1981).

⁶F. 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, p. 1604 (1969).

⁷F. C. Rauch and R. B. Wainright, "Studies on Composition B," *Final Report*, Contract No. DAAA 21-68-C-0334, February, 1969 (AD-850 928).

phase, followed by reaction in the gas phase. The NO₂ capacity of the system might then still be determined mainly by the container volume, although the data are not actually inconsistent with the idea that the interpretation adopted by the authors of references 6 and 7 is operative to some extent. Note also that NO₂ could form in the gas-phase from HONO formed by cyclic elimination reaction (see below).

There are several kinetic studies (references summarized in references 2 and 3) on gas-phase HMX and RDX decomposition, but the data in these are mostly either crude data obtained by DSC, or show a great deal of scatter. Furthermore, there is a great need for a better understanding of the effect on the kinetics and parameters for nitramine decomposition of such factors as reaction on the surface of the container (references summarized in reference 3). The importance, to an understanding of the gas phase nitramine decomposition, of an improved understanding of the role of such factors as wall reactions on the container surface cannot be overemphasized, since it has been reported⁸ that the decomposition kinetics of dimethylnitramine were dependent on the nature of the container surface. This effect may³ be less important for HMX and RDX, but in view of the report⁸ of wall-material dependence of decomposition rate for dimethylnitramine, further work is clearly needed.

The effect of chain reactions and other kinetic complexities should also be examined carefully. Some notion of what can be involved in being sure of one's ground when dealing with gas phase reactions can be gained

⁸ 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.

by reading references 9-12 and further references cited therein.

The above comments on the need for further work on sources of experimental error in gas-phase reaction studies also apply to other studies under conditions where gas-phase decomposition may be important, including many if not most studies of decomposition of HMX and RDX at temperatures below their respective melting points, and studies of the effect on decomposition of nitramines other than HMX and RDX of substances such as NO_2 and H_2CO (references summarized in reference 3), as well as the work summarized in references 6 and 7. It might be a good idea for future workers in these areas to examine the effect of increased surface area due to added glass wool, beads, etc., and if practicable the effect of varying the nature of the container surface.

In addition to techniques such as those described in references 5 and 8, laser-powered homogeneous pyrolysis¹³ might well be capable of providing information on this point. Note that care should be taken to work under conditions such that the results are not influenced by wall reactions.

C. Work Needed: Improved Understanding of the Nature and Occurrence of True Solid-State Decomposition of HMX and RDX

There is a need for improved understanding of the solid-phase decomposition of HMX and RDX. This can be seen by comparing discussions of Cosgrove and Owen (decomposition rate of RDX below its melting point found to be independent of sample weight, but to increase with increasing

⁹R. J. Robinson and M. A. Holbrook, "Unimolecular Reactions," Wiley-Interscience, New York, 1972.

¹⁰H. Davis, "Comments on the Paper 'Gas-Phase Pyrolysis of 2,2,3,3-Tetramethylbutane Using a Wall-less Reactor,'" *International Journal of Chemical Kinetics*, Vol. 11, p. 1131 (1979).

¹¹J. E. Taylor, *Ibid.*, "Reply to Comments on 'Gas-Phase Pyrolysis of 2,2,3,3-Tetramethylbutane Using a Wall-less Reactor,' by H. Davis," *Ibid.*, 1133, (1979).

¹²S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS 21, U. S. Department of Commerce, National Bureau of Standards, February 1970; for sale by the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402.

¹³K. E. Lewis, D. F. McMillen and D. M. Golden, "Laser-Powered Homogeneous Pyrolysis of Aromatic Nitro Compounds," *J. Phys. Chem.* Vol. 84, p. 226, (1980).

container volume),^{14,15} and of Batten¹⁶ (who interpreted his own results and those of Cosgrove and Owen in terms of effect of sample geometry on the interaction between gaseous decomposition products and undercomposed RDX in the gas phase). After reading the later¹⁵ discussion of Cosgrove and Owen, this writer tends to agree with them, but it seems as though further work is needed here also. In this connection, it also seems worth noting that Maksimov¹⁷ also reported a dependence of decomposition rate on volume for both HMX and RDX although the dependence was not as great for HMX as it was for RDX; one possible explanation for this might be that the solid phase decomposition is somewhat more important for HMX than for RDX. In any case, until the role of vapor and liquid-phase decomposition relative to true solid-phase decomposition is understood, it seems clear that the possibility should be considered that many studies of decomposition of "solid" HMX and RDX may actually have involved sublimation or vaporization followed by gas-phase decomposition. Thus, further work on the relative importance of gas, liquid and true solid-state decomposition is clearly needed, in order to extract the contribution due to true solid-state decomposition and, if possible, extend or extrapolate it meaningfully to combustion and explosion conditions.

One possible type of experiment that might help here 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 of sample size, configuration and reactor volume, each with the others held constant. This should be done for HMX as well as for RDX. In a possibly related approach (Belyayeva et al., (FTD-ID(RS)T-1209-8)) (AD-B033 572L), 0.2 gram samples of HMX and RDX were decomposed in containers of varying volumes and the rate of thermal decomposition was broken down into components due to gaseous and condensed phase decomposition; the gas phase reaction was reported to proceed faster than the condensed phase decomposition by a factor of 10^4 ; however sample configuration was not described.

¹⁴J. 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 (1965).

¹⁵J. 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, 13 (1974).

¹⁶J. 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).

¹⁷Yu. Ya. Maksimov, "Thermal Decomposition of Hexogen and Octogen," *Tr. Mosk. Khim.-Tekhnol. Inst.*, No. 53, 73 (1967), translated by H. J. Dahlby, Los Alamos Report LA-TR-68-36, Los Alamos, New Mexico, 1968.

In carrying out these and any other experiments under conditions possibly including gas-phase decomposition, attention should be paid to the possible effect of factors such as wall reactions and kinetic complexities of the types discussed in the preceding sections.

Only with a clear understanding of the relative roles of gas, solid and liquid-phase decomposition will it be possible to understand the decomposition of HMX and RDX at temperatures below their melting points, let alone under the much more severe conditions of temperature and pressure characteristic of combustion and explosion.

D. Work Needed: Temperature and Pressure Effects

There is also a need for improved understanding of the effect of temperature and pressure on the decomposition of HMX and RDX. In extending low-temperature, low-pressure results to combustion conditions, it should be remembered that the Arrhenius parameters, which are usually used to carry out these extensions, may themselves depend on temperature and pressure; improved understanding of these variations would enhance the reliability of the extension.

E. Work Needed: Autocatalysis

There is a need for improved understanding of the nature and occurrence of autocatalysis and autoinhibition in the thermal decomposition of HMX and RDX. This is especially true in view of apparent discrepancies between literature statements concerning acceleration or inhibition of HMX and RDX decomposition by known products such as formaldehyde and oxides of nitrogen.¹⁷⁻²⁰ (See also the discussion in reference 3, and references cited therein.) In studies of catalysis or inhibition by gas-phase products, the studies should be carried out in such a way as to exclude or at least understand the role of reactions on the container surface; and an understanding of the role of surface reactions in many of the existing studies would also be helpful.

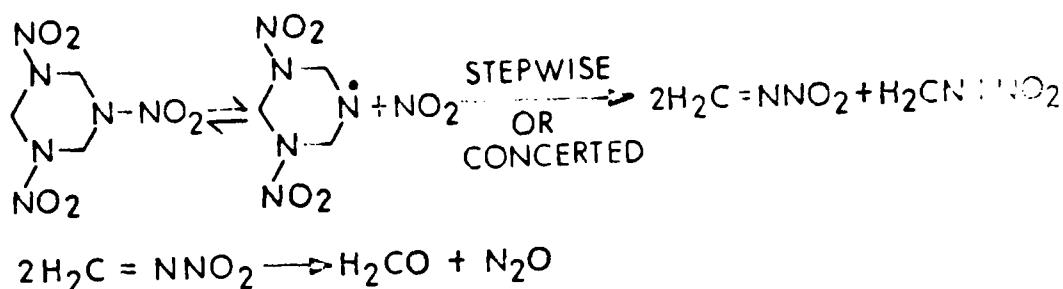
¹⁸J. J. Batten, "The Thermal Decomposition of RDX at Temperatures Below the Melting Point. III. Towards the Elucidation of the Mechanism," *Aust. J. Chem.*, Vol. 24, p. 945 (1971).

¹⁹J. 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).

²⁰D. 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, 201 (1976) (*Pu.* 1977).

F. Work Needed: Labelling Studies

Another area in which further work would be very beneficial is isotope labelling studies. Studies on decomposition of Nitro- ^{15}N -labelled HMX and RDX^{21,22} indicate that N_2O is formed as N^{15}NO (labelled adjacent to O), N_2 is formed as N^{15}N (singly labelled), NO is formed as ^{15}NO (labelled), and HCN is formed as unlabelled HCN . This indicates that N_2O and N_2 are formed with the original N-N bond in the nitramine intact; NO incorporates the nitro nitrogen and HCN incorporates the amine nitrogen of the starting HMX or RDX. It does not necessarily prove that C-N cleavage is the first step, or that N-N cleavage does not occur; the N_2O could be formed subsequently to initial N- NO_2 cleavage by decomposition of $\text{H}_2\text{C}=\text{NNO}_2$, for example as follows:



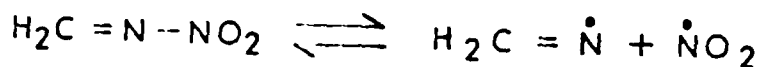
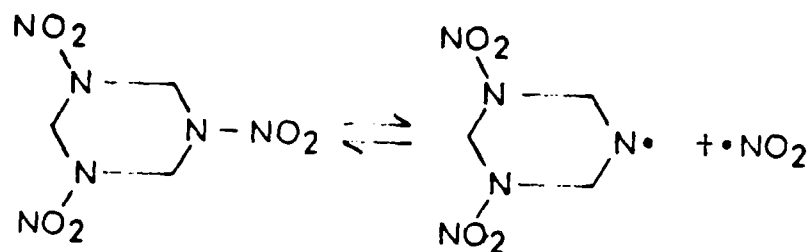
The decomposition of HMX (mp ca 285°C (dec)) was studied isotopically at 230° , 254° , and 285°C . It was stated (reference 21) that "at these temperatures, HMX exists as the δ -form" but it can also be seen (reference 22, table 3) that the products at 285°C are markedly different from those at 226 - 58°C ; possibly this is due to liquid-phase decomposition at 285°C , as opposed to gas and/or solid-phase decomposition at the below-melting-point temperatures. This is an important point, as it would help to have established for certain the degree of scrambling in the liquid-phase decomposition. RDX was studied at 190°C , ca 10 - 15°C below its melting point.

Mixtures of ^{13}C and ^{18}O labelled HMX were also decomposed; some scrambling was found but was attributed to secondary reactions such as polymerization/depolymerization of formaldehyde after formation.²²

²¹B. 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. and Ind.*, 2177 (1967).

²²B. Suryanarayana, J. R. Autera and R. J. Graybush, *Proceedings of the 1968 Army Science Conference (OCRD)*, West Point, New York, Vol. 2, p. 423 (1968), (AD-837 173).

Another very interesting set of isotope-labelling studies is being carried out at Eglin AFB.²³ These studies involve decomposition of mixtures of unlabelled and doubly-¹⁵N-labelled HMX. The results obtained from these studies will be very important, since the amount of scrambling observed in the unreacted starting material and in the various products such as N₂O, N₂, nitrosoamines, etc., would be expected to yield valuable information as to the possible occurrence of equilibria of the type



and of the importance and influence of these equilibria on the course of the decomposition.

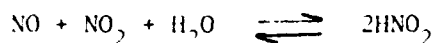
In view of²³ the potential importance of the results, it is to be hoped that this work²³ can be continued, confirmed and extended, or at the very least that the report describing it can be finished and published.

There is a need for further studies of this type. It would be a good idea to apply this approach (scrambling studies on singly-labelled compounds or on mixtures of doubly- and unlabelled HMX or RDX) on as many as possible of the types of studies and conditions reported in the literature, in order to get an idea of the effect of conditions of decomposition

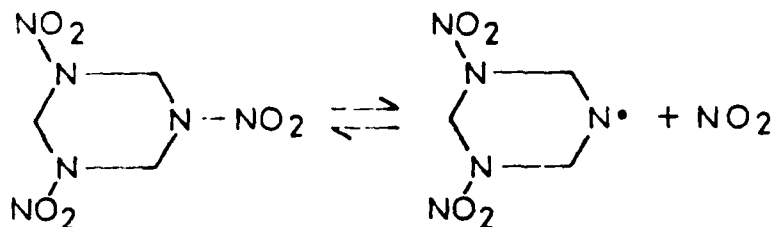
²³R. J. Powers, AFATL, Eglin AFB, Florida, Private Communication, 1980.

on the isotopic composition of unreacted starting material, and on as many of the products as possible. This would be expected to yield much useful information on decomposition mechanisms. For example, formation of N_2 with the same degree of scrambling as N_2O might suggest that it is formed either by deoxygenation of N_2O , or by some such pathway as deoxygenation of starting material, with the resulting nitrosoamine yielding N-nitrosoimine, which then breaks down to give N_2 and H_2CO . Formation of fully scrambled N_2 might suggest a similar pathway to N_2 , but with the nitrosoamine formed with complete scrambling by combination of NO with nitrogen-centered radical left from N- NO_2 cleavage of starting material, which would of course account for the scrambling. However, complete scrambling would not indicate complete absence of free-radical deoxygenation of the nitro groups unless it was established that the N-N bond in the nitrosoamines was stronger than that in the nitroamine.

Another possible labelling study might be exemplified by addition of labelled NO, or NO_2 followed by experiments to see if the label is incorporated into the NO, NO_2 , N_2O , N_2 and unreacted starting material through some such reaction as (see for example reference 24, and further references cited therein):

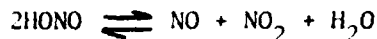


followed by incorporation of labelled NO_2 into unreacted starting material by the equilibrium



Further deuterium isotope effect studies should also be done. It has already been found²³ that liquid-phase decomposition of HMX gives no primary kinetic isotope effect when deuterium is substituted for hydrogen; since this indicates that hydrogen atoms are not involved in the rate-determining step, HONO elimination is apparently not the primary pathway in liquid-phase decomposition, at least for HMX. This is in agreement with the idea that the NO_2 observed in the liquid phase^{1,4} probably came from N- NO_2 cleavage, since it eliminates one obvious source of HONO, which might have given rise to NO_2 via the overall reaction

²⁴E.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).



However, the possibility of other sources for both HONO and NO₂ should still be considered. It has also been reported²³ that decomposition of HMX at temperatures below its melting point gave a primary H-D isotope effect on the induction time; possible explanations for this include (a) solid-state decomposition via HONO elimination; (b) the effect could be due to some such factor such as crystal quality; or (c) vaporization followed by decomposition via HONO elimination in the gas phase.

G. Work Needed: Chemistry of HMX and RDX Decomposition Intermediates

It would help to have a better understanding of the actual chemistry that takes place in HMX and RDX decomposition, subsequent to the initial step. Two (but not the only two) subjects of considerable interest are (a) the chemistry of the N-nitroformimine that appears to be involved in the decomposition, and (b) the question of bimolecular followup steps such as hydrogen and oxygen abstraction from unreacted HMX and RDX molecules. Some (but not the only) possible ways of attacking these problems are suggested in the attached copies of two ILIR Proposals, "Chemistry of HMX/RDX Thermal Decomposition Intermediates" and "Effect of Free Radical Sources on HMX and RDX Decomposition" (Appendices A and B, respectively). These are proposals for chemical-type studies on HMX/RDX decomposition chemistry. More studies of this type are needed and could be proposed, for example, this writer hopes to write one for some experiments on product analysis using a pyrolysis apparatus that has been used for pyrolysis studies at BRL.^{25,26}

H. Work Needed: Elementary Arrhenius Parameters for Decomposition of Nitramines, HMX and RDX in the Liquid Phase.

Suggested values for activation energies and frequency factors for decomposition of HMX and RDX in the liquid phase are given in references 2 and 3. However, these values are probably not the actual values for the elementary chemical steps involved in the decomposition (although for want of anything better, the present writer^{2,3} and others (see for example refer-

²⁵ J. J. Rocchio and A. A. Juhasz, "HMX Thermal Decomposition Chemistry and Its Relation to HMX-Composition Propellant Combustion," *Proceedings, 11th JANNAF Combustion Meeting, Volume 1*, p. 247.

²⁶ J. P. Pfau, J. J. Rocchio and R. A. Wires, "New Aspects of HMX Thermal Decomposition as Studied by Pyrolysis/Mass Spectrometry," *Proceedings, 15th JANNAF Combustion Meeting, Naval Underwater Systems Center, Newport, Rhode Island, September 11-15, 1978*, p. I-359.

ence 27) have at times made the assumption that they were); they are probably complicated by such factors as chain reactions and solvent "cage" effects.^{28,29} It would help if we had a better understanding of the nature and relative importance of these factors and of how to correct for them, in order to get a better idea of the elementary Arrhenius parameters for the actual reactions involved in liquid-phase decomposition of these molecules. Comparison of these values with predicted (see for example reference 27) values for various mechanisms would help in understanding the true nature of the first step of liquid phase decomposition of nitramines, HMX and RDX.

Some possible ways of checking the importance of bimolecular follow-up steps or chain processes are mentioned in Appendix B. Reviews on the subject³⁰⁻³² may suggest ways of evaluating cage effects.

²⁷R. Shaw and F. E. Walker, "Estimated Kinetics and Thermochemistry of Some Unimolecular Reactions in the Thermal Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetrazapalooostme in the Gas Phase," *J. Phys. Chem.*, Vol. 81, p. 2572 (1977).

²⁸C. E. Waring and G. Krastins, "The Kinetics and Mechanism of the Thermal Decomposition of Nitroglycerin," *J. Phys. Chem.*, Vol. 74, p. 999 (1970).

²⁹R. A. Fifer, report in preparation.

³⁰T. Koenig and H. Fischer, "Cage Effects," Chapter 4 in J. K. Kochi, Ed., "Free Radicals," Vol. 1, Wiley-Interscience, New York, 1973, p. 157ff.

³¹S. H. Northrup and J. T. Hynes, "Short Range Caging Effects for Reactions in Solution. I. Reaction Rate Constants and Short Range Caging Picture," *J. Chem. Phys.*, Vol. 71, p. 871 (1979).

³²N. J. Turro, "Micelles, Magnets and Molecular Mechanisms. Application to Cage Effects and Isotope Separation," *Pure and Applied Chemistry*, Vol. 53, p. 259 (1981).

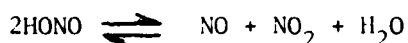
I. Work Needed: Critical and Interpretative Literature Reviews on Selected Topics

A number of these are needed; some of the more important ones are summarized below.

There is a need for a critical, interpretative review of the literature pertaining to autocatalysis, autoinhibition, etc., in decomposition of HMX, RDX and nitramines generally. Actually, this is the phase of the current review that is in progress right now.

There is also a need for a critical and interpretative review on additive effects on decomposition of HMX, RDX and related compounds. This could actually be regarded as being related to the autocatalysis and autoinhibition referred to in the preceding paragraph, and it is possible that the two of them may end up being done as one review.

Another possibility is the following: Reactions among nitrogen oxides, formaldehyde, water, etc., may be important even in low temperature (ca 200-300°C) decomposition. For example, care should be taken to rule out the reaction between O_2 and NO as a possible source of some of the NO_2 detected in HMX and RDX decomposition, in view of the known formation of NO^{1-4} and the possibility of traces of air in the apparatus, even when the reaction is carried out under vacuum or under an inert gas. This is especially true in the light of reports^{17,18} that originally-colorless product gas mixtures from HMX or RDX decomposition turned brown on admission of air to the apparatus. Another possibility is the reaction between H_2CO and NO_2 ; in fact right now this writer is in the habit of thinking of this reaction as being the source of much of the CO, CO_2 and NO that is found. Another possibility is the following (see for example reference 24 and additional references cited therein).



This might give rise to NO_2 even if the initial reaction was HONO elimination, and might account for some of the gas-phase NO_2 formation mentioned in the discussion of references 6 and 7. Other reactions of this same type might well be affecting the product distributions from HMX and RDX decomposition, and it might be a good idea to search the literature for as many of them as can be found, and try to estimate their rates under the conditions of existing HMX/RDX decomposition studies. (Another possible way to approach this problem might be through isotope scrambling or labelling studies, as mentioned earlier in the present report.)

It might also be a good idea to review the decomposition chemistry of nitramines other than HMX and RDX; this may well end up being covered to a significant degree in the autocatalysis/autoinhibition portion of the current review, but a separate portion devoted to full coverage of all nitramines would also be worthwhile.

Also, a review of such properties as conformations, electronic structures, crystallography, etc. of nitramines generally and of HMX and RDX in particular would make it easier to pull everything together to define the mechanisms of HMX and RDX decomposition.

Another possibility might be, as suggested in reference 4, to review the mass spectral studies on decomposing HMX in an effort to separate ion-fragmentation peaks from those that are parent peaks of true thermal-decomposition products, or are at least due to such products. Further discussion of this suggested topic is given in reference 4.

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APPENDIX A

CHEMISTRY OF HMX/RDX THERMAL DECOMPOSITION INTERMEDIATES

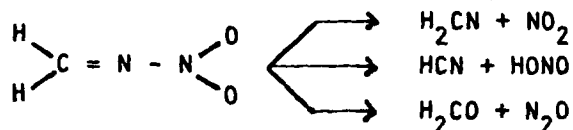
ILIR PROPOSAL

TASK TITLE: Chemistry of HMX/RDX Thermal Decomposition Intermediates

PRINCIPAL INVESTIGATORS: Michael A. Schroeder and Richard A. Beyer
Ignition and Combustion Branch
Interior Ballistics Division

OBJECTIVE: Determine the temperature and heating rate dependence of the thermal decomposition of nitroimine compounds analogous to those observed in HMX and RDX thermal decomposition.

BACKGROUND: An understanding of the thermal decomposition behavior of HMX and RDX is important in learning how to model and design propellants, and to develop additives to modify their ballistic properties. N-nitroformimine has been observed in the mass spectra of HMX and RDX thermal decomposition products. An understanding of its decomposition pathways is important because of the different subsequent chemistry of the possible products. Pathways which appear to be possible on the basis of studies of other compounds are the following:



Some studies indicate that HMX and RDX give increased yields of NO_2 and HCN and decreased yields of N_2O and H_2CO at higher decomposition temperatures. Therefore a study of the temperature dependence of the intermediate products such as the nitroimines is a logical starting point to obtain an understanding of the reasons for this behavior.

APPROACH: The compound $\text{H}_2\text{C}=\text{NNO}_2$ has apparently never been prepared, probably because of its volatility and instability. Analogous compounds such as $(\text{CH}_3)_2\text{C}=\text{NNO}_2$ have been prepared and should have the same major features in thermal decomposition. This analog would be prepared and its thermal decomposition studied as a function of temperature and heating rate. Heating would be done both with CO_2 laser radiation and on previously well characterized platinum ribbon heaters. Analysis of products would initially be with infrared absorption spectroscopy, as done previously for HMX by Beyer and Morgan. Other methods of product detection including electron spin resonance spectroscopy, mass spectroscopy, and Raman spectroscopy could be implemented if required.

RESOURCES: 1 man-year, 3K for expendables. Total 65K

PROGNOSIS: 2-Nitriminopropane ($(\text{CH}_3)_2\text{C}=\text{NNO}_2$) has been prepared and is described in the literature. Apparatus and chemicals from previous studies on HMX decomposition are still on hand at BRL, so that part of the work should present no problem. There is still some risk, however, the main problem that might arise concerns the fact that 2-nitriminopropane and related compounds are thermally unstable and are sensitive to moisture and to oxygen; if the limited synthetic facilities available at BRL proved insufficient to handle these problems, the approach might have to be modified, arrangements made to have the needed compounds prepared outside of BRL, or the project abandoned. If all experimental details proceed favorably, the prospect of observing a significant temperature variation in the product distribution is highly uncertain.

APPENDIX B

EFFECT OF FREE-RADICAL SOURCES ON HMX AND RDX
DECOMPOSITION

ILIR PROPOSAL

TASK TITLE: Effect of Free-Radical Sources on HMX and RDX Decomposition.

PRINCIPAL INVESTIGATOR: Michael A. Schroeder
Ignition and Combustion Branch
Interior Ballistics Division

OBJECTIVE: Attempt to evaluate the possible importance, to HMX and RDX decomposition, of bimolecular follow-up processes involving attack by intermediates or free radicals formed in the reaction, on unreacted HMX or RDX molecules.

BACKGROUND: An understanding of the thermal decomposition behavior of HMX and RDX is important in learning how to model and design propellants, and to develop additives to modify their ballistic properties. To date, most considerations of HMX and RDX decomposition mechanisms seem to have centered around the idea that the initial degradation of HMX or RDX molecules is a strictly unimolecular process, involving little or no interaction between unreacted HMX or RDX molecules, and intermediates or radicals formed in the decomposition. Such pathways presumably are in fact important. However, available literature analogies would appear to suggest that free radicals may be able to react with at least some nitro compounds under conditions milder than those usually encountered (200-300°C, < 1 atmosphere) in studies of HMX or RDX decomposition, although after a literature search the present writer remains unaware of an example of attempted reaction of a free radical with a nitroamine.

APPROACH: Decomposition of HMX and RDX in the presence of free radical sources would be examined. One possible and readily available source of free radicals would be azo-bis-isobutyronitrile; this compound decomposes thermally to give free radicals which have been shown to react with nitro-aromatic compounds to give products apparently derived from nitroso compounds formed by initial deoxygenation of nitro groups in the starting nitroaromatic. The first phase of the proposed research would probably consist of DSC studies on thermal decomposition of RDX and azo-bis-isobutyronitrile, first separately, then in mixtures. Since azo-bis-isobutyronitrile melts at ca 100°C with decomposition, the liquid phase from this melt might well dissolve some HMX or RDX, thereby facilitating any reaction due to the more efficient contact between the two materials in the dissolved state.

If negative results are obtained, attempts would be made to carry out the reaction in such a way as to get as intimate contact as possible between the two ingredients, for example, by dissolving them in a common solvent, evaporating the solvent, and studying the decomposition of a small sample of the resulting mixture, or by studying the decomposition of both materials in a stable, nonreactive, high-boiling solvent, or by carrying out the decomposition at a high heating rate so that there will be some free radical source left when the decomposition temperature of HMX or RDX is reached.

If positive results are obtained, the above experiments could be carried out, and in addition, some attempt could be made to identify the products of the decomposition in the presence of azo-bis-isobutyronitrile, for purposes of comparison with the products of decomposition of neat HMX or RDX.

RESOURCES: 1/2 man-team. 3K for expendables.

PROGNOSIS: Reportable results of some sort should be obtainable fairly quickly, but might be negative. The results might be suggestive rather than definitive since, although they would probably be of comparable reactivity, the free radical $(CH_3)_2CCN$, formed from decomposition of azo-bis-isobutyronitrile, is not actually one of the radicals formed in HMX or RDX decomposition. Also, negative results could be explained by saying that azo-bis-isobutyronitrile and HMX or RDX might be immiscible under the conditions of the experiment, hence allowing insufficient contact between radicals and HMX or RDX.

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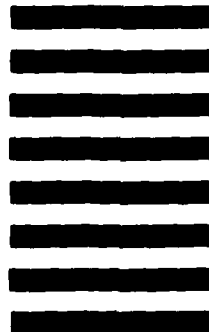


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