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CRITICAL ANALYSIS OF NITRAMINE
DECOMPOSITION DATA: ACTIVATION
ENERGIES AND FREQUENCY FACTORS
FOR HMX AND RDX DECOMPOSITION

Michael A. Schroeder

September 1985

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HMX	Arrhenius Parameters	Decomposition												
RDX	Activation Energy	Explosives												
Nitramines	Frequency Factor	Propellants												
Kinetics	Thermal Decomposition													
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) gkl A literature review is presented, on kinetic parameters for thermal decomposition of HMX and RDX in the homogeneous vapor, liquid, and dissolved states. The decomposition apparently fits first-order kinetics, and suggested values for Arrhenius parameters for HMX and RDX decomposition in the gaseous and liquid phases, and for decomposition of RDX in solution in TNT are given. The possible importance of autocatalysis is pointed out as are some possible complications that may be encountered in interpreting,														

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20. Abstract (Cont'd):

extending or extrapolating kinetic data for these compounds from measurements carried out below their melting points to the higher temperatures and pressures characteristic of combustion.

The mechanistic implications of the activation energies and frequency factors are discussed. In general, the recommended values seem consistent with the idea that under many conditions the first step is either HONO elimination, N-NO₂ cleavage or some combination of these two steps. However, it is difficult to rule out other processes. Some possible unimolecular and bimolecular followup steps and the possible role of factors such as chain reactions, cage effects and other solvent-related effects are also discussed briefly.

*Figure 1: Statistical analysis,
Vapor phase decomposition;
not liquid. ←*

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INTRODUCTION

There is currently considerable interest in the use of nitramine oxidizers in gun and rocket propellants (see for example Reference 1), due to their desirable properties, such as absence of noxious combustion products, high specific impulse and impetus, and thermal stability. The most commonly used nitramine oxidizers are RDX (I), (also known by such names as hexogen or cyclonite) and currently indexed in Chemical Abstracts under the heading "1,3,5-Triazine, hexahydro-1, 3, 5-trinitro" and HMX (II), also known by such names as Octogen and indexed in Chemical Abstracts under the heading "1,3,5,7-Tetrazocine, octahydro-1,3,5,7-tetranitro." (Octogen). 5473

Before the combustion and deflagration behavior of these materials can be understood and intelligently modified, it will be necessary to have an understanding of their thermal decomposition chemistry. This is true for several reasons. First, combustion modellers use the kinetics and kinetic parameters as input into their models. Second, the product distributions from the decomposition reactions are also needed as input for many of these models. Also, an understanding of the detailed chemical decomposition modes might well make it possible to suggest new types of additives for combustion modification.

At present, the chemical mechanisms involved in the decomposition of these materials are not at all well understood. There are a number of apparent conflicts in the literature with regard to such topics as kinetic parameters, product distributions, autocatalysis and acceleration and/or inhibition of the decomposition by substances, some of which are known products of the decomposition. Many of these apparent conflicts probably arise from the great complexity of the decomposition. The course of the reaction seems to be very dependent on experimental conditions due to the apparent operation of simultaneous gas, liquid and solid-phase decomposition, leading to products many of which are able to react among themselves and also to accelerate or inhibit the decomposition of starting material. In addition, the nature of even the first step of the decomposition reaction is not at all well understood, quite possibly as a result of variations with temperature, pressure and state of aggregation (gas, liquid, solid, dissolved in solvent) in the relative rates of the many reactions (N-NO₂ cleavage, HONO elimination, various forms of C-N cleavage, etc.) that have been proposed.

In view of these considerations, it appeared that there was a need for a critical, interpretative review of the literature on decomposition of nitramines, with the emphasis on HMX and RDX. Such a review would summarize what is known about the chemical and physical mechanisms involved, and involves an attempt to resolve conflicts and to suggest new experiments to elucidate the mechanisms involved.

The present report is one of a series describing such a review. This review is written from the point of view of an organic chemist and so is complementary to reviews such as that by McCarty,¹ which emphasize combustion

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

behavior as seen by a physical chemist or combustion engineer. In the present report, available information on kinetic parameters for HMX and RDX decomposition is summarized, and an attempt is made to arrive at suggested values for activation energies and frequency factors, and to discuss the results in terms of the possible chemical and physical mechanisms involved in the decomposition reactions. Brief preliminary discussions of possible chemical mechanisms and of needed research have already appeared,² and subsequent reports in the present series will deal with such topics as product distributions and autocatalysis. There have been a number of reviews of HMX and RDX decomposition,³⁻⁶ some of which came to our attention after the present work was in progress, but there still seems to be a definite need for a critical, interpretative review written from the point of view of an organic or physical-organic chemist.

In the present report, an attempt has been made to provide comprehensive literature coverage to approximately mid-1980, although some later reports and papers are included.

The scope and organization of the present report are as follows: The available values for activation energy and frequency factor A (expressed as log A) are summarized in Appendices A-D. Appendix A summarizes the very few available values for vapor-phase decomposition of HMX and RDX. Appendix B summarizes data for HMX decomposition in the neat liquid and dissolved states. Appendix C similarly summarizes data for RDX decomposition in the neat liquid and dissolved states. Appendix D covers decomposition of HMX and RDX at temperatures below their respective melting points. These Appendices

²(a) M. A. Schroeder, "Critical Analysis of Nitramine Decomposition Results: Some Comments on Chemical Mechanisms," Proceedings, 16th JANNAF Combustion Meeting, Naval Postgraduate School, Monterey, CA, Sep 10-14, 1979, Vol. 2, p. 17; (b) M. A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Some Suggestions for Needed Research Work," Memorandum Report ARBRL-MR- 3181, June 1982 (AD-A116 194).

³J. Wilby, "Thermal Decomposition of RDX/TNT Mixtures, Part 1," A.R.D.E. Report (MX) 16/59, August 1959 (AD-285 991).

⁴F. C. Rauch and R. B. Wainright, "Studies on Composition B," Final Report Contract No. DAAA21-68-C-0334, American Cyanamid Company, Feb. 1969 (AD-850 928).

⁵M. Benreuten and L. H. Caveny, "Nitramine Monopropellant Deflagration and General Nonsteady Reacting Rocket Chamber Flows," MAE Report No. 1455, Princeton University, Princeton, NJ, January 1980.

⁶Ye. 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).

are separately accompanied by discussions intended to justify the selection of best values and weights of data from each title. The reference numbers in these discussions correspond to references given in that particular Appendix. A more general discussion of sources of error, chemical mechanism, etc. is given in the main report; this more general discussion is intended to tie together the information in all of the tables, and to present suggested values for kinetic parameters of HMX and RDX decomposition in the liquid and gaseous states.

It should be understood that the entire decomposition process of HMX cannot be described by a single set of kinetics constants; the kinetics and parameters differ appreciably with experimental conditions such as confinement, temperature, pressure and phase (solid, liquid, gas, solution) and with extent of reaction. This is especially true for the physically-complex below-the-melting-point decomposition, in which considerable evidence seems consistent with the idea that initially, vaporization and gas-phase decomposition (in at least some cases probably proceeding side-by-side with true solid-state decomposition) leads to formation of liquid products which condense onto undecomposed solid and induce liquefaction, leading to acceleration of condensed-phase decomposition. However the rates differ appreciably even between the homogeneous solid, liquid, vapor and solution phases, and in many cases even the rate constants for homogeneous, single-phase decomposition seems subject to some autocatalysis. Thus, when rate data such as those summarized here are used for predictive purposes, care should be taken to understand as well as possible the physical and chemical mechanisms of HMX and RDX decomposition under the conditions of pressure and temperature for which predictions are being made; and to take as much account as possible of variations in physical and chemical mechanisms with temperature and pressure.

It should be remembered that the activation energies and frequency factors given here are the result of efforts to arrive at values characteristic of certain specific chemical decomposition reactions occurring in the homogeneous liquid or vapor phases (but see the discussion in the preceding paragraph). Consequently, they are strictly applicable to complex processes (such as combustion) only to the extent that these processes are representable in terms of these same specific, homogeneous decomposition steps. Therefore, when the values given here are used as input for combustion or explosive modeling studies, they can be expected to prove most useful when used in conjunction with other measured or estimated parameters, in models which take detailed account of the individual chemical and physical processes involved. There is a need for further development of propellant-combustion and explosive models which take detailed account of the chemical decomposition processes involved, especially since relative rates of various initial and follow-up steps may change with changes in pressure and temperature.

II. SOURCES OF ERROR

One important source of uncertainty in studies such as those summarized here is that use of a very short temperature range for the Arrhenius plot may lead to inexact values for the frequency factor and activation energies. Other important sources of error include self-heating; vaporization followed by vapor phase decomposition or by condensation onto the cooler parts of the apparatus; reactions taking place on or catalyzed by the container surface;

and autocatalysis or autoinhibition. Another problem is that it is often not stated whether or what sort of statistical analysis was employed. This can make a difference, as is shown by the following example: an activation energy of 48.7 kcal/mole is reported^{4,7} for the thermal decomposition of neat liquid RDX. In a later report⁸ in the same series, it was stated that least squares analysis of the data gave a $\log A$ (sec^{-1}) of 22.4 and an activation energy of 55.6 kcal/mole. This is a significant change from the earlier values which were stated to be the result of a preliminary analysis. This example illustrates the possible effect of statistical treatments on the results.

A. Temperature Range

Activation energy and frequency factors are determined from a logarithmic plot of rate constant k vs reciprocal temperature; clearly the longer the temperature range the more reliable will be the extrapolation to the much higher temperatures characteristic of combustion and explosive behavior. Most authors studying HMX and RDX decomposition kinetics have worked over relatively short temperature ranges, often 20° or less, possibly because temperature dependence due to the relatively high (ca 50 kcal/mole) activation energies results in shortening of the temperature range over which the decomposition proceeds at conveniently measurable rates. This problem is especially severe for liquid HMX, which is already within its decomposition range at the melting point of solid HMX (ca 280°). In spite of this problem, Robertson⁹ was able to study neat liquid RDX over the range of 213–99°C ($\Delta T = 86^\circ$) and HMX over the range 271–314°C ($\Delta T = 43^\circ$); the reaction at higher temperatures was followed using a membrane manometer attached to an optical lever, pressure-time traces being recorded on a moving strip of photographic paper.

In the present report, we will plot the most reliable data on common axes, hoping thereby to moot the question of differences in reliability due to use of different temperature ranges in the different studies by doing common statistical analysis on all data for the same compound and phase.

⁷F. 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.

⁸F. C. Rauch and W. P. Colman, "Studies on Composition B," Final Report, Contract No. DAAA21-68-C-0334, American Cyanamid Company, March 1970 (AD-869-226).

⁹A. J. B. Robertson, "The Thermal Decomposition of Explosives, Part II. Cyclotrimethylenetrinitramine and Cyclotetramethylenetetramine," Trans. Faraday Soc., Vol. 45, p. 85, 1949.

B. Self-Heating

Self-heating results when an exothermic reaction generates heat faster than the surroundings can conduct it away. Self-heating would be favored¹⁰ by large sample sizes and by higher pressure of gas over the sample since high pressure would lead to smaller bubbles of decomposition gases, hence to less efficient stirring of the sample. Thus two checks for self-heating would be whether or not the rate were independent of (a) sample size and of (b) pressure of inert gas atmosphere. Robertson⁹ found no self-heating by either methods for RDX with sample sizes from 4-45 mg, or for HMX with sample sizes from 1-7 mg. Thus, it would appear that in manometric kinetic apparatus of this general type, use of samples of these sizes or smaller should obviate the problem of self-heating. However, as indicated in Appendices B and C, use of larger samples did sometimes give evidence of self-heating. Furthermore, Goshgarian¹¹ in describing a DSC experiment states that "sample weight (of HMX) greater than 1.0 mg increased the isothermal temperature during HMX decomposition, apparently due to excess thermal evolution beyond the capabilities of the instrument to adequately regulate a constant temperature." Thus the permissible sample size in a DSC apparatus appears to be much smaller than in a standard kinetic apparatus.

If self-heating were important, it should give artificially high rate constants at high temperatures resulting in high values for activation energy and frequency factor.

C. Sublimation and Gas-Phase Reactions

Another possible important source of error in condensed-phase studies is vaporization of the sample followed by either gas-phase decomposition, or even sublimation of undecomposed HMX or RDX onto cooler portions of the apparatus. In most of the kinetic studies, sublimation was retarded either by carrying out the reaction under a pressure of inert gas or by carrying out the reaction in an apparatus designed in such a way that all parts were evenly heated to the temperature of the experiments. These precautions serve a purpose, since it is widely reported that in vacuum both HMX and RDX readily vaporize and condense on the cooler parts of the apparatus without appreciable decomposition; see for example Robertson.⁹

The vapor-phase reaction can interfere appreciably with determination of liquid-phase kinetic parameters, as shown by the results of Rogers,¹² who found that the vapor phase caused a quite noticeable hump on the tail of the

¹⁰A. J. B. Robertson, "The Thermal Decomposition of Explosives, Part I. Ethylenedinitramine and Tetryl," Trans. Faraday Soc., Vol. 44, p. 677, 1948.

¹¹B. B. Goshgarian, "The Thermal Decomposition of Cyclotrimethylene-trinitramine (RDX) and Cyclotetramethylenetetranitramine (HMX)," AFRPL-TR-78-76 (AD-B032-275L).

¹²R. N. Rogers, "The Determination of Condensed Phase Kinetics Constants," Thermochimica Acta, Vol. 9, p.444, 1974.

DSC curve of decomposing RDX. The gas-phase material disappears immediately after the liquid-phase is all gone; the result is a hump on the tail of the DSC curve at the point where liquid-phase decomposition ends and the gas-phase RDX starts to disappear. While liquid-phase is present, what is actually being observed is presumably a superposition of a first-order liquid phase reaction and a gas-phase reaction which reduces to apparent zero-order due to constant volume and to replenishment of gaseous material by vaporization of liquid. In the case of RDX this led¹² to an apparent $E_a = 43.1$ kcal/mole and $A = 2.44 \times 10^{16}$ sec⁻¹. When the vapor-phase reaction was taken account of by using a baseline based on the constant gas-phase decomposition, Rogers obtained $E_a = 47.1$ kcal/mole and $A = 2.02 \times 10^{18}$ sec⁻¹, in good agreement with Robertson's manometric values. In spite of Roger's publication, subsequent workers have generally continued to ignore the vapor-phase contribution to the decomposition of neat liquid HMX and RDX.

The above discussion refers to isothermal DSC. When temperature-programmed nonisothermal DSC is employed, the problem becomes even worse due to probable temperature dependence of the relative importance of vapor- and liquid-phase decomposition, as well as error introduced by the particular method of calculation employed.

Thus, out of the multitude of thermal analysis studies of Arrhenius parameters of HMX/RDX decomposition, the gas-decomposition-corrected values of Rogers^{12,13} are preferred. The 4 kcal/mole difference between Rogers' corrected and uncorrected activation energies for RDX suggests that a similar correction should be applied to all isothermal DSC results; examination of Appendix C suggests that application of such a correction would bring these values into the same range as those found from non-DSC kinetic studies on RDX. See also the discussion in Section II. F.

The effect of vapor-phase decomposition may be smaller for non-DSC studies. Rauch and Wainwright (see page 29 of Reference 4), in the course of their reactant-disappearance kinetic studies of the decomposition of liquid RDX, calculated (from vapor pressure) the percent RDX initially in the gas phase for several different combinations of reactor volume and initial weight of RDX at 212°C. These percentages varied from 0.3 to 3.6, and seemed unrelated to the rate constant which varied in the range $2.0 \pm 0.3 \times 10^{-3}$ sec⁻¹ in a manner unrelated to the amount of RDX present in the gas phase. This is surprising, since the liquid-phase rate constant at this temperature is calculated to be 1.25×10^{-3} sec⁻¹, using Robertson's values⁹ ($A = 3.16 \times 10^{18}$, $E_a = 47.5$ kcal/mole), and the gas-phase rate constant is calculated to be about ten times faster (1.35×10^{-2} sec⁻¹) using Rogers' values¹⁴ ($A = 3.14 \times 10^{13}$ sec⁻¹, $E_a = 34.1$ kcal/mole) for the gas-phase decomposition. However, this is in agreement with Robertson's statement⁹ that his manometric results were independent of sample weight and pressure of overlying gas. Thus, it appears that vapor reaction probably does not introduce as much error into non-thermal kinetic studies as into thermal analysis studies.

¹³R. N. Rogers, private communication, Los Alamos Scientific Laboratory, 1979.

¹⁴R. N. Rogers and G. W. Daub, "Scanning Calorimetric Determination of Vapor-Phase Kinetic Data," Anal. Chem., Vol. 45, p. 596, 1979.

Possible reasons for this discrepancy include the following: (a) The DSC experiment follows the decomposition by its heat release. If the gas-phase decomposition had a greater heat release per mole than the liquid-phase decomposition, the DSC apparatus would see the gas-phase reaction as being proportionately more important than would the conventional kinetic experiments, thereby necessitating a larger correction. (b) The m/V ratio for the DSC experiments (ca 0.5mg/0.022ml^{13,14} 23mg/ml is generally larger than those for conventional kinetic experiments (see for example Reference 4) (ca 40mg/26ml = 1.5mg/ml); this might promote any exothermic reaction of gaseous products with each other or with unreacted RDX, since the higher m/V ratio might tend to keep gaseous decomposition products in contact with unreacted liquid (see discussion under auto-acceleration). This effect might conceivably operate even though gaseous products are generally allowed to escape through a small hole in the top of the DSC pan. (c) The DSC apparatus might detect heat output from reaction of gaseous decomposition products with each other rather than just that from decomposition of RDX itself.

The possibility should be kept in mind that some of the heat evolution from the gas phase reaction may be due to reaction among the products rather than just decomposition of RDX; however, good first order plots and reaction orders of ca 0.9 were obtained for the gas phase reaction so it seems likely that the observed rate constants¹⁴ and Arrhenius parameters (Appendix A) obtained by DSC are actually those for the gas phase decomposition of RDX and HMX, although it is difficult to rule out the possibility of pseudo-first-order reaction of products. Expulsion of unreacted HMX or RDX vapor through the hole in the lid of the pan might also lead to artificially high rate constants.

The above discussion applies specifically to RDX but since HMX also exhibits a vapor phase reaction it should apply to HMX also. However, the situation may be more complicated for HMX; see discussion in Appendix B.

D. Reactions on the Container Surface

In connection with gas-phase decomposition, another possible (and often-overlooked) complication¹⁵ is the fact that reactions assumed to take place entirely in the homogeneous gas phase sometimes in fact take place on or are catalyzed by the wall of the reaction vessel. More work is needed, but wall reactions are probably not a very important source or error in studies of gas-phase decomposition of HMX and RDX themselves. This tentative conclusion is

¹⁵P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley-Interscience, New York, pp. 6-7, 1972.

based on two observations: First, it has been reported¹⁶ that the rate of gas-phase HMX pyrolysis is independent of the nature of the container surface (note however, that dimethylnitramine decomposition did exhibit such a dependency¹⁶); second, consider the gas-phase decomposition data for RDX plotted in Figure 2. As stated in Appendix A and in the section on "Statistical Analysis," the data plotted includes DSC data of References A-1 and A-4, and manometric data from Reference A-3. The DSC data were done in metal-walled DSC pans. The wall material of the manometric (Reference A-3) studies was not stated, but was presumably some kind of glass or quartz. If this is the case, the close correspondence (Figure 2) of data with the two types of wall material would seem to suggest that wall material doesn't make much difference, and hence that wall reactions are not too important. Note again, however, that the SRI workers¹⁶ found that the rate of dimethylnitramine decomposition did depend on wall material; thus wall material is apparently important at least for the case of this one nitramine. Note also the discrepancy between dimethylnitramine and HMX in this respect; possible explanations include structural effects on absorption characteristics, differences in decomposition mechanism, and difference in pressure at which the experiments were carried out. See also paragraph 6 of Note Added in Proof No. 3.

This apparent importance of wall reactions for at least some nitramines should be kept in mind when reading previous work on gas-phase decomposition of nitramines. Furthermore, it is recommended that future workers on decomposition of nitramines under conditions where gas-phase decomposition may be important, should at least check for wall reactions by examining the effect of added glass beads, glass wool, etc., if practicable it would probably also be a good idea to study the effect of variations in wall material.¹⁵ As discussed above, it appears that HMX and RDX themselves may not be affected too much by wall reactions, but more information is needed here also.

E. Autoacceleration, Chain Reaction and Cage Effects

In the homogenous liquid phase, autoacceleration of decomposition by products might be swallowed up in the overall first order rate constant if the autoacceleratory follow-up reactions were rapid and the chain lengths relatively short. Robertson⁹ reported some evidence of autocatalysis of RDX decomposition, apparently by a stable product formed in solution. Autoacceleratory behavior might in principle be expected to either raise or lower the apparent activation energy depending on the relative temperature dependencies of the initial cleavage and autocatalytic follow-up steps, but lowering seems to be the usual pattern. Evidence for some effect on liquid decomposition by gaseous products is provided by observations that the activation energies for RDX decomposition were about 15 kcal/mole lower for

¹⁶D. F. McMillen, J. R. Barker, K. E. Lewis, P. L. Tavor and D. M. Golden, "Mechanisms of Nitramine Decomposition: Very-Low Pressure Pyrolysis of HMX and Dimethylnitramine," Final Report, SRI Project "YU-5787, 18 June 1979 (SAN 0115/117). (Supported by Department of Energy through Lawrence Livermore Laboratories).

closed pan (sealed) than for open pan (1 hole) DSC experiments.¹⁷ Note however the possibility of heat effects due to confinement of reactive gaseous products. In general, however, the agreement of the most reliable rate constants and activation energies with each other and with the vapor-phase-reaction-corrected DSC results suggests that under these conditions of less confinement (lower m/V ratio), rate constants are not being affected by reaction of gaseous products with the liquid phase. It is also possible that case effects could affect rates and activation parameters. See also Section V A and Note Added in Proof No. 2.

F. Isothermal vs. Nonisothermal Thermal Analysis

Two general approaches are generally used in measuring activation energies and frequency factors by thermal analysis methods. We will refer to these as isothermal and nonisothermal approaches. In the first (isothermal) approach the decomposing sample is held at constant temperature and the plot of heat evolved vs time is used to derive the rate constant at that temperature; the rate constants derived in this way at several temperatures are then used in a conventional Arrhenius plot of log of k vs 1/T to derive E_a and A. In the second (nonisothermal) approach the activation energy is derived by any of a variety of calculation procedures from time-property curves derived from programmed temperature runs.

The isothermal method seems capable of giving good results for the liquid phase reaction provided a correction is made for the gas phase reaction which occurs simultaneously with liquid phase reaction; thus the activation energy and frequency factor found for decomposing liquid RDX¹² were 43.1 kcal/mole and $2.44 \times 10^{16} \text{ sec}^{-1}$ respectively without corrections for vapor phase reaction, and 47.1 kcal/mole and $2.02 \times 10^{18} \text{ sec}^{-1}$ with correction for gas phase reaction, the latter pair of values being in reasonable agreement with Robertson's values⁹ of 47.5 kcal/mole and $3.16 \times 10^{18} \text{ sec}^{-1}$ (not $2.17 \times 10^{18} \text{ sec}^{-1}$ as stated in Reference 12). As far as this writer is aware, this is the only attempt at correcting isothermal DSC data on liquid HMX and RDX for concurrent vapor phase reaction; since the correction in activation energy seems to be about $47.1 - 43.1 = 4.0$ kcal/mole and other isothermal DSC values (Appendix C, References 13, 14, 16, 20, 28-30) are generally in the range 40-44 kcal/mole it would appear that application of this correction would raise these values to the range 44-48 kcal/mole in better agreement with Robertson's value⁹ of 47.5 kcal/mole. A similar treatment suggests that the correction factor in A is about 10^2 or 10^3 ; thus it is recommended that whenever possible values of E_a and A measured by thermoanalytical methods for liquid phase HMX and RDX should be corrected for concurrent vapor phase decomposition.

In the case of the nonisothermal approach it is hard to know how to include a correction for the gas phase reaction. In addition these methods are generally subject to errors both experimentally and because of assumptions introduced in the course of deriving the equations used in the calculation

¹⁷K. 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.

(see for example References 18-21). Because of these considerations, and due to time limitations only a short discussion of non-isothermal DSC determinations will be given here. However, an attempt has been made at including in the Appendices all available values measured by these methods.

For example, it seems appropriate to point out that it appears¹⁸⁻²⁰ that one common method²¹ for calculating activation energies, namely the method of Kissinger,²¹ may be subject to errors, when used to study HMX and RDX decomposition. In particular Rogers and Smith reported²⁰ that the Kissinger method gave low values for activation energy (28 kcal/mole) and frequency factors ($\log A(\text{sec}^{-1}) = 10.6$) although several other methods gave values more in agreement with Robertson.⁹ However, Kishore^{17,22} found that the Kissinger method gave $E_a = 42$ kcal/mole, in approximate agreement with isothermal and other scanning methods. Thus, it would appear that until this situation is better understood, the Kissinger method and other nonisothermal methods should be used with caution; care should be taken that the system under study conforms to the assumptions made in deriving the method. Actually, the physical complexities alone may well render HMX and RDX decomposition unsuitable for study by many nonisothermal methods.

It also seems worth mentioning that several papers^{17,20,23} include comparisons of Arrhenius parameters, obtained by various dynamic or nonisothermal thermoanalytical methods, including DSC and TGA results. In general, the dependence of the results of these studies on experimental conditions and method of calculation appears to be such that, as suggested by Garn²⁴ (for systems other than HMX and RDX), it actually seems more appropriate to regard them as "Temperature Coefficients of Reaction" rather than "Activation Energies," since they almost certainly do not represent an energy of reaction for a single, homogeneous chemical process, but rather the

¹⁸W. W. Wendlandt, "Thermal Methods of Analysis," 2nd. Edition, John Wiley and Sons, New York, NY, p. 187-193, 1974.

¹⁹J. H. Sharp, "Differential Thermal Analysis," R. C. Mackenzie, ed., Vol. 2, Chapter 28, See especially p. 55, Academic Press, New York, NY, 1972.

²⁰R. N. Rogers and L. C. Smith, "Application of Scanning Calorimetry to the Study of Chemical Kinetics," Thermochimica Acta, Vol. 1, p. 1, 1970.

²¹H. E. Kissinger, "Reaction Kinetics in Differential Thermal Analysis," Anal. Chem., Vol. 29, p. 1702, 1957.

²²K. Kishore, "Comparative Studies on the Decomposition Behavior of Secondary Explosives RDX and HMX," Defense Science Journal, Vol. 18, p. 59, See Chem. Abstr., Vol. 90, 206758V, 1978.

²³B. D. Smith, "Differential Thermal Analysis and Dynamic Thermogravimetric Analysis Studies of RDX and HMX," NWL Technical Report TR-2316, July 1969 (AD-857 655).

²⁴P. D. Garn, "Temperature Coefficient of Reaction," Thermochimica Acta, Vol. 28, p. 185, 1977.

temperature dependence of a complex process involving both vapor and condensed phase, and most likely some degree of autocatalysis as well. Thus, although these methods may well have usefulness in studying trends in data for a series of experiments under similar conditions, the absolute values probably have meaning only under the exact conditions for which they were determined.

III. STATISTICAL ANALYSIS

The statistical analysis was carried out by two methods. The first method was the method of Cvetanovic and Singleton^{25,26} which involves fitting the logarithms of the data using a transformation of the weights. The result is a least squares fit of the original data. The program used had been written for another project by Dr. T. P. Coffee, and a copy of it is included as Appendix E. The second program fits data to the logarithmic form ($\log k_c = \log A - E_a/RT$) of the Arrhenius Equation. The result is a least squares fit of the logarithms of the data. This program was written by D.R. Crosley and G.E. Keller for other work. A copy of this program is included as Appendix F of the present report. The author thanks Drs. Coffee and Keller for carrying out the analyses of the data using their respective programs.

Data on gas-phase decomposition of HMX and RDX was taken from Tables A-2 and A-3 of Appendix A. These Tables include all data known to the present writer on gas-phase decomposition of HMX and RDX. Data analyzed for decomposition of neat liquid HMX were taken from Table B-3 of Appendix B; these are believed by the present writer to be the most reliable data on decomposition of neat liquid HMX. Although all three sets of data were analyzed and plotted together, it is suggested that until the question of the gas-phase correction for HMX decomposition is better understood, the best value for liquid HMX would probably be those derived from Robertson's work (Reference 9). The data analyzed for decomposition of neat liquid RDX were taken from Table C-3; for reasons discussed in Appendix C, these are believed by the present writer to be the best data for decomposition of neat liquid RDX. Since several authors reported data (Table C-4) on decomposition of RDX in TNT solution, these data were analyzed and plotted together also. The data for neat, liquid RDX, gaseous RDX, neat liquid HMX, gaseous HMX, and RDX in TNT solution are plotted in Figures 1-5 respectively, and the Arrhenius parameters obtained from the two programs are summarized in the first four columns of data in the Table. The last two columns of data in the Table list the values suggested by the present writer for decomposition of the indicated compounds in the indicated state of aggregation. In general, these are the values from the Cvetanovic-Singleton Program, as it seems that the direct fit to the logarithmic form should be more accurate.^{25,26}

²⁵R. J. Cvetanovic and D. L. Singleton, "Comment on the Evaluation of the Arrhenius Parameters by the Least Squares Method," Int. J. Chem. Kinet., Vol. 9, p. 481, 1977.

²⁶R. J. Cvetanovic and D. L. Singleton, "Comment on the Evaluation of the Arrhenius Parameters by the Least Squares Method," Int. J. Chem. Kinet., Vol. 9, p. 1007, 1977.

TABLE 1. SUGGESTED $\log_{10}A(\text{sec}^{-1})$ AND E_a (Kcal/Mole) FOR THERMAL DECOMPOSITION OF HMX AND RDX.

Compound	State	Cvetanovic-Singleton		Linear Least Squares		Suggested Values			$K(\text{sec}^{-1})$ at		
		log A	E_a	log A	E_a	log A	E_a		480°K	573°K	700°K
RDX	Neat Liquid	18.668	47.8	18.354±0.3	47.0±0.8	18.668	47.8		8.02 x 10 ⁻⁴	2.73	5.55 x 10 ³
	Vapor (low temp)	11.991	30.5	12.202±.4	31.0±0.9	11.991	30.5		1.27 x 10 ⁻²	2.28	2.94 x 10 ²
	(high temp)	a	a	a	a	a	a				
	TNT Soln. 91-5% TNT Soln. (20-60%)	15.383 14.992	41.1 39.4	15.498±0.4 15.198±0.7	41.4±0.8 39.7±1.4	15.383 14.992	41.1 39.4		4.68 x 10 ⁻⁴ 1.13 x 10 ⁻³	0.510 0.922	3.56 x 10 ² 4.91 x 10 ²
HMX	Neat Liquid ^b	21.734	57.9	21.227±1.1	56.6±2.7	19.950 (or 19.7)	53.1 (or 52.7)		5.93 x 10 ⁻⁵	0.498	2.35 x 10 ³
	Neat Liquid ^c	19.950	53.1	19.943±0.5	53.1±1.4						
	Vapor (low temp)	ca 12.8 ^d	30-35	a	a	ca 12.8	ca 32.5		1.01x10 ⁻²	2.54	4.50 x 10 ²
	(high temp)	a	a	a	a	a	a				

^a See discussion, pp. 26-27.

^b Best three sets of data (Appendix B)

^c Robertson's data only (Best single set)

^d Due to scatter in data, log A = 12.8 was assumed in order to get a reasonable fit, following Reference 16. (A point at $1/T = j$, log K = 12.8 was included in the data fitted, and weighted heavily).

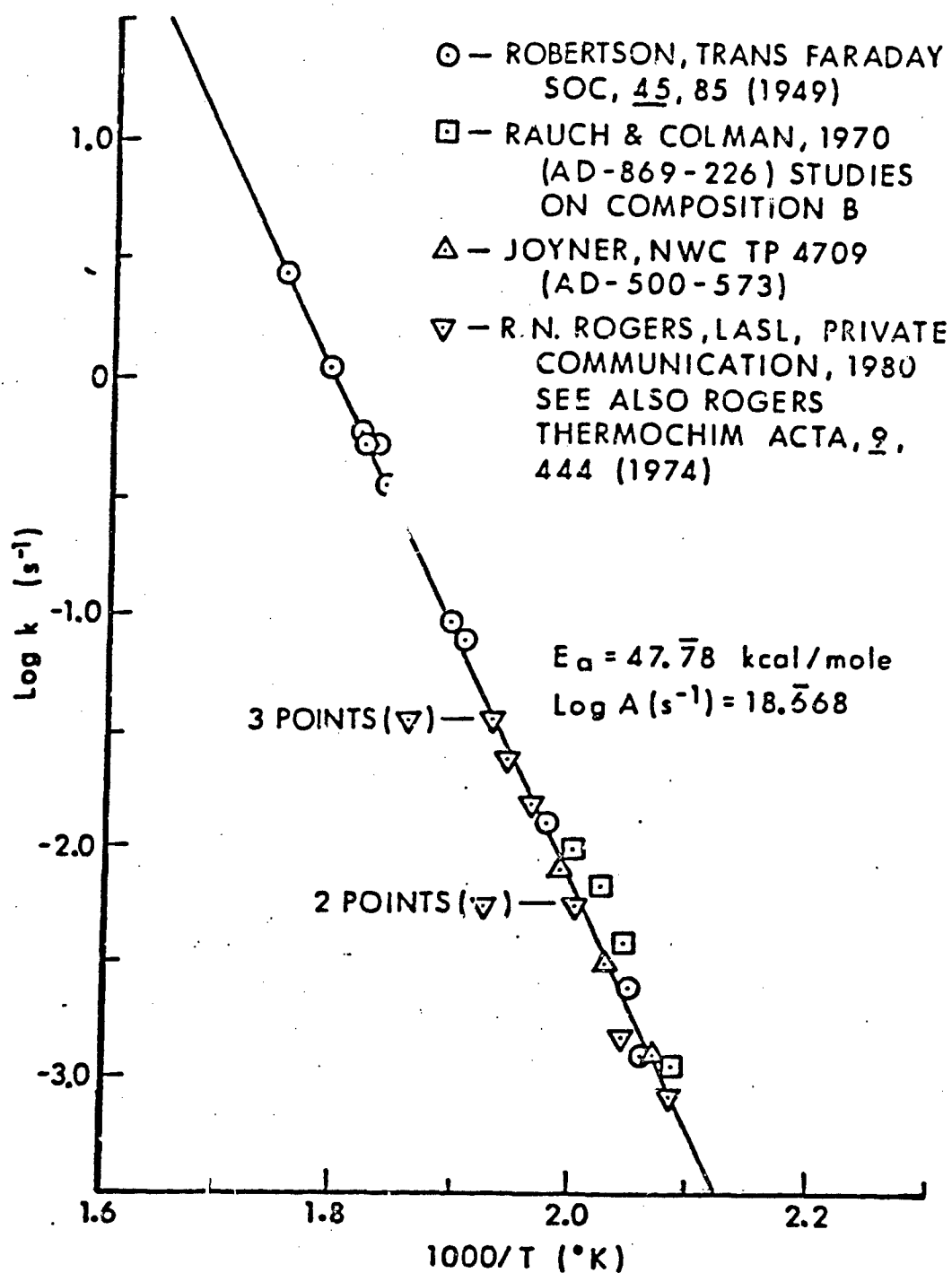


Figure 1. Plot of $\text{Log } k$ vs $1000/T$ for Liquid RDX Decomposition.

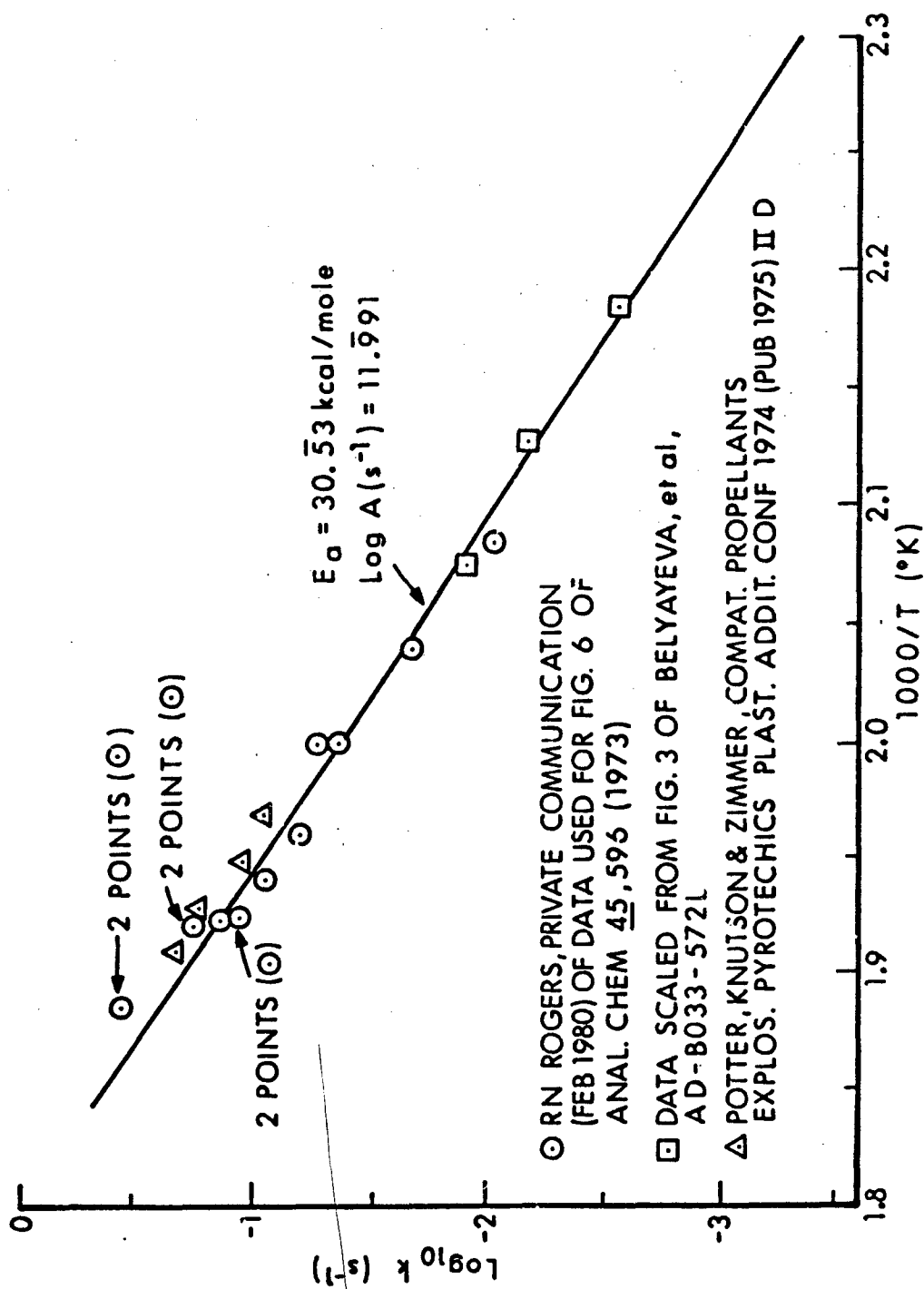


Figure 2. Plot of $\text{Log } k$ vs $1000/T$ for Decomposition of Gaseous RDX.

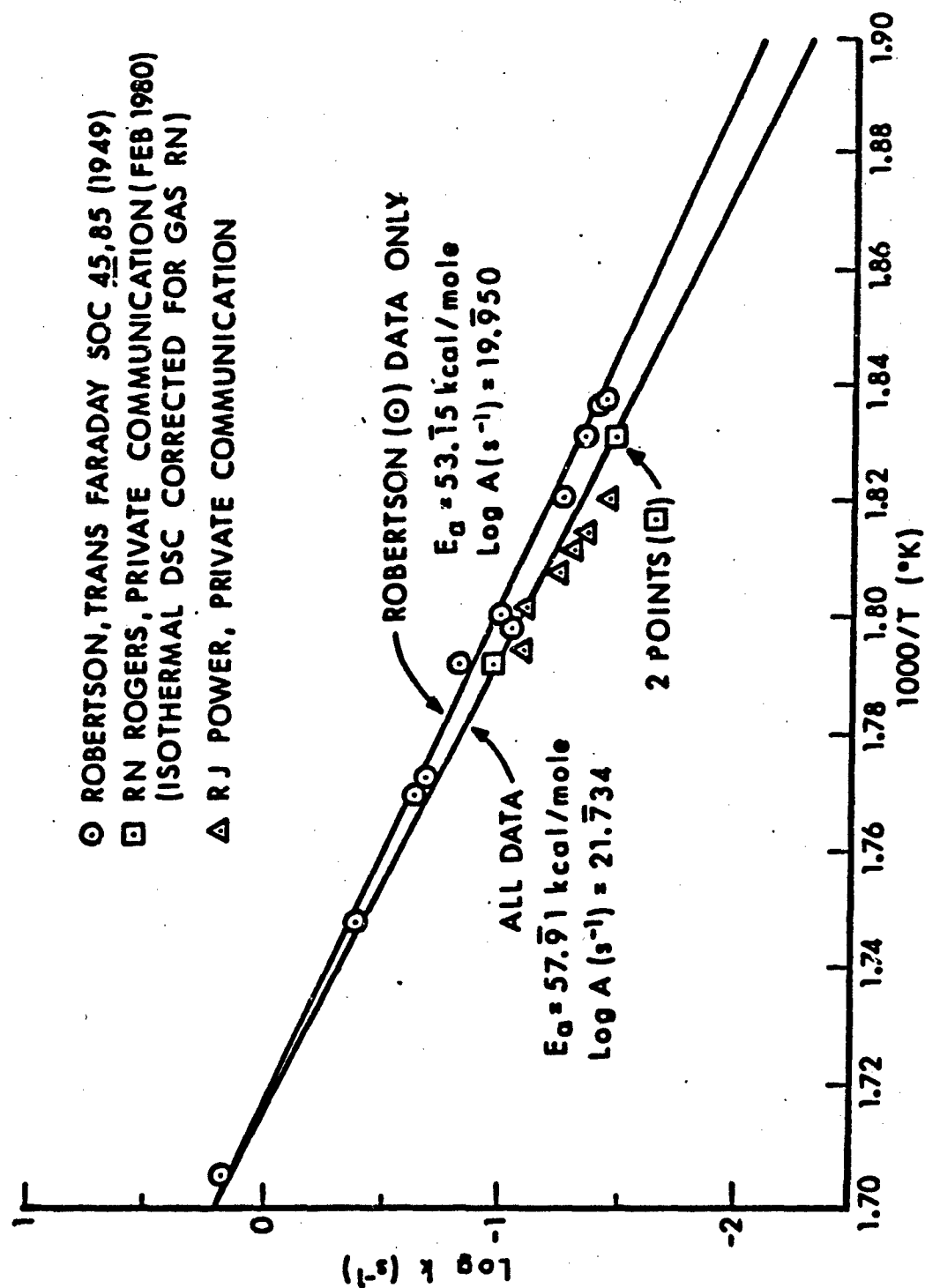


Figure 3. Plot of $\text{Log } k$ vs $1000/T$ for Liquid HMX Decomposition.

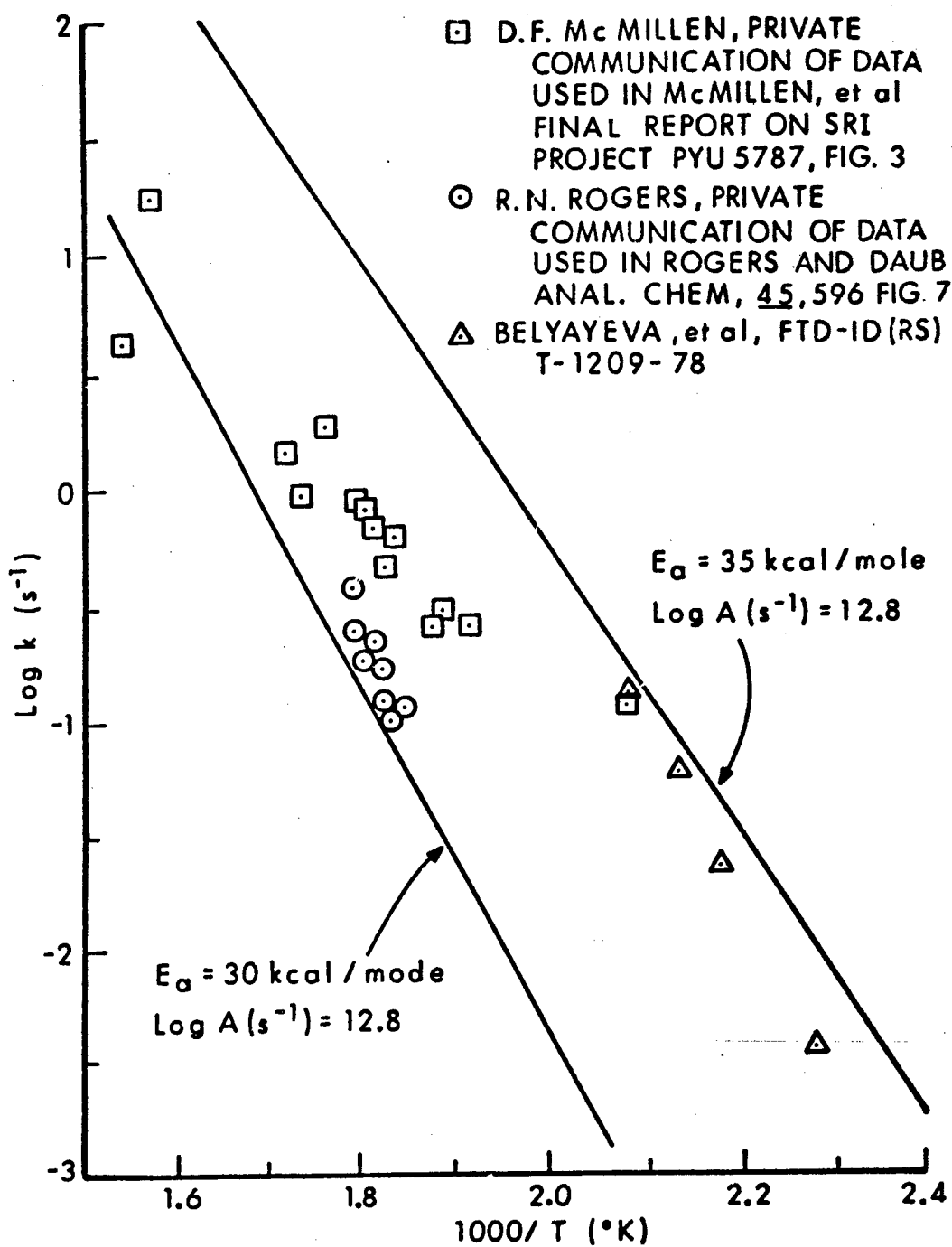


Figure 4. Plot of Log k vs 1000/T for Gas-Phase HMX Decomposition.

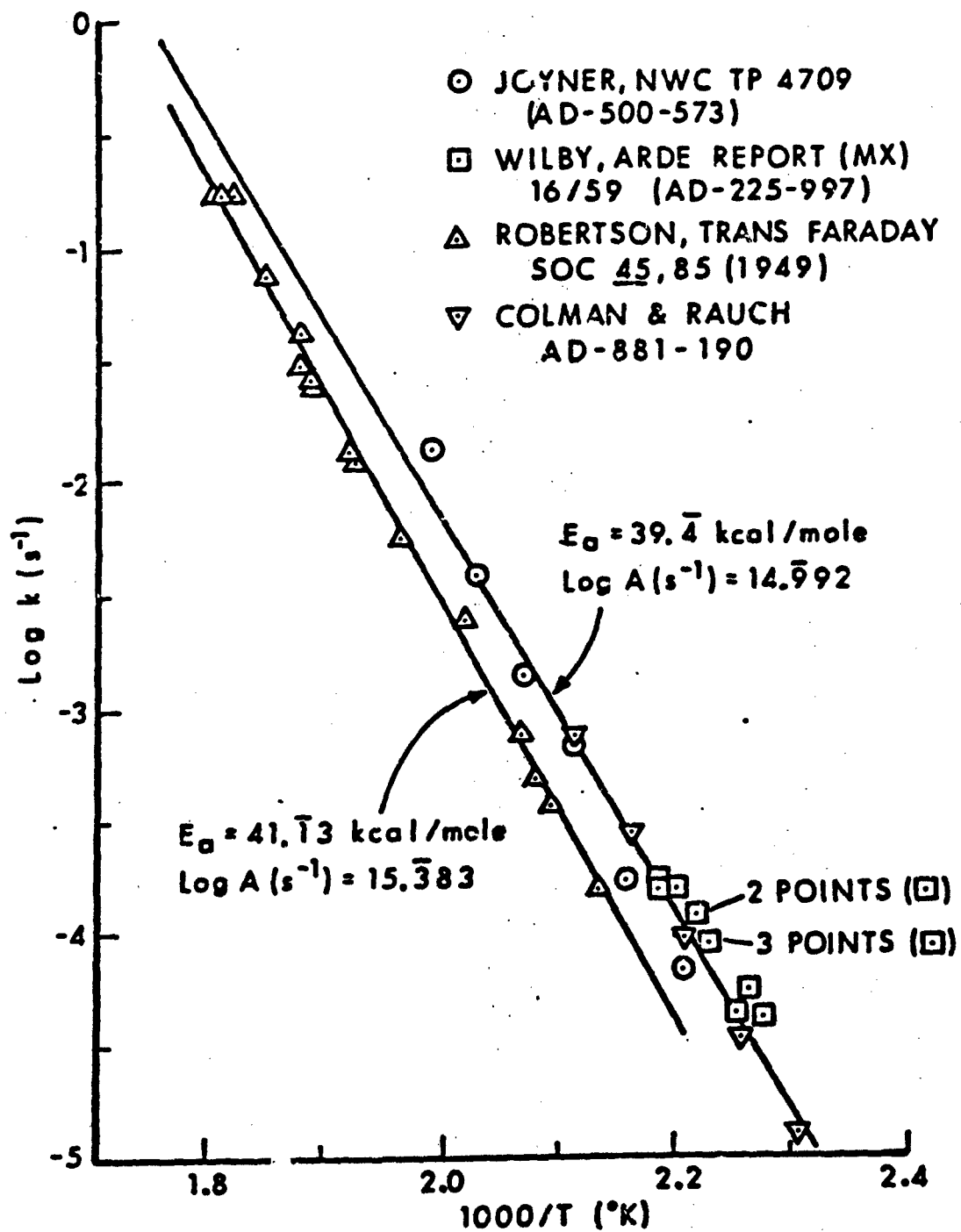


Figure 5. Plot of Log k vs 1000/T for Decomposition of RDX in Solution in TNT.

The values of $\log_{10} A$ listed in the Table are given to three significant figures past the decimal point, although it is highly questionable whether the accuracy of the intercepts themselves justifies more than one such figure. The other figures are given because it is felt that modelers may find more precision useful in interpolating within the temperature range covered by the actual measurements, or for extrapolating to temperatures not too far outside these ranges. Note that the original rate constants and temperatures on which the values given are based, are for the most part given to three or four significant figures by the original authors.

IV. GENERAL DISCUSSION AND SUGGESTED VALUES FOR KINETIC PARAMETERS

A. Gas-Phase

There is a need for more work on the gas-phase kinetic parameters for HMX and RDX decompositions, as mentioned in the discussion of data in Appendix A. The best values for use in modeling studies involving gas-phase decomposition at relatively low temperatures (ca 200-300°C) would probably be $\log A$ (sec^{-1}) = 11.991 and E_a = 30.5 kcal/mole for RDX, based on the plot and statistical analysis of all data (Table and Figure 2). For HMX, the data is too scattered to allow choice of a single recommended value (Table, Figure 4) but the values are most likely in the range 30-35 kcal/mole and $\log A$ (Sec^{-1}) = 12.8 respectively. Until more data is available, E_a = 32.5 kcal/mole would probably be as good as anything.

Furthermore, there is reason to suspect that as temperature rises the Arrhenius parameters may change appreciably, due to a change in decomposition mechanism. This follows from the report by McMillen et al.,¹⁶ who carried out thermochemical estimations, very low pressure pyrolysis and mass spectral studies on gas phase HMX and dimethyl-N-nitroamine decomposition; their results were in agreement with the idea that at lower temperatures the principal reaction in the vapor phase was HONO elimination, and at higher temperatures N-NO₂ cleavage, with the cross-over point occurring at about 500°K or 300°C. If this is the case, it might be a good idea if possible to represent the low temperature reaction by the values given above. The high temperature N-NO₂ cleavage reaction could be represented by the parameters estimated by Shaw and Walker²⁷ for N-NO₂ cleavage of HMX: $\log A$ (sec^{-1}) = 16.4 and E_a = 46.2 kcal/mole. For RDX E_a should be about the same but $\log A$ might be expected to be lowered from 16.40 to 16.28 since RDX has only three equivalent N-NO₂ groupings. If possible it would probably be best for modelers to incorporate this possible mechanism shift by representing low temperature reactions as proceeding on the basis of whatever temperature is predicted by the model under consideration. Note also that the exact location of the crossover point is uncertain; thus Shaw and Walker,²⁷ using a somewhat different set of parameters, got a crossover point of ca 60°C. In closing, we

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

point out again that there is a need for more data on the gas-phase decomposition of both HMX and RDX, especially in the high-temperature range, where $N-NO_2$ cleavage may become important.

Available data on gas-phase decomposition of nitramines other than HMX and RDX has been summarized by the SRI group,¹⁶ who also carried out additional measurements themselves, on dimethylnitramine and HMX. The literature²⁸⁻³¹ activation energies and frequency factors varied widely (E_a values reported for dimethylnitramine varied from 37 to 53 kcal/mole, for example), and were generally interpreted as being consistent with $\log A(\text{sec}^{-1}) = 12.4$ and $E_a = 35-39$ kcal/mole, or with $\log A(\text{sec}^{-1}) = 16.5$ and $E_a = 43-48$ kcal/mole. These values were of interest because they are characteristic of HONO elimination, and of $N-NO_2$ cleavage respectively. The SRI workers interpreted their results in terms of temperature-variation of the relative importance of these two mechanisms, see the preceding paragraph. However, the role of wall reactions seems uncertain at this point. As pointed out by the SRI workers,¹⁶ the apparent lack of surface effects on HMX decomposition seems puzzling, since dimethylnitramine decomposed faster with a normally aged or oxygen cleaned surface than with a carbon-coated surface. On the other hand, the decomposition rate of N-methyl-N-chloromethylnitramine was unaffected by increasing the specific surface area of the container by over an order of magnitude,³¹ and Figure 1 of Reference 30 suggests that decomposition kinetics of diethylnitramine were not greatly affected by filling the reaction vessel with glass packing. The explanation for these results seems uncertain; differences in pressure between experiments may make a difference, or possibly the surface reaction has a steric requirement that is satisfied only by the relatively unhindered dimethylnitramine. In any case, there is clearly a need for further work on the nature and occurrence of surface reactions in the gas phase decomposition of gaseous nitramines, if the gas-phase decomposition itself is to be understood.

B. Liquid Phase

The activation energy and frequency factors from the four apparently most reliable data sources on decomposition of liquid RDX have been described in Appendix C and accompanying discussion. A plot of the data for all four sources on one axis is given in Figure 1, and a statistical analysis of the

²⁸J. M. Fluornoy, "Thermal Decomposition of Gaseous Dimethylnitramine," J. Chem. Phys., Vol. 36, p. 1106, 1962.

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

³⁰B. 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, (Eng. Transl. p. 1405), 1967.

³¹B. L. Korsunskii, F. I. Dubovitskii and V. I. Losenova, "Thermal Decomposition Kinetics of N-Methyl-N-Chloromethylnitramine," Russian J. Phys. Chem., Vol. 43, p. 645, 1969.

points for all four sources by the procedure of Cvetanovic and Singleton (pp. 19-26) gave $A = 2.46 \times 10^{18}$ ($\log A = 18.668$) and $E_a = 47.8$ kcal/mole; these are our suggested values for decomposition of neat liquid RDX.

The values for neat liquid HMX were similarly discussed in the discussion accompanying Appendix B. The most reliable values^{9,13,32} are those that were plotted (Figure 3), and analyzed similarly to the RDX values giving values for $\log A$ and E_a which could possibly be presented as recommended values for modeling studies involving decomposition of pure liquid HMX. Note, however, that while the picture of concurrent gas and liquid phase reactions^{12,14} still seems to hold for RDX, it has recently begun to appear that the situation for HMX may be more complicated,^{32,33} and until this situation is understood better than at present, it may be a good idea to just use Robertson's manometric data⁹ as the best data for decomposition of neat liquid HMX: as shown in Appendix B, this gives $E_a = 53.1$ kcal/mole and $\log A$ (sec^{-1}) = 19.950. Note also that the values of $\log A$ (sec^{-1}) (= 21-21.5) obtained from all three sets of data together seem unreasonably high. Alternatively, Robertson's values of $E_a = 52.7$ kcal/mole and $\log A$ (sec^{-1}) = 19.7 could be used, especially since some of the discrepancy between the two sets was presumably introduced by the present writer in the course of reading numbers off Robertson's published graph.

³²R. J. Powers, AFATL, Eglin AFB, FL, Private Communication, 1980.

³³R. N. Rogers, Los Alamos Scientific Laboratories, Private Communication, 1980.

Activation energies for thermal decomposition of nitramines other than HMX and RDX^{10,34-39} in the neat liquid state are generally in the range 40±5 kcal/mole, with frequency factors correspondingly decreased. The values have been observed to decrease with increasing confinement in at least one case,³⁵ namely that of di-(2-nitroxyethyl)-N-nitroamine; this was attributed³⁵ to autoacceleration due to a combination of hydrolysis and oxidation involving water and NO₂ formed in the decomposition.

C. Solution-Phase Decomposition of RDX and HMX

Activation energies and log A for solution phase decomposition of HMX and RDX are summarized in Appendix B (HMX) and Appendix C (RDX). Like the gas-phase values the values for frequency factors and activation energy are generally lower for decomposition in solution than in pure liquid. There was enough data on the decomposition of RDX in solution in TNT to allow statistical analysis by the procedure of Cvetanovic and Singleton; a plot is given in Figure 5. The line for the three studies at concentration of 20-60% falls above the line defined by the studies of Robertson (carried out at concentrations of 1-5% RDX) within the region studied experimentally, although the frequency factor for the 20-60% points is lower than that for the 1-5% points; apparently there is a line crossing resulting from a slightly higher activation energy for the 1-5% studies. It is not certain whether this line crossing is real or is an artifact resulting from scatter in the experimental data. If, as it does not seem altogether unreasonable, the line-crossing is a artifact, then it would appear that the studies at 20-60% concentration have a frequency factor higher by a factor of ca 2-3 than the studies at 1-5% RDX.

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- ³⁴F. I. Dubovitskii, G. B. Manelis and L. P. Smirnov, "Kinetics of the Thermal Decomposition of N-Methyl-N, 2, 4, 6-Tetranitroaniline (Tetryl)," Russian Journal of Physical Chemistry, Vol. 35, p. 255, 1961.
- ³⁵F. I. Dubovitskii, Yu. I. Rubtsov, V. V. Barykin and G. B. Manelis, "Kinetics of Thermal Decomposition of Diethylnitramine Dinitrate," Bull. Acad. Sci. USSR, Div. Chem. Sci., p. 1126, 1960.
- ³⁶B. S. Svetlov and B. A. Lur'e, "Thermal Decomposition of Di(nitroxyethyl) nitramine," Russian Journal of Physical Chemistry, Vol. 37, p. 1073, 1963.
- ³⁷N. 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," Russian Journal of Physical Chemistry, Vol. 44, p. 22.
- ³⁸B. L. Korsunskii, L. Ya. Kiseleva, V. I. Ramushev and F. I. Dubovitskii, "Kinetics of the Thermal Decomposition of bis-(2,2-Dinitropropyl)-N-nitroamine," Izv. Akad. Nauk. SSSR, Ser. Khim., p. 1778, (Eng. Transl., p. 1699) 1974.
- ³⁹G. V. Sitonin, B. L. Korsunskii, N. F. Pyamakov, Y. G. Shvaiko, I. Sh. Abrahmov and F. I. Dubovitskii, "The Kinetics of the Thermal Decomposition of N,N-Dinitropiperazine and 1,3-Dinitro-1,3-Diazacyclopentane," Izv. Akad. Nauk. SSSR, Ser. Khim., p. 311, (Engl. Transl., p. 284) 1979.

However, the possibility of a systematic error in the 1-5% studies should be kept in mind, since these studies are all taken from a single publication. Continuing this possible trend, the frequency factor for decomposition of neat liquid RDX is considerably higher than for the reactions in solution ($2.46 \times 10^{18} \text{ sec}^{-1}$, Figure 1). The values for gas-phase decomposition (Table, p. 26-27) are also lower than for the neat liquid; possible reasons for this increase in frequency factor with concentration include (a) a difference in mechanism of energy transfer leading to an increase with RDX concentration in the efficiency of energy transfer into RDX molecules; (b) an increase with RDX concentration in the importance of bimolecular follow-up steps such as those discussed in our discussions^{2a} of possible mechanisms involved in HMX and RDX decomposition; and (c) catalysis of TNT decomposition by solute RDX.⁴⁰

For both HMX and RDX, the activation energies for decomposition in solution (Appendices B, C and Figure 5) are generally lower (ca 40-45 kcal/mole) than those (ca 50 kcal/mole) for decomposition in the neat liquid phase (Appendices B, C and Figures 1 and 3). The best values for the vapor-phase decomposition of both compounds are also lower than for the neat liquid. Possible reasons for this include the following: (a) the mechanism changes from one unimolecular mechanism to another on going from gas phase or solution to neat liquid HMX; (b) the mechanism stays the same, but neat liquid HMX and RDX exerts a different solvent effect than the inert solvents studied; (c) the mechanism shifts from unimolecular in the gas-phase or in dilute solutions, to bimolecular, possibly chain or autocatalytic, in neat liquid HMX or RDX. Possible bimolecular steps might include reaction of a nitro group on one molecule of HMX or RDX with a CH_2 grouping of another HMX or RDX molecule, as illustrated in Scheme VI of Reference 2-A, or electron transfer between two molecules of HMX or RDX. A bimolecular first step for the decomposition in the neat liquid is not inconsistent with the observed first-order kinetics, since the concentration of HMX/RDX seen by any given molecule of HMX/RDX would remain constant throughout the reaction; hence the reaction would be zero-order in the second molecule of HMX/RDX and first-order overall. However, (c) seems unlikely in view of the high ($\log A = 10^{18} - 10^{20}$) frequency factors for the liquid-phase reaction, and of the apparent first-order kinetics in solution. See also the discussion of cage effects in Note Added in Proof No. 2.

In connection with the discussion of the decomposition of RDX in TNT solution, it seems worth mentioning that while RDX catalyzed the thermal decomposition of TNT,⁴⁰ the TNT acts as an inert solvent with regard to the decomposing RDX.^{9,40}

⁴⁰W. P. Colman and F. C. Rauch, "Studies on Composition B," Final Report, Contract No. DAAA21-70-0531, American Cyanamid Company, February 1971 (AD-881 190).

The above values for $\log A$ and E_a are approximately in agreement with those measured⁴¹ for a series of substituted dialkylnitroamines in dibutylphthalate solutions; these measurements gave $\log A(\text{sec}^{-1}) = 13.7-14.4$ and $E_a = 40-42$ kcal/mole. However studies on a series of 4-substituted-2,6-dinitrophenylmethyl-N-nitroamines in dinitrobenzene solution gave somewhat lower values: $\log A(\text{sec}^{-1}) = 12.4-13.5$ and $E_a = 32-36$ kcal/mole.

D. Decomposition of "Solid" HMX and RDX

The reason for putting quotation marks around the word "solid" is that in most low temperature (100-300°C) work the decomposition of RDX and (possibly with somewhat less certainty) HMX below their melting point may well involve the liquid and vapor phases in addition to, if not instead of, true solid-state decomposition. For example, Cosgrove and Owen⁴²⁻⁴⁴ found that the rate of decomposition of RDX at 195°C (ca 5-10° below its melting point) 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 pressure of inert gases, for example, nitrogen. They concluded that RDX does not decompose in the solid state to any significant degree at that temperature. Rather, in the early stages of the decomposition, the RDX was considered to vaporize and the vapor to decompose to liquid products which dissolve the solid and thus accelerate the decomposition.

In agreement with this, studies⁴⁵ on decomposition of RDX at high (up to 5 kbar) pressures indicate that decomposition of RDX is much slower in the solid state just below its melting point, than in the liquid state at its melting point.

Since HMX and RDX are very similar chemically, these results raise strong suspicions that HMX may behave in a similar manner when decomposed below its

⁴¹R. S. Stepanov, V. N. Shan'ko, I. P. Medvetskaya, and V. M. Gorodetskaya, "Kinetics and Mechanism of Thermal Degradation of Certain Alkyl- and Arylalkyl nitroamines," 5th All-Union Symposium on Combustion and Detonation, p. 56-9. (FTD-JD(RS)T-1208-78) (AD-B033 622), Sept. 1977.

⁴²J. D. Cosgrove and A. J. Owen, "The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-triazine (RDX)," Chem. Commun., Vol. 286, 1968.

⁴³J. 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," Combust. Flame, Vol. 22, p. 13, 1974.

⁴⁴J. 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," Combust. Flame, Vol. 22, p. 19, 1974.

⁴⁵P. J. Miller, G. W. Naufflett, D. W. Carlson and J. W. Brasch, "The Thermal Decomposition of 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX) and RDX_{d6} at High Pressures," Proceedings of the 17th JANNAF Combustion Meeting, Vol. II, p. 479, Hampton, VA, 22-26 Sept. 1980.

melting point. In fact, Maksimov⁴⁶ found that HMX did behave similarly to RDX when it was decomposed below its melting point, although in the case of HMX, the volume dependence was not as great as for RDX. Thus the true solid-state decomposition may well be more important for HMX than for RDX, possibly because HMX is solid at temperatures higher than the melting point of RDX, or because of lower vapor pressure for HMX than for RDX at the temperatures of the respective experiments.

However, there is another point of view in the question of vapor-phase involvement in "solid" HMX/RDX decomposition: Batten⁴⁷⁻⁵⁰ has also studied the decomposition of RDX below the melting point and has interpreted his 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 Owen⁴³ argued again in favor of the gas-phase decomposition, saying that the results quoted by Batten are not at variance with the suggestion^{42,43} 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 that it is worth noting that Batten⁴⁷ 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 vaporization and 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, it seems to this writer that the increase in rate with increasing reactor volume, or amount of free space, spreading, etc., and its independence on 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

⁴⁶Yu. Ya. Maksimov, Tr. Mosk. Khim-Tekhnol. Inst. No. 53, p.73, 1967; see Chem. Abstr., Vol. 68, p. 41742r. Translated by H. J. Dahlby, Los Alamos, Report LA-TR-68-30, Los Alamos, NM, 1968.

⁴⁷J. 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.

⁴⁸J. 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.

⁴⁹J. 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.

⁵⁰J. 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.

decomposition residue is apparently a positive catalyst^{9,49,51} and that such apparent products as formaldehyde, NO₂ and hydroxymethylformamide can catalyze the reaction either positively or negatively depending on the exact reaction conditions (see for example References 44 and 49). Thus, it may well be possible to explain just about any set of results by some combination of inhibition and catalysis of the condensed phase reaction by gaseous products such as formaldehyde and NO₂, especially when the possibility of reaction between these products is considered.

Clearly, there is a need for more work on the relative roles of vapor-phase, liquid-phase, and true solid-state reaction in the decomposition of HMX and RDX below their melting points, in order that the contribution due to true solid-state decomposition can be extracted and, extrapolated intelligently to combustion and explosion conditions. One possible type of experiment that might help here would be to use various amounts of sample in varying amounts 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.

Thus, these below-melting point activation parameters are actually overall numbers for complex processes, and it is difficult to relate them to any single, homogeneous chemical reaction. Garn²⁴ has suggested the use of the term "Temperature Coefficient of Reaction" rather than "Activation Energy" in situations of this type; the present writer agrees with this suggestion.

Furthermore, Arrhenius parameters for decomposition below the melting point seem to be dependent on such factors as degree of spreading of the sample, which are difficult to evaluate in view of the limited information given in many of the reports. For example, Batten and Murdie⁴⁸ found that activation energies for decomposition of RDX below its melting point were dependent on the degree of spreading of the sample.

For these reasons and because of time limitations, a complete discussion and evaluation of Arrhenius parameters for decomposition of nominally "solid" HMX and RDX below the melting point does not, at this time, seem justified in terms of its relevance to any true solid-state decomposition of propellants that may occur under combustion conditions. Consequently, although for future reference an attempt has been made at including all available activation energies for decomposition of HMX and RDX below their melting points in Appendix D, they will not be discussed in detail; only a few trends and particularly relevant points will be considered.

It seems worthwhile to begin the discussion of these points by saying something about the relative rates of the gas, liquid and solid decomposition and their relations to combustion modeling efforts. The above-mentioned work

⁵¹B. Suryanarayana and R. J. Graybush, "Thermal Decomposition of 1,3,5,7-tetranitro-1,3,5-Tetrazacyclooctane (HMX); A Mass Spectrometric Study of the Products from β -HMX," Ind. Chim. Belg., Vol. 32, Spec. No. Part 3, p. 647, 1967.

of Cosgrove and Owen⁴²⁻⁴⁴ indicates that the gas-phase reaction is much faster than the solid-state decomposition. Furthermore, the liquid-phase decomposition is faster than the solid-phase reaction,^{3,11,14,52} even up to pressures of 5 kbar.⁴⁵ A liquid/solid rate ratio of 10/1 or greater seems reasonable for RDX at its melting point, based on examination of the pressure-time data in Figure 8 of Reference 3. Also, decomposition of HMX accelerates sharply when it is heated past its melting point. In view of these results, it seems quite reasonable for combustion modelers to assume that the solid-phase decomposes relatively slowly, and that primary decomposition takes place, almost entirely in the liquid layer or in the vapor phase. However some, albeit slow, solid state reaction apparently does take place,⁵³ even for RDX and pressures and temperatures of combustion are much higher than those at which the decomposition studies are carried out; it is quite possible that these higher temperatures and pressures may lead to accelerated solid state decomposition. This point seems especially relevant to conditions where there is no liquid layer. It would also help to know whether at the heating rates involved in combustion, HMX has time to transform from the β - to the δ -polymorph.

Another interesting trend is that, in many cases (Appendix D) HMX exhibits a change in activation energy in the region 240-260°C. Sometimes there are two changes separated by ca 10-20°. This break appears in the results of studies by thermal analysis and or manometric studies, so it is not a peculiarity of any one experimental method. One possible explanation for this might be as follows: Goshgarian (p. 13 of Reference 11) has observed an endotherm in DSC curves of HMX samples, as well as increased gas evolution, at ca 250°C. He tentatively attributes this to melting of β -HMX left over from the β - δ phase transition at ca 190°C, apparently following an earlier report by Tetstov and McCrone⁵⁴ that some β -HMX survives the β - δ phase transition and melts at 240°C; these observations are described more fully in Reference 54 of the present report than in Reference 6 of Reference 11. Photographs of this effect are shown on pages 19-21 of Reference 1. If the β -HMX melts, it presumably exhibits a tendency to solidify into δ -HMX, seeded by the δ -HMX already present. While liquid HMX was present it might decompose at a faster (preceding paragraph) rate than the solid HMX and changes with temperature in the amount of liquid HMX present might cause a shift in temperature-dependence of the decomposition rate, as observed. Even if the β -HMX melt hypothesis proves incorrect, the activation energy shift might still be related to the endotherm and increase in gas evolution at 250°C.

⁵²T. B. Joyner, "Thermal Decomposition of Explosives. Part I. Effect of Asphalt on the Decomposition of Asphalt-Bearing Explosives," NWC TP 4709, March 1969 (AD-500 573).

⁵³J. 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.

⁵⁴A. S. Tetstov and W. C. McCrone, Jr., "The Microscopical Study of Polymorph Stability Diagrams," Miscrosc Cryst-Front, Vol. 15, p. 13, 1965.

Another interesting aspect is that DSC and Flow Reactor Mass Spectrometric (FRMS) studies on pure HMX and RDX decomposing at or very close to their melting points (Appendix D) often show very high activation energies of 100-200 kcal/mole or more. These have been attributed^{55,56} to thermal chain reactions,⁵⁷ or to the complexity of the decomposition reaction⁵⁷ or to the occurrence of processes involving the simultaneous breaking of more than one chemical bond,¹¹ although this last seems more likely to lower than to raise the activation energy. In view of the faster decomposition rate for the liquid than for the solid state, the following explanation might also be worth considering: over the melting range of HMX (or RDX) a small increase in temperature will cause some of the solid to melt. Because of the greater decomposition rate of the liquid, this causes the rate to increase, resulting in an artificially large temperature-dependence of the decomposition rate, until the solid is entirely melted and the temperature dependence of the decomposition becomes that of the neat liquid.

V. CHEMICAL MECHANISMS

A. Autocatalysis

When decomposition takes place under very confined conditions, activation energies for liquid decomposition of HMX and RDX can apparently be lowered due to autocatalysis by gas-phase products. For example, when RDX was decomposed¹⁷ in an open (one hole in lid) DSC pan, E_a was ca 41 kcal/mole but when the decomposition took place in a closed pan, the rate was faster and activation energy was ca 10-15 kcal/mole lower. A similar pattern has also been observed for dinitroxydiethylnitramine; it was attributed by the authors to a combination of hydrolysis and oxidation by NO_2 formed in the decomposition. A similar effect may hold at high pressure, where products would have a more difficult time escaping from the surface. Thus, serious consideration should be given to the possibility that apparent activation energy (or temperature coefficient of reaction) might be lower under the higher pressure characteristic of combustion conditions than the values given above. However, it is difficult to rule out the possibility that the above effects might be heat effects due to confinement of reactive products near the starting material. Also, under the higher temperatures of combustion conditions, higher activation-energy unimolecular reactions might predominate.

⁵⁵R. N. Rogers and E. D. Morris, Jr., "On Estimating Activation Energies with a Differential Scanning Calorimeter," Anal. Chem., Vol. 38, p. 412, 1966.

⁵⁶P. G. Hall, "Thermal Decomposition and Phase Transitions in Solid Nitramines," J. Chem. Soc., Faraday Trans. Pt. 2, Vol. 67, p. 556, 1971.

⁵⁷B. V. Novazhilov, "The Temperature Dependence of the Kinetic Characteristics of Exothermic Reactions in the Condensed Phase," Dokl. Akad. Nauk. SSSR, Vol. 154, p. 106, 1964.

Dimethylnitramine decomposition also appeared subject to autocatalysis by NO_2 .^{29,58} Thus, other nitramines also seem to show autocatalysis. Furthermore, HMX and RDX decompositions have been reported to be accelerated or retarded by addition of known decomposition products such as formaldehyde and oxides of nitrogen.^{44,46,49}

There are also a number of reports (see for example References 9, 11, 49, 51) of residues or stable products that are capable of accelerating the decomposition or of lowering the decomposition temperature.

More work is needed in the area of autocatalysis of nitramine, HMX and RDX decomposition. Since many of the references cited in the preceding paragraph do not specifically allude to the possibility of surface catalysis of gas-phase reactions, and since the SRI workers¹⁶ found that at least some of the rates were affected by the nature of the container surface, it would be helpful to have a better understanding of the role of surface reactions here.

B. Initial Step

As discussed previously,² these are complex systems. However, at present, the available data seems consistent with the idea that the most likely mechanism for the initial decomposition in the gaseous phase is a combination of HONO elimination at lower temperatures and N- NO_2 cleavage at higher temperatures, with the crossover point occurring at about 300°C ¹⁶ or 600°K .²⁷ This is based on thermochemical estimates of temperature-variation of relative rates for the possible decomposition steps,¹⁶ on comparison of the preliminary best values (Table) for activation energies and frequency factors with values estimated²⁷ for the individual processes, and on the results of very low pressure pyrolysis studies¹⁶ on dimethylnitramine decomposition.

For decomposition in the pure liquid phase, the above values for the activation energies for decomposition of RDX (47.8 kcal/mole) and HMX (53-57 kcal/mole) seem reasonably close to the values estimated²⁷ for gas-phase N- NO_2 cleavage (46.2 kcal/mole), although the value for HMX does seem uncomfortably close to the 60 kcal/mole estimated²⁷ for gas-phase unassisted C-N cleavage and is also associated with a $\log A$ (sec^{-1}) value of $10^{20} - 10^{21}$, which seems unexpectedly high. However, without more detailed knowledge of the molecular and electronic structure of the transition state, it is difficult to evaluate the effect of such factors as (a) the electrostatic effect of the other N- NO_2 groupings in the starting HMX or RDX, or (b) "solvent" as opposed to the gas-phase effects of neat liquid HMX and RDX on the observed activation energies.

The activation energies for decomposition of HMX and RDX in solution are difficult to interpret. They tend to be around 40 kcal/mole, which is several kcal/mole lower than those of the neat liquids, although not quite as low as the vapor-phase values (ca 30-35 kcal/mole). The reasons for this are uncertain, in view of the difficulty in evaluating the solvent effects on

⁵⁸B. 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 (Engl. Transl., p. 436).

these activation energies. One possible explanation might be that in the gas-phase and in solvents studied to date the first step is HONO elimination, while in the neat liquid it is N-NO₂ cleavage, although without more information it is difficult to suggest why the "solvent effect" exerted by neat liquid HMX or RDX should be so different from the other solvents. Note, however, that the studies have apparently been carried out in a temperature range where the intrinsic (gas phase) reactivities toward HONO elimination and N-NO₂ cleavage are near the crossover point; thus small variations in solvent effects could conceivably have more dramatic effects on the nature of the principal pathway.

Possibly the main conclusion to be drawn from the activation energies is that the observed values for HMX and RDX decomposition in the gaseous and liquid phases seem to be in a region (ca 30-50 kcal/mole) that is more characteristic of HONO elimination and N-NO₂ cleavage than of the higher values estimated²⁷ for C-N cleavage, although it is difficult to rule out all possible variations on the general theme of C-N cleavage, such as C-N cleavage involving two or more bonds simultaneously, especially since unexpectedly low activation energies for depolymerization of trioxane to formaldehyde (a reasonable model for depolymerization of RDX to N-nitroformine) have been interpreted in terms of a concerted ring cleavage.^{59,60} However, some degree of N-N cleavage must be capable of taking place, since isotope-labeling studies on mixtures of un- and fully N-15 labelled HMX³² show some scrambling of the labelled and unlabelled nitrogens. The scrambling most likely takes place during the primary decomposition step, since HMX labelled in the nitro group with N-15 decomposes to give unscrambled N₂O with the labelled nitrogen still attached to the oxygen.^{32,61} The most straightforward explanation for the scrambling³² is a preliminary equilibrium involving dissociation and recombination of the N-NO₂ bond.

However, it should be remembered that the activation energy for the decomposition of neat liquid HMX and RDX may be influenced by factors other than the occurrence of a single, homogeneous process. For example, it has

⁵⁹S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas-Phase Unimolecular Reactions," NSRDS-NBS 21, p. 314ff. For sale by the Superintendent of Documents, US Printing Office, Washington, DC 20402, February 1970.

⁶⁰S. W. Benson, "Thermochemical Kinetics," Wiley Interscience, New York, p. 117, 1976.

⁶¹B. 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.

been suggested^{62,63} that the higher values observed for decomposition of nitrate esters in the liquid than in the vapor phase may be due to a decrease with increasing temperature, in the inhibition of the reaction due to recombination of NO_2 and alkoxy radical formed in the primary O- NO_2 bond breaking step. This decrease was suggested^{62,63} to be due to increased mobility and to increased tendency for the NO_2 to undergo further reaction rather than recombination, as temperature increases. Like the nitrate esters, the nitramines exhibit higher activation energies for decomposition in the liquid than in the vapor phase, although in the case of the nitramines, the gas-phase activation energies and frequency factors seem more characteristic of HONO elimination than of N- NO_2 cleavage. However the above "cage" effect could conceivably be raising the neat-liquid activation energies for HMX and RDX decomposition. In this connection it seems worth mentioning that nitroalkanes appear to undergo HONO elimination rather than C-Nitro cleavage in the gas phase, at least up to temperatures of about 450°C.^{64,65}

The frequency factors are somewhat more difficult to interpret, especially the condensed phase values. The frequency factors for the neat-liquid decompositions (Table) RDX, $\log A (\text{sec}^{-1}) = 18.7$; HMX $\log A (\text{sec}^{-1}) = 19-22$ seem unexpectedly high for a first order reaction. Although this is consistent with the occurrence of bimolecular follow-up reactions of the type discussed previously,² it should be remembered that little if anything is known about energy transfer processes in liquid HMX and RDX. These high frequency factors seem inconsistent with bimolecular initial steps, or with anchimerically assisted C-N cleavage, since such mechanisms would be expected to lead to low frequency factors due to the high degree of ordering in the transition states.

C. Unimolecular Follow-Up Steps

Some possible unimolecular follow-up steps have been discussed previously;² these include (a) ring opening by β -cleavage reactions, and elimination of N-Nitroformimine ($\text{H}_2\text{C}=\text{NNO}_2$) from the ring-opened open-chain intermediates by further β -cleavage reactions; and (b) further reaction of $\text{H}_2\text{C}=\text{NNO}_2$, most likely to give formaldehyde and N_2O (both of which are known (see for example References 1, 7-9, 43, 44 and 51) to be formed in large

⁶²C. E. Waring and G. Krastins, "The Kinetics and Mechanism of the Thermal Decomposition of Nitroglycerin," J. Phys. Chem., Vol. 74, p. 999., 1970.

⁶³R. A. Fifer, "A Hypothesis for the Phase Dependence of the Decomposition Rate Constants of Propellant Molecules," in the abstract booklet for ONR-AFOSR-ARO Workshop on Fundamental Research Directions for the Decomposition of Energetic Materials, Berkeley, CA, January 1981.

⁶⁴R. G. Coombes, "Nitro and Nitroso Compounds," D. Barton and W. D. Ollis, ed., Comprehensive Organic Chemistry, Pergamon Press, Elmsford, NY, Vol. 2, Chapter 7, p. 439, 1979.

⁶⁵G. M. Nazin, G. B. Manelis and F. I. Dubovitskii, "Thermal Decomposition of Aliphatic Nitro-Compounds," Russ. Chem. Rev., Vol. 37, p. 603, 1968.

amounts in HMX and RDX decomposition), although at higher temperatures it is possible that N-N cleavage of N-Nitroformimine to NO_2 and H_2CN might also occur.

D. Bimolecular Follow-up Steps

As discussed earlier,² possible bimolecular follow-up steps include (a) abstraction of hydrogen from starting HMX and RDX by free radicals formed in the reaction, and (b) attack on nitro oxygen by free radicals formed in the reaction, possibly followed by N-O or N-N cleavage of the resulting oxynitroxide radical to give a nitrosoamine or a denitro nitrogen-centered radical. Available literature analogies and thermo-chemical estimates² are consistent with the idea that these are both reasonable follow-up steps. Possibly steps such as these, involving radicals formed either (a) directly from HMX or RDX decomposition or (b) by reaction between primary products such as NO_2 or $\text{H}_2\text{C=O}$, are at least partly responsible for the high frequency factors and apparent autocatalysis of nitramine decomposition referred to above.

More work is needed on all aspects of HMX and RDX decomposition mechanisms. While the above and similar mechanisms seem reasonable and consistent to the present writer, the individual mechanisms are not firmly established and in fact are at present best considered only as a basis for further discussion. The formation of other known products of HMX and RDX decomposition, such as N_2 and NO , can be explained by adaptations or combinations of the above mechanisms. Products such as O , O_2 , and H_2O , could be formed by reaction among primary products, for example NO_2 and H_2CO .

E. Extension to Combustion Conditions

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

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; 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 earlier in the present report; these are the apparent temperature dependence of the relative rate of N- NO_2 cleavage and of HONO elimination in the gas-

phase decomposition,¹⁶ and the possible tendency for cleavage of $\text{H}_2\text{C}=\text{NNO}_2$ to H_2CN and NO_2 to become more important relative to formation of N_2O and H_2CO , as temperature rises. 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 first-order 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 or heating rate. The temperature and pressure effects on the unimolecular/bimolecular ratio apparently work in opposite direction but complete compensation is of course 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 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.

VI. WORK NEEDED

More work is needed in a number of areas. Several of these seem particularly worth mentioning, among them the following:

1. The first step of the decomposition of 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, $\text{N}-\text{NO}_2$ cleavage, $\text{C}-\text{N}$ 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^{66,67} at least for the vapor-phase decomposition.

⁶⁶B. 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.

⁶⁷K. 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.

2. There seems to be very little work available on the gas-phase decomposition of HMX and RDX. There is a need for more understanding of this with regard to both the kinetics and the product distributions, especially since the gas-phase decomposition would most reflect the intrinsic behavior of the 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. In addition to techniques such as those described in References 16 and 66, laser-powered homogeneous pyrolysis⁶⁷ 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.

3. There is a need for improved understanding of the solid-phase decomposition. In view of the discussions of Cosgrove and Owen⁴²⁻⁴⁴ and of Batten,⁴⁷ it seems clear that in studying the behavior of HMX and RDX below their melting points, care should be taken to separate the true solid-state decomposition from concurrent sublimation followed by gas-phase decomposition and to understand the relative roles of gas, liquid, and solid-state decomposition; see the discussion on pages 31-35 of the present report.

4. 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.

5. 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.^{44,46,49,68} See also the discussion above under "Autocatalysis" and references cited therein.

6. There is also 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,⁶⁹ 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

⁶⁸D. 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, 1976., Pub. 1977.

⁶⁹D. A. Flanigan and B. B. Stokes, "HMX Deflagration and Flame Characterization. Volume I. Phase II Nitramine Decomposition and Deflagration Characterization," Thiokol Corporation, Huntsville Division, Huntsville, AL, Report AFRPL-TR-79-94, October 1980 (AD-B053 058L).

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,⁷⁰ 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 report¹⁷ that the activation energy for decomposition of RDX was ca 15 kcal/mole lower when measured by closed-pan than by open-pan DSC. Pressure effects on product distributions from HMX and RDX decomposition have been summarized briefly.⁷¹ In view of the differences between experimental conditions and results reported in these studies,^{11,69-71} it is clear the pressure effects on HMX and RDX decomposition are far from well understood, and much more work in this area is required.

VII. NOTES ADDED IN PROOF

A. Note Added in Proof No. 1 While this report was being proofread, the author became aware of a review article⁷² in the Russian literature; although as this is written this review probably will not be available in English translation for several months, it seems worth while to call it to the attention of anyone reading the present report.

B. Note Added in Proof No. 2 Brill and Karpowicz^{73,74} have recently suggested that the decomposition reactions of condensed-phase HMX and RDX may be governed by release of intermolecular interactions occurring prior to unimolecular decomposition, rather than by the decomposition steps themselves. This is based on large (ca 40-50 kcal/mole) activation energies observed for phase transitions among the solid polymorphic forms of HMX; Brill and Karpowicz feel that the large activation energies for these phase transitions (much larger than the net energies of reaction for the same transitions) represent energy needed for "freeing-up" of HMX or RDX molecules

⁷⁰E. R. Lee, R. H. Sanborn and H. D. Stromberg, "Thermal Decomposition of High Explosives at Static Pressures 10-50 Kilobars," Proceedings 5th Symposium (International) on Detonation, 1970, p.331-337, for sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

⁷¹M. A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Product Distributions from HMX and RDX Decomposition," Proceedings 18th JANNAF Combustion Meeting, Pasadena, CA, Vol. 2, p. 395, CPIA Publication 347, October 19-23, 1981.

⁷²F. I. Dubovitskii and B. L. Korsunskii, "Thermal Decomposition Kinetics of N-Nitro Compounds," Usp. Khim., Vol. 50, p. 1828, 1981, cited in Current Contents, Physical, Chemical and Earth Sciences, Vol. 22, p.144, No. 2, January 11, 1982.

⁷³T. B. Brill and R. J. Karpowicz, "Solid Phase Transition Kinetics The Role of Intermolecular Forces in the Condensed-Phase Decomposition of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine," J. Phys. Chem., Vol. 86, p. 4260-5, 1982.

⁷⁴R. J. Karpowicz, L. S. Gelfand and T. B. Brill, "Application of Solid-Phase Transition Kinetics to the Properties of HMX," AIAA Journal, Vol. 21, p. 310-12, 1983.

which presumably must take place before decomposition. The magnitudes of the energies involved are such as to raise at least the possibility that the freeing-up of the molecules may be the rate-determining step, at least for the solid-state decomposition.

Note that this treatment depends critically on the assumption that the rate constants measured in References 73 and 74 and attributed to solid-solid phase transitions in HMX, are actually rate constants for true first-order processes and hence that the activation energies are also true activation energies for a specific first-order process, not merely effective temperature coefficients of reaction (see Reference 24) for a complicated assembly of processes.

In addition, Fifer⁷⁵ has published a more recent and accessible discussion than reference⁶³ of the cage effect hypothesis. The basic idea of this hypothesis is that the relative ordering of the rates and Arrhenius parameters for the gas, liquid and solid-state thermal decomposition of nitramines and nitrate esters (Gas phase rates faster than liquid, which in turn are faster than solid-state rates of decomposition; Arrhenius parameters follow the opposite ordering) is explainable in terms of greater confinement of radicals (such as NO_2 and denitro-HMX/RDX) formed in the initial step of decomposition. This is in agreement with recent work⁷⁶ on the thermolysis of 1,2-diphenylethane.

Note that this hypothesis applies only to radical-producing reactions and not, for example, to HONO elimination. However, even if the gas-phase reaction were found ultimately to proceed via some other mechanism, for example HONO elimination, the cage-effect hypothesis might well still be useful to understand quantitative differences between the observed liquid-phase decomposition kinetics and parameters, and values reliably estimated for the hypothetical gas-phase radical pathways.

Furthermore it was argued⁷⁵ that a practical implication of the cage effect hypothesis was that at higher temperatures the condensed phase rates would approach those for the gas phase; so that at the higher temperature characteristic of combustion it might be a reasonable approximation to use the gas phase kinetic parameters to represent the condensed phase decomposition. The present writer suggests it may also be worthwhile to consider the possibility that, at the higher pressures characteristic of combustion, the density of the gas phase might be increased to the point where it might resemble the liquid more than what would be thought of at more moderate pressures as a vapor; if this is true, the system might exhibit behavior such that it would be the vapor phase that would assume Arrhenius parameters characteristic of the liquid, rather than the other way around.

⁷⁵R. A. Fifer, "Cage Effects in the Thermal Decomposition of Nitramines and Other Energetic Materials," Proceedings 19th JANNAF Combustion Meeting, Greenbelt, MD; Vol. I, CPIA Publication 366, p. 311-319, October 1982.

⁷⁶S. E. Stein, D. A. Robaugh, A. D. Alfieri and R. E. Miller, "Bond Homolysis in High-Temperature Fluids," J. Amer. Chem. Soc., Vol. 104, p. 6567-70, 1982.

At the very least, both of the effects⁷³⁻⁷⁶ described in the above paragraphs will have to be better understood than at present before Arrhenius parameters applicable to combustion conditions can be reliably derived from studies of decomposition under more moderate temperatures and pressures. It will also of course be necessary to understand the role of such factors as dielectric constant of the medium, and other types of solvent effects and intermolecular interactions.

C. Note Added in Proof No. 3 It also seems worthwhile to mention an interesting paper in which Burov and Nazin⁷⁷ have very recently reported some kinetic measurements on gas phase thermal decomposition of several nitramines including HMX and RDX. Other compounds studied included N,N-dinitropiperazine and 1,3-dinitrazacyclopentadiene. The decompositions of all of these compounds except HMX were studied in the presence of NO, addition of which noticeably affected the kinetics, resulting in lower rates by factors of 2 to 4 at 200°C, as well as noticeable changes in Arrhenius parameters; thus chain reactions or autocatalysis are apparently of some importance here. The decompositions were studied manometrically, at pressures of 0.05-0.1 mm Hg. Gas phase and solution kinetic measurements on the above nitramines as well as dimethyl and diethyl nitramines and N-nitropiperidine were summarized in a table.⁷⁷

The authors⁷⁷ make the interesting suggestion that differences in decomposition rates of these nitramines are determined by the configuration of the amino nitrogens, the more-rapidly decomposing, low-activation-energy compounds, including RDX, being those with tetrahedral or pyramidal nitrogens, while the slower-decomposing, higher activation energy compounds have trigonal coplanar nitrogens. This will be discussed further in a final, wrap-up portion of the present review, which will be devoted to chemical and physical mechanisms of decomposition.

It also seems worth mentioning that the authors of Reference 77 are of the opinion that the N-NO₂ bond dissociation energy of nitromethane is about 40 kcal/mole, giving as their authority a Russian book⁷⁸ which, as far as the present writer is aware, is not available in English translation. This value is considerably lower than the 46.2 kcal/mole estimated by Shaw and Walker for dimethylnitramine and applied also to HMX. Korsunskii and Dubovitskii⁷² also seem to feel that the N-NO₂ bond dissociation energy for simple nitramines is around 40 kcal/mole. This discrepancy should be checked into further, in view of the obvious importance of an accurate knowledge of the N-NO₂ dissociation energies of dimethylnitramine and other nitramines to the decomposition chemistry of these compounds. In view of the possible importance of wall reactions and autocatalysis, and of decomposition pathways such as HONO

⁷⁷Yu. M. Burov and G. M. Nazin, "Influence of Structure on Rate of Decomposition of Secondary Nitramines in the Gas Phase," Kinetika i Kataliz, Vol. 23, No. 1, pp. 12-17, 1982 (English Translation, p. 5-10).

⁷⁸L. V. Gurvich, G. V. Karachevtsev, V. N. Kondrat'ev, Yu. A. Lebedev, V. A. Dedvedev, V. K. Potapov and Yu. S. Khodiev, "Chemical Bond Rupture Energy, Ionization Potentials and Electron Affinity," Nauka, Moscow, 1974, (Reference 15 of reference 77 above).

elimination, this knowledge should be obtained from sources, such as thermochemical studies, that are independent of kinetic measurements on the decomposition reactions of the nitramines.

It seems worth noting that Reference 77 says that Shaw and Walker's estimated parameters for N-NO₂ bond dissociation were taken from a private communication concerning DMNA. The value of E was stated to have been adopted without change, and log A to have been multiplied by 4. However, an examination of Shaw and Walker's paper (Reference 27 of the present report) shows that they are based on heats of formation and frequency factors given in References 12-14 and 21 of Reference 27 of the present report; these references are not to any private communications but to two journal articles and to two standard compilations of data. In particular the N-NO₂ dissociation energy is based on, in addition to (CH₃)₂NNO₂,⁷⁹ heats of formation for (CH₃)₂N[•] and NO₂, which are the same as those given in standard compilations of data.^{80,81} Shaw and Walker also cite a number of reported values for the N-NO₂ bond dissociation energy, nearly all of which are higher than 40 kcal/mole, ranging from 47 to 66 kcal/mole. Thus the 46.2 kcal/mole estimated by Shaw and Walker for the N-NO₂ dissociation energy of dimethylnitramine seems to be reasonably well-founded in the literature.⁷⁷ However it would be most helpful to have access to the reference⁷⁸ cited⁷⁷ as supporting an upper limit of 170 kJ/mole (40.6 kcal/mole) for the N-NO₂ bond energy of dimethylnitramine; especially since additional measurements might lead to revision of the heats of formation on which the figure of 46.2 kcal/mole was based. The frequency factor (log A = 15.8) suggested by Shaw and Walker²⁷ was based on an average of values from decomposition of nitromethane and N₂O₄; possibly more elaborate thermochemical calculations would be helpful in arriving at a firmer value.

Activation energies and frequency factors (log A(sec⁻¹)) reported in Reference 77 were as follows: for RDX, 146.6 kJ/mole (35.04) kcal/mole) and 13.5 without NO; 167.6 kJ/mole (40.06 kcal/mole) (see footnote, p. 6 of Reference 77) and 15.6 with NO. For HMX, the values were 165.5 kJ/mole (39.56) kcal/mole) and 14.2 without added NO. N,N'-dinitropiperazine gave 160 kJ/mole (38.2 kcal/mole) and 13.6 alone, but 151.2 kJ/mole (36.14 kcal/mole) and 12.0 in the presence of NO, while 1,3-dinitrazacyclopentane gave 146.6 kJ/mole (35.04 kcal/mole) and 13.5 alone and 169.3 kJ/mole (40.46) kcal/mole) and 15.6 in the presence of NO.

When the results for RDX are plotted alongside those given in Figure 2, they do not fall on the same line as the other results plotted in Figure 2,

⁷⁹R. C. Cass, S. E. Fletcher, C. T. Mortimer, P. G. Quincey and H. D. Springall, "Heats of Combustion and Molecular Structure, Part IV. Aliphatic Nitroalkanes and Nitric Esters," *J. Chem. Soc.*, p. 958-63, 1958.

⁸⁰R. C. Weast and M. J. Astle, eds., *CRC Handbook of Chemistry and Physics*, p. F-204, 63rd. edition, CRC Press, Inc., Boca Raton, FL, 1982-1983.

⁸¹S. W. Benson, "Thermochemical Kinetics," 2nd. edition, Wiley, New York, NY, 1976, p. 292.

but lie on a parallel line, about 0.5 log unit below those plotted in the figure. However, they do not seem to fit the other points on the graph as well as the data of Belyaeva et al., judging from the degree of scatter when the line defined by the points of Reference 77 is extended through the other points.

There also seems to be a series of typographical errors in Table 1, column 6 of Reference 77; the values given do not match those calculated from the values of E and $\log A$ (sec^{-1}) in columns 4 and 5. The present writer recalculated the numbers in column 6 of Table 1 of reference 77 and obtained the following values: line 1, 0.268 instead of 4; line 2, 1.67 instead of 0.158; line 3, 5.0 instead of 0.525; line 4, 721 instead of 0.676; line 5, 2.12 instead of 0.2; line 6, 31.2 instead of 2.9; line 7, 22.5 instead of 2.24; line 8, 8.73 instead of 0.87; line 9, 530 instead of 50; line 10, 666 instead of 63; line 11, 207 instead of 20; line 12, 81.3 instead of 8; line 13, 1.7 instead of 0.56; line 14, 5.20 instead of 0.56; line 15, 255 instead of 2500; line 16, 8.50 instead of 0.8; line 17, 0.631 instead of 0.063; line 18, 8.64 instead of 0.83; line 19, 2.03 instead of 0.22; line 20, 24.5 instead of 2.5; line 21, 207 instead of 20; line 22, 81.3 instead of 8.

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APPENDIX A.

REPORTED ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION
OF HMX AND RDX IN THE VAPOR PHASE

APPENDIX A.

REPORTED ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF HMX AND RDX IN THE VAPOR PHASE

Available values^{A-1-4} for gas-phase decomposition of HMX and RDX are summarized in Table A-1, together with temperature ranges, kinetics, etc. The activation energy and frequency factor for gas phase decomposition of HMX have been determined by isothermal DSC^{A-1,4} (see discussion accompanying Appendix B, p. 70-72), by very-low-pressure pyrolysis^{A-2} and by a method^{A-3} involving combined manometric study of gas- and condensed-phase decomposition in the very early stages of the reaction. The DSC values^{A-1} are much higher than those determined by the other methods.^{A-2,A-3} Both DSC and VLPP data for HMX^{A-1,2} show considerable scatter, but the VLPP^{A-2} values seem more reliable due to the larger temperature range (135° as compared to 12°); thus, the activation energy for gas-phase HMX decomposition in the temperature range ca 250-400°C would appear to be ca 33 kcal/mole, with a frequency factor of $\log A$ (sec^{-1}) ca 12.8 although the authors point out that their data are too scattered to completely rule out that 45.50 kcal/mole that would signify initial N-NO₂ bond scission.^{A-1} This value of ca 33 kcal/mole is in agreement with the manometric values.^{A-3}

The DSC values^{A-1,4} for RDX decomposition in the vapor phase were measured over a wider temperature range (51°) than for HMX (12°), and the plot shows considerably less scatter; thus the RDX values measured by DSC seem much more reliable than the HMX values measured by DSC. For further discussion of DSC studies on vapor-phase HMX and RDX decomposition, see Appendix B.

Since HMX and RDX might be expected to decompose by similar mechanisms, it is interesting to note the general agreement between the manometric^{A-3} and VLPP^{A-2} values for HMX and the values for RDX.^{A-1,3,4}

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As discussed in the main body of the report, reactions on the container surface probably are not influencing these values too much, although more work on this point would help since wall reactions do seem to influence dimethylnitramine decomposition.

Tables A-2 and A-3 show the actual data points reported by the authors of References A-1-4 these were analyzed statistically as described in the main report (p. 19-26). Recommended values are given in the table in the main report, and the points are plotted in Figures 2 and 4 of the main report.

TABLE A-1. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF HOMOGENEOUS GASEOUS HMX AND RDX

Compound	Temperature Interval (°C)	Temperature Interval (°K)	Type of Kinetics	Log A (A in sec ⁻¹)	Activation Energy (E _a) (kcal/mole) (kJ/mole)	Reference	Method
HMX	273-85	546-58	order 0.9	20.179	52.9	221	A-1 Isothermal DSC
RDX	207-58	480-531	order 0.94	13.497	34.1	143	A-1 Isothermal DSC
HMX	248-383	521-656	first order		< 40	< 167	A-2 VLPP
				ca 12.8	ca 33	140	A-2 VLPP; log A estimated by authors
RDX	166-208	439-81	first order	11.7	30	125	A-3 Manometric
HMX	166-208	439-81	first order	13.5	32	134	A-3 Manometric
RDX	230-50	503-23	first order	11.70±0.78	29.61±1.85	124±8	A-4 Isothermal DSC

TABLE A-2. RATE DATA USED IN STATISTICAL ANALYSIS OF GAS-PHASE DECOMPOSITION OF HMX

Temperature (°C)	1000/T	k(sec ⁻¹)	log ₁₀ k	Remarks
558	1.792	0.3738	-0.42736*	*Data used in Reference A-1, communicated privately by R. N. Rogers, LASL. Least-squares analysis gave log A(sec ⁻¹) = 17.736 and E _a = 46.7 kcal/mole (Cvetanovic-Singleton); and log A(sec ⁻¹) = 18.859 ± 2.4 and E _a = 49.5 ± 6.1 kcal/mole (ordinary least squares).
558	1.792	0.2420	-0.61618*	
554	1.805	0.1767	-0.75276*	
552	1.812	0.2172	-0.66314*	
550	1.818	0.1555	-0.80827*	
548	1.825	0.1198	-0.92154*	
546	1.832	0.1026	-0.98885*	
546	1.832	0.0999	-1.000*	
544	1.838	0.1057	-0.97593*	†Data read with an expandable ruler from Figure 3 of Reference A-3. Least-squares analysis gave log A(sec ⁻¹) = 15.497 and E _a = 36.1 kcal/mole (Cvetanovic-Singleton) and log A(sec ⁻¹) = 15.519 ± 0.3 and E _a = 36.1 ± 0.9 kcal/mole (ordinary least squares).
439	2.280	0.00316	-2.500†	
459	2.180	0.01995	-1.700†	
469	2.130	0.05248	-1.280†	
480	2.082	0.1122	-0.950†	
521	1.919	0.25	-0.602‡	Data used in Reference A-2, communicated privately by D. F. McMillen, SRI International. Least-squares analysis with assumed log A(sec ⁻¹) = 12.8 gave E _a = 35.4 kcal/mole (Cvetanovic-Singleton); and log A(sec ⁻¹) = 12.558 ± 0.4 and E _a = 32.4 ± 0.9 kcal/mole (ordinary least squares).
529	1.890	0.29	-0.538‡	
532	1.879	0.24	-0.620‡	
545	1.835	0.62	-0.208‡	
546	1.832	0.43	-0.366‡	
551	1.815	0.66	-0.180‡	
554	1.805	0.84	-0.0757‡	
556	1.799	0.86	-0.655‡	
569	1.757	1.81	0.2577‡	
575	1.739	0.96	-0.01773‡	
581	1.721	1.43	0.1553‡	
637	1.570	17.2	1.236‡	
649	1.541	4.30	0.6335‡	

TABLE A-3. RATE DATA USED IN STATISTICAL ANALYSIS OF GAS-PHASE DECOMPOSITION OF RDX

Temperature (°C)	(°K)	1000/T	k(sec ⁻¹)	log ₁₀ k	Remarks
480		2.083	0.00975	-2.011 *	*Data used in Reference A-1, communicated privately by R.N. Rogers, LASL. Least-squares analysis gave log A(sec ⁻¹) = 13.00256 and E _a = 32.9 kcal/mole (Cvetanovic-Singleton); and log A(sec ⁻¹) = 13.423 ± 0.9 and E _a = 33.9 ± 2 kcal/mole (ordinary least squares).
490		2.041	0.0223	-1.652 *	
500		2.000	0.0562	-1.250 *	
500		2.000	0.0453	-1.344 *	
510		1.961	0.0630	-1.201 *	
515		1.942	0.0890	-1.051 *	
520		1.923	0.1788	-0.74763*	
520		1.923	0.1813	-0.74160*	
520		1.923	0.1314	-0.88140*	
520		1.923	0.118	-0.9281 *	
520		1.923	0.116	-0.9355 *	†Data read with an expandable rule from Figure 3 of Reference A-3. Least-squares analysis gave log A(sec ⁻¹) = 11.0278 and E _a = 28.4 kcal/mole (Cvetanovic-Singleton) and log A(sec ⁻¹) = 11.050 ± 0.3 and E _a = 28.5 ± 0.6 kcal/mole (ordinary least squares).
530		1.887	0.3717	-0.42981*	
530		1.887	0.3605	-0.44309*	
438		2.285	0.000661	-3.181†	
458		2.184	0.00288	-2.54†	
470		2.127	0.00692	-2.16†	
481		2.077	0.0126	-1.90	
508.0		1.969	0.0889	-1.051†	‡508° point read from Figure 3 of Reference A-4; all others from Table 1 of Reference A-4. Least-squares analysis gave log A(sec ⁻¹) = 12.143 and E _a = 30.7 kcal/mole (Cvetanovic-Singleton) and log A(sec ⁻¹) = 12.184 ± 0.9 and E _a = 30.8 ± 2.0 kcal/mole (ordinary least squares).
513.0		1.949	0.1142	-0.9423†	
518.0		1.930	0.1707	-0.7678†	
523.0		1.912	0.204	-0.6904†	

APPENDIX B.

**REPORTED ARRHENIUS PARAMETERS FOR DECOMPOSITION
OF NEAT LIQUID AND DISSOLVED HMX**

APPENDIX B.

REPORTED ARRHENIUS PARAMETERS FOR DECOMPOSITION OF NEAT LIQUID AND DISSOLVED HMX

Available values^{B-1-10} for liquid-phase decomposition of HMX are summarized in Table B-1, and solution-phase values in Table B-2, together with temperature ranges, kinetics, etc.

The best literature set of Arrhenius parameters for thermal decomposition of neat liquid HMX (Table B1) seems to be the 52.7 kcal/mole and $\log A(\text{sec}^{-1})$ of 19.7 reported by Robertson; this is based on the long temperature range

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- B-1 A. J. B. Robertson, "The Thermal Decomposition of Explosives. Part II Cyclotrimethylenetrinitramine and Cyclotetramethylenetetranitramine," Trans. Faraday Soc., Vol. 45, p. 85, 1949.
- B-2 R. N. Rogers and E. D. Morris, Jr., "On Estimating Activation Energies with a Differential Scanning Calorimeter," Anal. Chem., Vol. 38, p. 412, 1966.
- B-3 R. N. Rogers and L. C. Smith, "Estimation of Preexponential Factor from Thermal Decomposition Curve of an Unweighed Sample," Anal. Chem., Vol. 39, p. 1024, 1967.
- B-4 E. K. Rideal and A. J. B. Robertson, "The Sensitiveness of Solid High Explosives to Impact," Proc. Roy. Soc., Vol. 195A, p. 135, 1948.
- B-5 R. N. Rogers, "Differential Scanning Calorimetric Determination of Kinetic Constants of Systems that Melt with Decomposition," Thermochimica Acta, Vol. 3, p. 437, 1972.
- B-6 B. B. Goshgarian, "The Thermal Decomposition of Cyclotrimethylene-trinitramine (RDX) and Cyclotetramethylenetetranitramine (HMX)," AFRPL-TR-78-76 (AD-B032 275L).
- B-7 D. A. Flanigan and B. B. Stokes, "HMX Deflagration and Flame Characterization. Volume I. Phase II Nitramine Decomposition and Deflagration Characterization," Thiokol Corporation, Huntsville Division, Huntsville, AL, Report AFRPL-TR-79-94, October 1980 (AD-B053 058L).
- B-8 R. J. Powers, "Hazards Due to Precombustion Behavior of High Energy Propellants," AFATL, Private Communication, June 1980, of data presented at JANNAF Workshop, Eglin AFB, April 1980.
- B-9 Yu. Ya. Maksimov, "Thermal Decomposition of Hexagen and Octogen," Tr. Mosk. Khim-Tekhnol. Inst. No 53, p. 73, 1967; see Chem. Abstr., Vol. 68, p. 41742r. Translated by H. J. Dahlby, Los Alamos Report LA-TR-68-30, Los Alamos, 1968.
- B-10 Maksimov (presumably), work summarized in K. K. Andreyev, "Thermal Decomposition and Combustion of Explosives," FTD-HT-23-1329-68, p. 87, p. 130 (AD-693 600).

covered (44°); on the fact that the absence of any effect of sample size (varied from 1-7mg) suggests that self heating is not important; and on the low degree of scatter in the Arrhenius plot. However some of the other authors do not state temperature range or provide enough information to enable the degree of scatter to be evaluated. On reading Robertson's paper and experimental reference cited therein, no obvious sources of systematic error were evident to this writer.

Most of the values^{B-1-5,7} of A and E_a , measured at or below atmospheric pressure, given in Table B1 for decomposition of neat liquid HMX agree within a few kcal/mole with those of Robertson. The exceptions are the values of References B-6 and B-8. However, these points were measured over the shortest temperature ranges in Table B-1 and it is difficult to rule out the possibility of self heating, since Reference B-6 states (p.10) that the sample size was 2 mg, but it is stated on page 34 that "sample weight greater than 1.0mg increased the isothermal temperature during HMX decomposition, apparently due to excess thermal evolution beyond the capabilities of the instrument to adequately regulate a constant temperature."

Reference B-8 used sample sizes on the order of 1.5 mg, so self-heating may not be quite as bad. Robertson used sample sizes of 1-7 mg and found no effect of mass i.e., apparently no self-heating. Possibly this is because in the 2-cm glass bulb or copper oven apparatus used by Robertson, the sample would be more spread out than in a millimeter sized DSC pan.

Judging from the results in Table B-1, activation energies and frequency factors seem to be independent of type and pressure of inert gases present up to 1 atmosphere; however, judging from the data of Reference B-7 it would appear that on going from 1 to 70 atmospheres, the activation energy decreases noticeably, from ca 56 kcal/mole at 1 to ca 42 kcal at 70 atmospheres. These results are least squares averages and appear independent of particle size.

In addition to the data given in Tables B-1 and B-2, R. N. Rogers^{B-11} furnished several points for decomposition of neat liquid HMX, measured by isothermal DSC with correction for the concurrent gas-phase reaction. Powers,^{B-8} on the other hand, in his studies of the decomposition of neat liquid HMX by isothermal DSC, felt that the gas-phase decomposition was sufficiently unimportant to be neglected; this is in agreement with Goshgarian's^{B-6} observation that the decay portion of HMX decomposition curves appeared smooth throughout the decomposition. However for spread sample a gas-phase "hump" could be seen. Thus the gas-phase decomposition seems less important for HMX than for RDX. In any case, Powers' data were obtained in the initial phase of the liquid decomposition, where the vapor phase should be proportionately least important; thus they were included along with Robertsons^{B-1} and Rogers' gas-phase-corrected data, in the best three sets of data on liquid-phase HMX decomposition.

The actual data points obtained by Robertson,^{B-1} Rogers^{B-11} and Powers^{B-8} are given in Table B-3. These points were analyzed statistically as given in

^{B-11}R. N. Rogers, Los Alamos Scientific Laboratories, Private Communication, February 1980.

the main report, and plotted in Figure 3 of the main report. Note, however, that while the picture of concurrent liquid and vapor-phase reactions being the main contributors to the shape of the DSC curves still seems to hold for RDX, it has recently begun to appear^{B-8,11} that the situation for HMX may be more complicated, possibly as a result of complications due to presence of the non-volatile residue. Until this situation is understood better than it is at present, it may well be a good idea to just use Robertson's manometric data as the best data for decomposition of liquid HMX. As shown in Table B-3, this gives $E_a = 53.1$ kcal/mole and $\log A (\text{sec}^{-1}) = 19.950$.

There are only a few values for decomposition of HMX in solution. The value of 50.3 kcal/mole in Convalex-10 was measured by dynamic DSC, and there is no information on the temperature range covered. The data of Maksimov^{B-9,10} were done over a fairly large (54°C) temperature range, and the degree of scatter in the Arrhenius plot given^{B-9} does not seem unreasonable. Thus it does not seem unreasonable to conclude from the data in Tables B-2 and B-1, that the activation energy and frequency factor for decomposition of HMX in an inert solvent are somewhat lower than those for neat liquid HMX, although the data for HMX in solution were not reanalyzed statistically by the present writer.

TABLE B-1. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF NEAT LIQUID HMX

Temperature Interval (°C) (°K)	Type of Kinetics	Log A (A in sec ⁻¹)	Activation Energy (kcal/mole) (kJ/mole)	Method	References	Remarks
271-315 544-88	First order	19.7	52.7 ± 2.0 220	Pressure rise	B-1	In vacuum; 5 cm Air or H ₂ present to retard vaporization; sample size 1-7 mg.
Not Stated	First order	18.1		DSC	B-2, B-3	A calculated in Ref. B3, using E _a from Ref. B2. Does not state which of several E _a 's was used. Sample size < 1 mg.
Not Stated	First order	18.9	(52.7) (220)	DSC	B-3, B-4	A calculated in Ref. 3, using E _a from Ref. 4 (apparently based on work described in Ref. 1). A independent of heating rate and sample size. Sample size < 1 mg.
271-85 544-58	First order	18.81	51.3 214	Isothermal DSC	B-5	Sample size not stated (< 1 mg? (by analogy with Ref 3 by same author using same instrument)).
274-80 547-53	First order		67 280	Isothermal DSC	B-6	Sample size 2 mg. Self-heating?
283-302 556-75	First order		55.87 233.8	Isothermal DSC	B-7	Pressure 14.7 psi, 20 μ particle size.
287-308 560-81	First order		49.71 208.0	Isothermal DSC	B-7	Pressure 500 psi, 20 μ particle size.

TABLE B-1. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF NEAT LIQUID HMX (Cont't)

Temperature Interval (°C) (°K)	Type of Kinetics	Log A (A in sec ⁻¹)	Activation Energy (kcal/mole) (kJ/mole)	Method	References	Remarks
283-307 556-80	First order		48.50 212.9	Isothermal DSC	B-7	Pressure 500 psi, 135 μ particle size
283-308 556-81	First order		49.28 206.2	Isothermal DSC	B-7	Pressure 500 psi, recrystallized HMX
283-310 556-83	First order		41.77 174.8	Isothermal DSC	B-7	Pressure 1000 psi 20 μ particle size.
274-84	Order 0.9-1.0	24.450	67.742	Isothermal DSC	B-8	Done in region where gas reaction is least important.
274-84	Order 0.9-1.0	25.384	67.174	Isothermal DSC	B-8	Fully Deuterated HMX

TABLE B-2. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF HMX IN SOLUTION

Temperature Interval (°C) (°K)	Type of Kinetics	Log A (A in sec ⁻¹)	Activation Energy (kcal/mole) (KJ/mole)	Method	References	Solvent and Remarks
171-215 449-503	First order	15.0	50.3 ± 6.4 210 ± 27	DSC	B-2	Solvent: Convalex-10 (polyphenyl ether)
			44.9	Manometric	B-9	Solvent: m-Dinitrobenzene Initial rate Russian original gives Log A variously as 15.0 and 16.0
176-230 449-503		14.9	42.6	Manometric	B-10	Solvent: m-Dinitrobenzene

TABLE B-3. RATE DATA USED IN DERIVATION OF RECOMMENDED VALUES OF ARRHENIUS PARAMETERS FOR DECOMPOSITION OF NEAT LIQUID HPOX

Temperature (°C)	1000/T	k(sec ⁻¹)	log k	Remarks
587	1.7050		0.170	*Values read from Figure 4 of Reference B-1. Least squares gave E _a = 53.1 kcal/mole and log A (sec ⁻¹) = 19.950 (Cvetanovic-Singleton); and E _a = 53.1 ± 1.4 kcal/mole and log A (sec ⁻¹) = 19.943 ± 0.6 (ordinary least squares).
572	1.7487		-0.385	
565	1.7697		-0.600	
564	1.7732		-0.705	
558	1.7922		-0.720	
556	1.7987		-1.020	
554	1.8052		-0.955	
549	1.8217		-1.220	
546	1.8315		-1.330	
544	1.8370		-1.365	
544	1.8379		-1.390	
546	1.832	0.0362	-1.4413†	†Data corrected for gas-phase reaction; communicated privately by R. N. Rogers, LASL.
546	1.832	0.0369	-1.4330†	
558	1.792	0.113	-0.9469†	
276	1.821	0.039	-1.409#	‡Data obtained in region where order = 0.9-1.0 and gas-phase reaction is proportionately least important. Communicated privately by R. J. Powers, AFATL, Eglin AFB. Least squares gave E _a = 62.2 kcal/mole and log A (sec ⁻¹) = 23.337 (Cvetanovic-Singleton); and E _a = 63.0 ± 6 and log A(sec ⁻¹) = 23.690 ± 2.2 (ordinary least squares).
278	1.815	0.046	-1.337#	
279	1.812	0.053	-1.276#	
280	1.808	0.058	-1.237#	
282	1.802	0.082	-1.0862#	
284	1.795	0.085	-1.0706#	

APPENDIX C.
REPORTED ARRHENIUS PARAMETERS FOR DECOMPOSITION
OF NEAT LIQUID AND DISSOLVED RDX

APPENDIX C.

REPORTED AR. WENIUS PARAMETERS FOR DECOMPOSITION
OF NEAT LIQUID AND DISSOLVED RDX

Available kinetic parameters^{C-1-31} for decomposition of RDX in the neat liquid phase and in solution are summarized in Tables C-1 and C-2, respectively.

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- C-1 A. J. B. Robertson, "The Thermal Decomposition of Explosives. Part II. Cyclotrimethylenetrinitramine and Cyclotetramethylenetetranitramine, Trans. Faraday Soc., Vol. 45, p. 85, 1949.
- C-2 A. J. B. Robertson, S.A.C. No. 4885, referred to in Reference 5.
- C-3 G. K. Adams, S.A.C. No. 5766, "The Thermal Decomposition of RDX," February 1944.
- C-4 A. J. B. Robertson, S.A.C. No. 3264, referred to in Reference 5.
- C-5 J. Wilby, "Thermal Decomposition of RDX/TNT Mixtures, Part I," A.R.D.E. Report (MX) 16/59, AD-225 991, August 1959.
- C-6 C. E. H. Bawn, J. K. Hays and F. H. Pollard, "The Thermal Decomposition of Tetryl and RDX," S.A.C. No. 2025, April 1942.
- C-7 A. J. B. Robertson and R. P. Sinclair, "The Thermal Sensitivity of Explosives," S.A.C. No. 1596, January 1942.
- C-8 F. C. Rauch and R. B. Wainwright, "Studies on Composition B," Final Report, Contract No. DAAA21-68-C-0334, American Cyanamid Company, February 1969, AD-850-928.
- C-9 F. C. Rauch and A. J. Fanelli, "The Thermal Decomposition Kinetics of Hexahydro-1,3,5-trinitro-s-triazene above the Melting Point: Evidence for both a Gas and Liquid-Phase Decomposition," J. Phys. Chem., Vol. 73, p. 1604, 1969.
- C-10 F. C. Rauch and W. P. Colman, "Studies on Composition B," Final Report, Contract No. DAAA 21-68-C-0334, American Cyanamid Company, March 1970, AD-869 226.
- C-11 R. N. Rogers and E. D. Morris, Jr., "On Estimating Activation Energies with a Differential Scanning Calorimeter," Anal. Chem., Vol. 38, p. 412, 1966.
- C-12 R. N. Rogers and L. C. Smith, "Estimation of Preexponential Factor from Thermal Decomposition Curve of an Unweighed Sample," Anal. Chem., Vol. 39, pp. 1024-5.

- C-13 R. N. Rogers and G. W. Daub, "Scanning Calorimetric Determination of Vapor-Phase Kinetics Data," Anal. Chem., Vol. 45, p. 596, 1973.
- C-14 R. N. Rogers, "Determination of Condensed-Phase Kinetics Constants," Therochimica Acta, Vol. 9, p. 444, 1974.
- C-15 P. G. Hall, "Thermal Decomposition and Phase Transitions in Solid Nitramines," J. Chem. Soc., Faraday Trans., Part II. Vol. 67, p. 556, 1971.
- C-16 K. Kishore, "Thermal Decomposition Studies on Hexahydro-1,3,5-trinitro-s-triazene (RDX) by Differential Scanning Calorimetry," Propellants and Explosives, Vol. 2, p. 78, 1978.
- C-17 T. B. Joyner, "Thermal Decomposition of Explosives. Part I. Effect of Asphalt on the Decomposition of Asphalt-Bearing Explosives," NWC TP 4709, March 1969, AD-500 573.
- C-18 J. Harris, "Autoignition Temperatures of Military High Explosives by Differential Thermal Analysis," Thermochimica Acta, Vol. 14, p. 183, 1976.
- C-19 J. Harris and E. Demberg, "Autoignition Temperatures of Military High Explosives by Differential Thermal Analysis," PATR 4481, March 1973, AD-908 846L.
- C-20 T. G. Floyd, "Reaction Kinetics of Temperature-Cycled Cyclotrimethylene-trinitramine (RDX)," Journal of Hazardous Materials, Vol. 2, p. 163, 1977/78.
- C-21 W. P. Colman and F. C. Rauch, "Studies on Composition B," Final Report, Contract No. DAAA21-70-0531, American Cyanimid Company, February 1971., AD-881 190.
- C-22 J. Wilby, "Thermal Decomposition of RDX/TNT Mixtures, Part I.," A.R.D.E. Report (MX) 16/59, August 1959, AD-225 991.
- C-23 J. Wilby, "Thermal Stability of RDX and HMX Compositions, Particularly their Mixtures with TNT," Symp. Chem. Probl. Connected Stab. Explos., (Proc.), pp. 51-65, 1967, for availability see Reference C-24, 1968.
- C-24 D. F. Debenham and A. J. Owen, "The Thermal Decomposition of 1,3,5-trinitro-hexahydro-1,3,5-triazine (RDX) in 1,3,5-Trinitrobenzene," Symp. Chem. Probl. Connected Stab. Explos., (Proc.) 1976; Vol. 4, pp. 210-20; 1977, can be ordered from the Secretary, Tekn Lic Stig Johansson, Sektionen for Detonik och Forbranning, Box 608, S-551 02 Jonkoping, Sweden. Postal Account No. 507690-6, Banking Account Gotabanken No. 652-4383.
- C-25 Yu. Ya. Maksimov, "Thermal Decomposition of Hexogen and Octogen," Tr. Mosk. Khim.-Tekhnol. Inst. No. 53, p. 73, 1967, see Chem. Abstr., Vol. 68, p. 41742r., Translated by H. J. Dahlby, Los Alamos Scientific Laboratory Report LA-TR-68-30, Los Alamos, NM, 1968.

- C-26 Maksimov (Presumably), work summarized in K. K. Andreyev, "Thermal Decomposition and Combustion of Explosives," FTD-HT-23-1329-68, p. 87, p. 130 (AD-693 600).
- C-27 K. K. Miles, "The Thermal Decomposition of RDX," Master's Thesis, Naval Postgraduate School, Monterey, March 1972 (AD-743 762).
- C-28 D. A. Flanigan and B. B. Stokes, "HMX Deflagration and Flame Characterization," Volume I. Phase II Nitramine Decomposition and Deflagration Characterization," Thiokol Corporation, Huntsville Division, Huntsville, AL, Report AFRPL-TR-79-94, October 1980 (AD-B053 058L).
- C-29 R. M. Potter, G. J. Knutson, and M. F. Zimmer, "Effect of Dibutyl Tin Dilaurate on the Thermal Decomposition of RDX," Compat. Propellants, Explos. Pyrotechnics Plast. Addit., Conf. 1974, II-D, 1975.
- C-30 K. Kishore, "Comparative Studies on the Decomposition Behavior of Secondary Explosives RDX and HMX," Defense Science Journal, Vol. 18, p. 59, 1978, summarized in Chem. Abstr., Vol. 90, 206758v.
- C-31 P. W. M. Jacobs and A. R. T. Kureishy, J. Chem. Soc., p. 4718, 1964.

Due to the long temperature range, low degree of scatter in the Arrhenius plots, and care to avoid such sources of error as self heating, the best pair of Arrhenius parameters for the decomposition of liquid RDX is probably that given by Robertson^{C-1,2} (Table C-1).

However, there remains the problem of vaporization followed by gas-phase reactions. Robertson's other set of data^{C-4} are probably in error as Wilby^{C-5} quotes Reference C-4 as saying that the values may be in error due to poor equilibrium and to gas-phase decomposition. The values of Rawn, Hays and Pollard^{C-6} and of Robertson and Sinclair^{C-7} are probably in error^{C-5} due to short temperature range and large sample sizes leading to self heating. Along with Robertson's values, ^{C-1,2} the values of G. K. Adams^{C-3} were accepted by Wilby^{C-5} as the best values. However, examination of Table 1 of Adams' report^{C-3} reveals that while the values for the experimentally determined $\log_{10} k_{\text{exp}}$ and the calculated $\log_{10} k_{\text{calc}}$ match each other they did not match values calculated from the stated Arrhenius parameters, and the plot of the values given for $\log_{10} k_{\text{calc}}$ shows a large degree of scatter. The source of this discrepancy is unknown to the present writer. Until it is explained it would probably be best to disregard the data given in Reference C-3.

The group at American Cyanamid^{C-8,9,10} decomposed RDX in reactors of constant known volumes and followed the reaction by gas chromatographic analysis of the undecomposed RDX. This has an advantage over manometric determination, since it is not subject to errors due to secondary reactions among gaseous products, although the manipulations necessary to quench the reaction in each reactor individually appear to have limited the temperature range to 20°. The rate constants were independent of initial mass, reactor volume or added pressure of NO₂ or helium.

The results described in this series of reports illustrate the importance of statistical analysis. The preliminary values^{C-8,9} ($\log A = 19.2$, $E_a = 48.7$) were obtained from a preliminary analysis, but a subsequent least squares analysis^{C-10} yielded $\log A = 22.4$ and $E_a = 55.6$ kcal/mole. The difference seems large enough to be chemically significant. This illustrates the importance of applying statistical analysis when estimating Arrhenius parameters from kinetic data, since it is evidently difficult to "eyeball" a slope and intercept with sufficient accuracy.

Joyner^{C-17} carried out manometric studies on the decomposition of RDX; the data were believed satisfactory despite some problems with sublimation and pressure fluctuation. In agreement with this the three points, plotted for neat liquid RDX appear to fall on the same line (main report, Figure 1) and the rate constants seem to agree reasonably well with those of Robertson^{C-1,2} and of the American Cyanamid group.^{C-10}

Thermal analysis studies will be considered in two parts - first the isothermal DSC and DTA, then dynamic or temperature-programmed studies. We begin with isothermal DSC results. The best isothermal DSC result is that of Rogers,^{C-14} who obtained $\log A$ (sec^{-1}) = 18.3 and $E_a = 47.1$ kcal/mole from experiments in which correction was made for gas-phase reaction which proceeds concurrently with the liquid reaction. To this writer's knowledge, this is the only study in which a quantitative correction for vapor-phase reaction has been carried out. Comparison with the uncorrected values^{C-13,14} of $\log A$ (sec^{-1}) = 16.4 and $E_a = 43.1$ kcal/mole reveals that the correction is of the

order of a factor of 100 in A and a difference of 4 kcal/mole in activation energy for DSC measurements of heat output using the Perkin-Elmer DSC-1B apparatus of Reference C-14; but the magnitude of the correction will of course vary with the mass/volume ratio and the geometry of the system. Since the other isothermal DSC studies^{C-16,20,28-30} made no attempt to correct their results specifically for the gas-phase reaction it is not surprising to note that their activation energies and frequency factors fall somewhat lower than the best DSC^{C-14} and kinetic^{C-1,2,8-10,17} values.

In addition to the above error (previous paragraph) due to vapor-phase reaction, non-isothermal thermal analysis experiments would be affected by a variation with temperature of the proportion of the vapor-phase reaction; this is in addition to any errors introduced in the derivation of the Kissinger equation (see p. 17-19) or other method used to estimate kinetic parameters. None of these studies attempts to correct for gas-phase reaction. Consequently, while all non-isothermal thermal analysis studies of which this writer is aware have been tabulated they will not be discussed individually.

Activation energies for decomposition of RDX in solution (Table C-2) seem to be generally several kcal/mole lower than the values (Table C1) for the neat liquid. Robertson^{C-1} found values for log A (sec^{-1}) and activation energy (ca 15.5 and 41 kcal/mole respectively) that were noticeably lower than his values (18.5 and 47.5) for the neat liquid. However, the values in TNT may be affected by concomitant decomposition of TNT; see following paragraph.

The work of Wilby^{C-22,23} was done over a short (17-18°) temperature range, using large samples which might have led to self-heating; furthermore, Wilby pointed out that TNT was decomposing at the same time as RDX and that this might have complicated matters. However, the Arrhenius parameters were in reasonable agreement with those of Robertson.^{C-1} This agreement for such large sample size may suggest that self heating is not a source of error for decomposing RDX in TNT and possibly in inert solvents generally; however, note the short temperature range in Wilby's measurements. The Russian workers also found^{C-25,26} that log A (sec^{-1}) and E_a were lower in solution in dinitrobenzene than were the best values for liquid RDX.

The value of 17.13 obtained by Joyner^{C-17} is somewhat higher than the value of about 14-16 obtained in the other entries of Table C-2. However, this is to be expected since it was obtained by assuming an activation energy (44.2 kcal/mole) determined for neat liquid RDX; this value is higher than most of those in Table C-2 and would thus be expected to lead to a higher frequency factor.

The above studies were all done manometrically. Colman and Rauch^{C-21} studied the decomposition in TNT kinetically, by analysis of undecomposed RDX; this would reduce errors due to vaporization followed by decomposition of RDX in the vapor phase. This is especially pertinent since while RDX decomposition seems unaffected by TNT, the TNT decomposition is accelerated in the presence of more than a 5% concentration of decomposing RDX; the composition of the gaseous products appears to be a superposition of those from RDX and TNT alone. Thus, while Robertson's values for 1% and 5% RDX in TNT are probably not in error from this source, studies using more than about 5-10% RDX and TNT may be in error. However, the errors in E_a and Log A may

not be too great since it was found^{C-21} that activation energies for decomposition of RDX and of solvent were about the same within the rather large (± 5 kcal/mole) error limits.

Debenham and Owen^{C-24} also followed the reaction by analysis of undecomposed RDX. Considering the short (10°) temperature range, their approximate activation energy of 46 kcal/mole seems essentially the same as the other values in Table C-2 although a bit on the high end of the range.

Rogers and Morris^{C-11} obtained an activation energy of 48.4 kcal/mole by DSC, in Convalex-10 (polyphenyl ether). This value is about the same as the best values in Table C-2 for the decomposition of neat liquid RDX, but significantly lower than the value (67.4 kcal/mole) reported on the same apparatus by Rogers and Morris^{C-11} for decomposition of liquid RDX; thus, the activation energy for RDX in solution is still less than for the neat liquid, when the two are determined by the same method on the same apparatus.

Table C-3 lists the rate constant and temperature data used^{C-1,10,14,17} in what, on the basis of the above discussion, the present writer feels to be the most reliable studies on decomposition of liquid RDX. These data were analyzed together on a common axis (main report, Figure 1, Table and accompanying discussion) to give the best values for $\log A$ (sec^{-1}) and E_a reported there. Table C-3 also gives the values obtained when the programs used in the present report were applied to the data from the individual data sets; values reported by the individual authors are given in Table C-1.

Table C-4 lists the actual rate constant and temperature data,^{C-1,17,21,22} used in what the present writer feels, on the basis of the above discussion, to be the most reliable data for decomposition of RDX in solution in TNT. These data were plotted together on a common axis (main report, Figure 5) and the data were analyzed statistically as described in the main report (Table and accompanying discussion) to give the suggested values for $\log A$ (sec^{-1}) and E_a reported there. Table C-3 also gives the values obtained when the programs used in the present report were applied to the data from the individual data sets; values reported by the individual authors are given in Table C-2.

TABLE C-1. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF HOMOGENEOUS LIQUID RDX

Temperature Interval (°C) (°K)	Type of Kinetics	Log A (A in sec ⁻¹)	Activation Energy (kcal/mole) (kJ/mole)	Method	References	Remarks
213-99 486-572	First order	18.5	47.5 ± 2.0 199	Pressure Rise	C-1, C-2	In vacuum or in pressure of Air, N ₂ or H ₂ at pressures up to atmospheric. Sample size 4-45mg. Least squares employed
203.5-61 476.5-534	First order	17.7 ± 0.7	45.5 ± 2.0 190	Pressure Rise	C-3	In vacuum; 10cm of Air or N ₂ present; disregard these data. (see discussion, p. C-1).
257-370 530-643		13	34.5 144	Pressure Rise	C-4	Wilby (Ref C-5) quotes Ref C-4 as saying these results may be inaccurate due to poor equilibration and gas-phase decomposition.
201-18 474-491	First order (slower towards end)	23	57 238	Pressure Rise	C-6	Less N ₂ O and NO, more CO ₂ at end. Fairly large samples (up to 0.2g) were used. Are results inaccurate due to self-heating leading to high A and E _a ? See also p. 2 of Reference 5.
240-60 513-33	First order	13	34.5 144	Pressure Rise	C-7	Much scatter done under air at normal pressure. Reaction became explosive at 261°C.
207-27 480-500	First order	19.23	48.7 204	Sealed reactor analysis of undecomposed RDX	C-8, C-9	Preliminary; sample size 12.5-40mg; initially under vacuum.
207-27 480-500	First order	22.4 ± 0.8	55.6 ± 1.7 233		C-10	Final value; least squares fitted.
Not stated			67.4 ± 3.0 282	DSC	C-11	Little detailed information.

TABLE C-1. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF HOMOGENEOUS LIQUID RDX (Cont'd)

Temperature Interval (°C) (°K)	Type of Kinetics	Log A (A in sec^{-1})	Activation Energy (kcal/mole (kJ/mole))	Method	References	Remarks
Not Stated	First order	18.4		DSC	C-12	Obtained as described in Reference 12, using E_a from Reference C-11. <u>ca</u> 1mg samples
Not Stated	First order	18.2		DSC	C-12	Obtained using Robertson's (Ref.1). E_a as described in Reference C11. <u>ca</u> 1mg samples.
207-58 480-531	First order	16.387	43.1 180	Isothermal DSC	C-13	<u>ca</u> 1mg sample; preliminary values.
207-58 480-531	First order	18.305	47.1 197	Isothermal DSC	C-14	Final values; corrected for vapor-phase decomposition.
210-61 483-534			45.2 $\pm$ 0.4 189 $\pm$ 2	DSC	C-15	Calculated as described in Ref C-11.
207-27 480-500	Order 0.6		41 $\pm$ 2 172 $\pm$ 8	Isothermal and Nonisothermal DSC	C-16	Open pan result; closed pan E was ~ 15 kcal lower. Table 2 of Ref. C-16 says 480-500°C (presumably a misprint). Sample size 0.1-1.2 mg. Open pan.
209-33 482-506	First order	17.09	44.2 185	Pressure rise	C-17	Sample size <u>ca</u> 5mg. Most runs at 640 torr of N_2 , some at lower pressures. Data believed OK despite problems with sublimation and pressure fluctuations.

TABLE C-1. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF HOMOGENEOUS LIQUID RDX (Cont'd)

Temperature Interval (°C) (°K)	Type of Kinetics	Log A (A in sec ⁻¹)	Activation Energy (kcal/mole (kJ/mole))	Method	References	Remarks
220-48 493-521		14.7004	34.68	DTA (peak temp)	C-19, C-19	Calculated by Kissinger
207-35 480-508		15.1430	34.00	DTA (slope temp)	C-18, C-19	method.
232-70 505-43	Order 0.7-1.2	17.069±2.530	44.569±2.069	Isothermal DSC	C-20	Uncycled RDX
232-70 505-43	Order 0.7-1.2	15.858±2.743	41.649±2.580	Isothermal DSC	C-20	Temperature cycled, cycle A3
232-70 505-43	Order 0.7-1.2	15.097±2.324	39.915±2.373	Isothermal DSC	C-20	Temperature cycled, cycle D3
						1.5-1.9mg samples.
231-255 504-28		20.8	49.5	DTA	C-27	Calculated by Kissinger Method, 43mg sample.
						Pressure 14.7 psi
			41.2	Isothermal DSC	C-28	Pressure 500 psi, least squares.
			41.8	Isothermal DSC	C-28	
230-50 503-23	Order 1.0-1.1	18.97 ±0.56	48.78 ±1.29	Isothermal DSC	C-29	
207-27 480-500			41 ±1	Isothermal DSC	C-30	Calculated by Kishore Method (Ref. C-16).
			32 ±1	Isothermal DSC	C-30	Calculated by Jacobs-Kureishy Method (Ref. C-31)
207-27 480-500			42	DSC	C-30	Scanning (2-32°C/min.)
						Calculated by Kissinger Method, Scanning (2-32°C/mole)
			42 ±3	DSC	C-30	Calculated by Kishore Method (Ref. C-16).

TABLE C-2. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF RDX IN SOLUTION

Temperature Interval (°C) (°K)	Type of Kinetic	Log A (A in sec ⁻¹)	Activation Energy (kcal/mole (kJ/mole))	Method	Ref	Solvent and Remarks
201-80 474-553	First order	15.46	41 172	Pressure rise	C-1	Solvent: Dicyclohexylphthalate Concentration - 2% and 5% Sample size 4-40mg.
194.5-281 467.5-554	First order	15.55	41.5 174	Pressure rise	C-1	Solvent: TNT Concentration 1% and 5% Sample size 4-40mg.
160-200 433-473	First order		48.4±2.6 203±11	DSC	C-11	Solvent: Convalex - 10 Little detailed information.
167-84 440-57	First order		41±5 172±21	Sealed reactor; analysis of undercomposed RDX	C-21	Solvent: TNT Least squares employed.
175-93 448-466	First order to 70% reaction	13.9±1.4	36.9±2.9 154±12	Pressure Time	C-22, C-23	Solvent: TNT
173-83 446-56	First order	14.5±2.5	37.8±11.3 158±47	Pressure Time	C-22, C-23	Solvent: Benzophenone Scatter on both TNT and benzophenone plots. Sample size ~ 300-600mg (~20% RDX); Deviations from first-order after 70% reaction.
150-97 423-470	First order	14.3	46 192	Sealed reactor; analysis of undercomposed RDX	C-24	Solvent: 1,3,5-trinitrobenzene.
182-222 455-95	First order	17.13	39.7 166 41.3 173	Pressure rise Pressure rise	C-25 C-26	Solvent: m-Dinitrobenzene. Solvent: m-Dinitrobenzene Could not obtain complete reference.
				Pressure rise	C-17	Based on assumed E _a = 44.2 kcal/mole from neat liquid work (Table C-1).

TABLE C-3. RATE DATA USED IN DERIVING RECOMMENDED VALUES OF ARRHENIUS PARAMETERS FOR DECOMPOSITION OF NEAT LIQUID RDX

Temperature (°C)	Temperature (°K)	1000/T (°K)	k(sec ⁻¹) x 10 ³	log ₁₀ k	Remarks
572	1.748			0.440 *	*Values read from Figure 1 of Reference C-1. Least squares in present report gave log A(sec ⁻¹) = 18.706 and E _a = 47.8 kcal/mole (Cvetanovic-Singleton); and log A(sec ⁻¹) = 18.564 ± 0.264 and E _a = 47.4 ± 0.6 (ordinary least squares).
561	1.7825			0.030 *	
552	1.812			-0.250 *	
549	1.822			-0.265 *	
550	1.8185			-0.265 *	
546	1.832			0.485 *	
529	1.892			-1.055 *	
526	1.901			-1.110 *	
519	1.928			-1.440 *	
507	1.974			-1.920 *	
498	2.0085			-2.230 *	†Values given in Table 2 of Reference C-10. Least squares in present report gave log A(sec ⁻¹) = 21.487 and E _a = 53.7 kcal/mole (Cvetanovic-Singleton); and log A(sec ⁻¹) = 21.514 ± 0.793 and E _a = 53.7 ± 1.8 kcal/mole (ordinary least squares).
488	2.0495			-2.620 *	
487	2.0545			-2.700 *	
486	2.0585			-2.925 *	
207			1.05	†	
212			2.02	†	
217			3.75	†	
222			6.41	†	
227			9.80	†	
210			1.26	‡	#Values given in Table 2 of Reference C-17 Least squares in present report gave log A(sec ⁻¹) = 17.147 ± 0.503 and E _a = 44.3 ± 1.1 (ordinary least squares).
220			3.00	‡	
230			7.86	‡	
480			0.816	-3.08831**	
490			1.48	-2.8297**	
500			5.71	-2.2434**	
500			5.50	-7.2596**	
510			14.5	-1.8386**	
515			23.9	-1.6216**	
520			32.9	-1.4828**	
520			33.5	-1.4750**	**Values for K and T(°K) communicated privately by R. N. Rogers, LASL; used in Reference C-14 Least squares gave log A(sec ⁻¹) = 19.186 and E _a = 49.1 (Cvetanovic-Singleton); and log A(sec ⁻¹) = 18.813 ± 0.607 and E _a = 48.2 ± 1.4 kcal/mole (ordinary least squares).
520			33.8	-1.4711**	

TABLE C-4. RATE DATA USED IN DERIVING RECOMMENDED VALUES OF ARRHENIUS PARAMETERS FOR DECOMPOSITION OF RDX IN TNT SOLUTION

Temperature (°C)	1000/T (°K)	k(sec ⁻¹) x 10 ⁴	log ₁₀ k	Remarks
554	1.804		-0.790 *	*Values read from Figure 3 of Reference C-1; concentration 1Z or 5Z. Least squares in the present report gave log A(sec ⁻¹) = 15.384 and E _a = 41.1 kcal/mole (Cvetanovic-Singleton); and log A(sec ⁻¹) = 15.498 ± 0.4 and E _a = 41.4 ± 0.8 kcal/mole (ordinary least squares).
551	1.815		-0.795 *	
542	1.845		-1.130 *	
533	1.875		-1.379 *	
534	1.874		-1.520 *	
531	1.882		-1.595 *	
531	1.884		-1.635 *	
521	1.919		-1.880 *	
521	1.921		-1.935 *	
510	1.960		-2.260 *	
495	2.0185		-2.645 *	
486	2.0685		-3.145 *	
481	2.0785		-3.340 *	
478	2.0925		-3.450 *	
468	2.139		-3.805 *	
473	2.114		-3.148 †	†Values read from Figure 11-4 of Reference C-21; concentration 60 RDX/40 TNT, except 30 RDX 70 TNT at 160°C. Statistical analysis in the present report gave log A(sec ⁻¹) = 15.929 and E _a = 41.4 kcal/mole (Cvetanovic-Singleton); and log A(sec ⁻¹) = 15.991 ± 0.4 and E _a = 41.5 ± 0.8 kcal/mole (ordinary least squares).
463	2.160		-3.638 †	
453	2.208		-4.0482†	
443	2.257		-4.478 †	
433	2.309		-4.938 †	
180	453	0.645	*	*Taken from Table 2 of Reference C-17; concentration 44-64% RDX by weight. Statistical analysis in the present report gave log A(sec ⁻¹) = 18.565 and E _a = 47.3 (Cvetanovic-Singleton); ordinary least squares gave log A(sec ⁻¹) = 18.697 ± 0.6 and E _a = 47.6 ± 1.3 kcal/mole.
190	463	1.64	*	
200	473	5.30	*	
210	483	13.5	*	
220	493	37.4	*	
230	503	132	*	

TABLE C-4. RATE DATA USED IN DERIVING RECOMMENDED VALUES OF ARRHENIUS PARAMETERS FOR DECOMPOSITION OF RDX IN TNT SOLUTION (Cont'd)

Temperature (°C)	(°K)	1000/T (°K)	k(sec ⁻¹) x 10 ³	log ₁₀ k
184.3	457.3		1.96	-3.7707
181.3	454.3		1.43	-3.8447
178.0	451.0		0.84	-4.0737
175.9	448.9		0.88	-4.0570
168.7	441.7		0.52	-4.2823
166.8	439.8		0.39	-4.4078
170.3	443.3		0.41	-4.3893
177.0	450.0		0.93	-4.0306
177.1	450.1		0.85	-4.0691
184.3	457.3		2.31	-3.6364

Remarks

Taken from Table 7 of Reference C-22.; concentration ca 20% RDX by weight. Note that k and log₁₀ k do not always agree exactly; values of log₁₀ k were used in Figure 5 of main report and statistics. Author states (Reference C-22) that temperatures were accurate to 1°C. Statistical analysis in the present report gave log A(sec⁻¹) = 14.00432 and E_a = 37.2 kcal/mole (Cvetanovic-Singleton). Ordinary least squares gave log A(sec⁻¹) = 13.926 ± 1.5 and E_a = 37.0 ± 3.1 kcal/mole.

APPENDIX D.

**REPORTED ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITIONS OF
HMX AND RDX AT TEMPERATURES BELOW THEIR MELTING POINTS.**

APPENDIX D.

REPORTED ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITIONS OF HMX AND RDX AT TEMPERATURES BELOW THEIR MELTING POINTS.

Available values^{D-1-27} for decomposition of HMX and RDX at temperatures below their melting points are summarized in Tables D-1 and D-2.

- D-1 B. B. Goshgarian, "The Thermal Decomposition of Cyclotrimethylene-trinitramine (RDX), and Cyclotetramethylenetetranitramine (HMX)," AFRPL-TR-78-76, October 1978 (AD-B032 275L).
- D-2 Yu. Ya. Maksimov, "Thermal Decomposition of Hexogen and Octogan," Tr. Mosk. Khim. Tekhnol., Inst. No. 53, p. 73, see Chem. Abstr., Vol. 68, p. 41742r, Translated by H. J. Dahlby, Los Alamos Report LA-TR-68-30, Los Alamos, NM, 1968.
- D-3 Maksimov, work summarized in K. K. Andreyev, "Thermal Decomposition and Combustion of Explosives," FTD-HT-23-1329-68, p. 87, 130 (AD-93 600).
- D-4 G. K. Adams, "Chemistry of the Solid State," personal communication referred to by C. H. Bawn, W. H. Garner, ed., Butterworths, London, p. 265, 1955.
- D-5 G. K. Adams, "The Thermal Decomposition of RDX," S. A. C. 5766, 1 February 1944.
- D-6 C. E. H. Bawn, "Chemistry of the Solid State," W. E. Garner, ed., Butterworths, London, p. 261, 1955.
- D-7 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.
- D-8 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, pp. 2025-9, 1971.
- D-9 K. K. Miles, "The Thermal Decomposition of RDX," Master's Thesis, U.S. Naval Postgraduate School, Monterey, CA, March 1972 (AD-743762).
- D-10 P. G. Hall, "Thermal Decomposition and Phase Transitions in Solid Nitramines," J. Chem. Soc., Faraday Trans. Part 2, Vol. 67, p. 556, 1971.
- D-11 A. E. Medvedev, G. V. Sakovich, and V. V. Konstantinov, "Nonisothermal Kinetics of the Solid-phase Decomposition of Octogen," Tezisy Dokl. Sovesh. Kinet. Mekh. Khim. Reakts. Tverd. Tele., 7th., Vol. 1, pp. 163-5, 1977, Chem. Abstr., Vol. 88, p. 177810g, 1978.

- D-12 R. R. Miller, R. C. Musso, and A. F. Grigor, "Combustion Mechanisms of Low Burning Rate Propellant," AFRPL-TR-69-130, May 1969 (AD-502957).
- D-13 S.(sic) Goshgarian, private communication cited in K. P. McCarty, HMX Propellant Combustion Studies," AFRPL-TR-76-59 (AD-B017 527L).
- D-14 W. Hoondée, "The Thermal Decomposition of β -HMX," Master's Thesis, Naval Postgraduate School, Monterey, CA, June 1971 (AD-728 582).
- D-15 J. E. Sinclair and W. Hoondée, "The Thermal Decomposition of β -HMX," Proc. Symp. Explos. Pyrotechnics, 7th, I-5, 1-4, (Chem. Abstr., Vol. 76, 143050w), 1971.
- D-16 J. N. Maycock and V. R. Pai Vernecker, "Thermal Decomposition of β -HMX (Cyclotetramethylene Tetranitramine)," Explosivstoffe, Vol. 17, p. 5, 1969.
- D-17 B. 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 β -HMX," Ind. Chim. Belg., Vol. 32, Spec. No. Part 3, pp. 647-50, 1967.
- D-18 B. Suryanarayana, V. I. Siele, and J. Harris, unpublished work cited in Reference 19.
- D-19 B. Suryanarayana, J. R. Autera, and R. J. Graybush, "Mechanism of Thermal Decomposition of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetraazacyclooctane)," Proceedings of the 1968 Army Science Conference, (OCRD) West Point, Vol. 2, p. 423, 1968 (AD-837 173).
- D-20 J. E. Sinclair and W. Hoondée, "Thermal Decomposition of β -HMX," Jahrestag, Inst. Chem. Treib., Explosivstoffe Fraunhofer-Ges. 1971, Pub. 1972, 57, Chem. Abstr., Vol. 81, 108070j.
- D-21 R. N. Rogers and E. D. Morris, Jr., "On Estimating Activation Energies with a Differential Scanning Calorimeter," Anal. Chem., Vol. 38, p. 412, 1966.
- D-22 M. S. Belyayeva, G. K. Klimenko, L. T. Babaytseva and, P. N. Stolyarov, "Factors Determining the Thermal Stability of Cyclic Nitroamines in the Crystalline State," FTD-ID (RS) T-1209-78, AD-B033 572L.
- D-23 J. Kimura and N. Kubota, "Thermal Decomposition Process of HMX," Propellants and Explosives, Vol. 5, p. 1, 1980.
- D-24 K. Takaira and K. Okazaki, M.S. Thesis, National Defense Academy, 1974, cited in Reference 23, 1974.
- D-25 B. Goshgarian, Private Communication, August 1976, cited in Reference 23.
- D-26 M. Farber and R. D. Srivastava, "A Mass-Spectrometric Investigation of the Decomposition Products of Advanced Propellants and Explosives," Space Sciences, Inc., August 1979 (AD-A074-963).

D-27 K. Kishore, "Comparative Studies on the Decomposition Behavior of Secondary Explosives RDX and HMX," Defense Science Journal, Vol. 18, p. 59, (summarized in Chem. Abstr., Vol. 90, 206758), 1978.

As discussed elsewhere (Section IV. D. of the main report), decomposition of HMX and RDX at temperatures below their melting points is most likely a complex process involving the liquid and vapor states as well as the solid state. Furthermore, the activation energies and frequency factors appear to be dependent on factors like degree of spreading of the sample (see for example Reference D-7) which are often difficult to evaluate in view of the limited information given in many of the reports. Therefore, although an attempt has been made to include all available values in Tables D-1 and D-2, we will confine ourselves to pointing out some of the main trends in the data.

One trend is a tendency for activation energies measured at or near the melting point by TGA^{D-25}, DSC^{D-9,10,21,23,24} or FRMS^{D-1} techniques to have what seem to be unreasonably high values, sometimes well over 200 kcal/mole. Possibly these values are artifacts resulting from complexity in the behavior of the material as it simultaneously melts and decomposes (see p. 35 of the main report).

Another pattern is that many^{D-11,14,15,17-20,25} (but not all) of the studies on HMX decomposition show changes in activation energy in the region around approximately $245 \pm 15^\circ\text{C}$. The magnitude and exact locations of these changes are not reproducible from study to study, except that they generally fall in the approximate range $230\text{--}60^\circ\text{C}$.

An attempt^{D-28} at applying autocatalytic solid reaction kinetics to HMX decomposition yielded an activation energy of 140 kcal/mole and a frequency factor of 4.76×10^{35} . However, the significance of these numbers seems uncertain; for one thing, the k_R in equation 6.4.2 of Reference D-29, which is equated by the authors of Reference D-28 to a rate constant, is described in Reference D-29 as an "adjustable parameter;" the justification for relating it to a rate constant is not obvious. Also, according to this treatment the rate constant comes out with units of time raised to the power of -3.5 , although rate constants generally, because of the manner of their derivation, are expected to be expressed in terms of reciprocal (time multiplied by concentration ^{$n-1$}). If the term $k t^\beta$ in equation 6.4.2 of Reference D-29 is replaced by $(kt)^\beta$, and $k (= (k_R)^{1/\beta})$ is considered as a rate constant having dimensions sec^{-1} , it would yield values of $\log_{10} A$ and E_a that would be lower by a factor of $\beta (=3.5, \text{Reference D-28})$ than those ($\log_{10} A = 35$ and $E_a = 140$ kcal/mole) given in Reference D-28, or $\log_{10} A(\text{sec}^{-1}) \approx 10$ and $E_a \approx 40$ kcal/mole.

Belyaeva et al.^{D-22} have reported a series of manometric studies on HMX and RDX decomposition in which separate account was taken of the gas and

D-28 A. E. Axworthy, J. E. Flanagan, and J. C. Gray, "Interaction of Reaction Kinetics and Nitramine Combustion," Rocketdyne Division, Rockwell International, Canoga Park, CA, Report AFATL-TR-80-58, May 1980 (AD-B052 861L).

D-29 M. Boudart, "Kinetics of Chemical Processes," Prentice-Hall, New York, Chapter 6, 1968.

condensed phase decompositions; the gas- and condensed-phase rates were evaluated separately from the following equation:

$$\frac{dn}{dt} = AK_1 \frac{V}{m_0} P_2 + B_2 K_2 (1 - n)$$

where $A = 273/760V_\infty T$, $B = 273R/760M$; K_1 and K_2 are the decomposition rates in the gas and condensed phases respectively; V is the volume of products up to a given point in time; V_∞ is the final volume of conversion products; m_0 is the sample weight, and M is molecular weight; and dn/dt is the total rate of thermal decomposition.

Initial rate data in the gas- and condensed phases are given in Appendix A and in the final lines of Tables D-1 and D-2 respectively. The condensed-phase Arrhenius parameters in Tables D-1 and D-2 are based on statistical analyses done by the present writer; the original Russian authors of Reference D-22 did not report Arrhenius parameters from their condensed phase data; it should be noted that this may well be the result of well-founded doubts as to their exact significance. Nevertheless, it seemed worthwhile to carry out the statistical analyses whose results are summarized in the last two lines of Tables D-1 and D-2. The "condensed phase" Arrhenius parameters or temperature coefficients of reaction are significantly lower for HMX than for RDX; in fact the frequency factor for HMX ($\log A(\text{sec}^{-1}) = 9.1$, Table D-2) is in a range that in the gas phase would be characteristic of a bimolecular reaction, while that for ($\log A(\text{sec}^{-1}) = 13.5$) is in a region that in the gas phase would be more characteristic of a unimolecular reaction. Possible reasons for this discrepancy include (a) differences in chemical mechanisms for the solid-state decomposition of HMX and RDX; and (b) differences in kind or contribution of physical mechanisms, in particular vaporization and gas-phase decomposition of HMX and RDX, and liquefaction of the solid phase due to condensation of products such as hydroxymethylformamide.

TABLE D-1. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF RDX AT AND BELOW ITS MELTING POINT

Temperature Interval (°C) (°K)	Region or Type of Kinetics	Log A (A in sec ⁻¹)	Activation Energy (kcal/mole) (kJ/mole)	Method	Ref	Remarks
150-80 423-53			25.3 106	Flow reactor mass spectrometry	D-1	Attributed to sublimation. sample size 2-5 mg.
150-97 423-70	Initial	19.1	52.0 218	Pressure rise	D-2	
150-97 423-70	Initial	18.6	51.0 213	Pressure rise	D-3	
177-200 450-72	Initial	16.7	45.5 190	Pressure rise	D-4, D-5	Ref. D-4 gives values shown; Ref. D-5 text implies values shown (p. 2); ca 4 mg samples, under 10 ² at 10 cm.
177-200 450-73	Initial		ca 49 ca 205	Pressure rise	D-7	Calculated from data in Ref. D-6.
171-93 444-71	Induction (7/τ ₇)		64.3 269	Pressure rise	D-7	Sample spread, 100 mm N ₂ , 0.2 g sample.
180-98 453-71	Induction (τ ⁻¹)		62.2 260	Pressure rise	D-7	Sample spread, 100 mm N ₂ , 0.2 g sample.
171-98 444-71	Induction (7/τ ₇)		49.4 207	Pressure rise	D-7	Sample unspread, 100 mm N ₂ , 0.2g sample.
171-98 444-71	Acceleration (10/(t ₂₀ -t ₁₀))		59.7 250	Pressure rise	D-7	Sample spread, 100 mm N ₂ , 0.2 g sample
171-90 444-63	Acceleration (10/(t ₂₀ -t ₁₀))		43.1 180	Pressure rise	D-7	Sample unspread, 100 mm N ₂ , 0.2 g sample
171-90 444-63	Acceleration (20/(t ₄₀ -t ₂₀))		42.2 177	Pressure rise	D-7	Sample unspread, 100 mm N ₂ , 0.2 g sample
180-98 453-71	Maximum (ρ max)		63.6 266	Pressure rise	D-7	Sample spread, 100 mm N ₂ , 0.2 g sample

TABLE D-1. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF RDX AT AND BELOW ITS MELTING POINT (Cont'd)

Temperature Interval (°C)	Region or Type of Kinetics	Log A (A in sec ⁻¹)	Activation Energy (kcal/mole) (kJ/mole)	Method	Ref	Remarks
180-98	453-71 Maximum (Prout-Tompkins k)	64.8	271	Pressure rise	D-7	Sample spread, 100 mm N ₂ , 0.2 g
180-38	543-71 Maximum (ρ _{max})	62.2	260	Pressure rise	D-7	Sample unspread, 100 mm N ₂ , 0.2 g sample.
170-97	443-70 Induction (7/t ₇)	44.3	185	Pressure rise	D-8	Sample spread, 130 mm H ₂ O=0, 0.2 g sample.
170-97	443-70 Acceleration (10/(t ₂₀ -t ₁₀))	43.8	183	Pressure rise	D-8	Sample spread, 130 mm H ₂ O=0, 0.2 g sample.
170-97	443-70 Acceleration (20/(t ₄₀ -t ₂₀))	45.9	192	Pressure rise	D-8	Sample spread, 130 mm H ₂ O=0, 0.2 g sample.
170-97	443-70 Maximum (ρ _{max})	43.8	183	Pressure rise	D-8	Sample spread, 130 mm H ₂ O=0, 0.2 g sample.
194-204	467-77 Melting	159.0282	665.36212	Isothermal DTA	D-9	From time elapsed to initiation of exothermic reaction (induction time).
194-204	467-77 Melting	131.0144	548.15447	Isothermal DTA	D-9	From time elapsed to peak of exotherm (time to deflagration)
194-204	467-77 Melting	160.9012	673.19861	Isothermal DTA	D-9	From (induction time)/t ²
194-204	467-77 Melting	132.8778	555.95080	Isothermal DTA	D-9	From (time to deflagration)/t ² ; 43 mg samples; curves appear s-shaped.
130-80	403-53 Initial (up to 0.15)	11.7	39.5	Pressure rise	D-22	

TABLE D-1. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF RDX AT AND BELOW ITS MELTING POINT (Cont'd)

Temperature Interval (°C) (°K)	Region or Type of Kinetics	$\log A$ (A in sec^{-1})	Activation Energy (kcal/mole) (kJ/mole)	Method	Ref	Remarks
167-98 440-71		13.51	40.3 169	Manometric (corrected for gas Reaction)	D-22	Ovetanovic-Singleton Analysis of Data 2n Figure 3, of Reference D-22. Are these values and those in the following decent estimates of true solid- state decomposition of RDX? 167- 200 mg.
167-98 440-71		13.50	40.3 169		D-22	Ordinary least squares analysis of Data on preceding line.

TABLE D-2. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF HMX AT AND BELOW ITS MELTING POINT

Temperature Interval (°C)	Type of Kinetics or Region	Log $10 A$ (sec^{-1})	Activation Energy (kcal/mole) (kJ/mole)	Method	Ref	Remarks
250-70	523-43		38 ± 2 159 ± 8	Flow reactor Mass spec. (FRMS)	D-1	Attributed by author to sublimation followed by vapor phase decomposition 2-5 mg. sample.
271-80	544-53		42 ± 2 176 ± 8	FRMS	D-1	Attributed by author to solid phase reactions. 2-5 mg. sample.
281-4	544-7 Melting		120 ± 10 502 ± 8	FRMS	D-1	Melting; 2-5 mg. sample.
261-76	534-49 Melting	17.83	50 ± 2 209 ± 8	Isothermal FRMS	D-1	2-5 mg. sample. Temperature range and slope of lines in Figure 11 suggest these are for HMX below the mp.
176-230	449-503 Initial	11.2	37.9 159	Pressure rise	D-2	
176-230	449-503 Initial	10.7	36.5 153	Pressure rise	D-3	
ca 267	ca 540 Melting		ca 210 870	DSC	D-10	Starting with α -HMX
ca 267	ca 540 Melting		180 ± 15 753 ± 63	DSC	D-10	Starting with β -HMX
185-280	458-553		41.2 173	DTA, TGA	D-11	Due to sublimation (see ref D-1).
		22	57.8	DSC	D-12	Exotherm covered ~500-560°K (227-870) Sample on cab-o-sil due to self heating of neat HMX.
>240	>513		67.4 282		D-13	
>240	>513		29.9 125		D-13	

TABLE D-2. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF HMX AT AND BELOW ITS MELTING POINT (Cont'd)

Temperature Interval (C)	Temperature Interval (°K)	Type of Kinetics or Region	Log 10 A (sec ⁻¹)	Activation Energy (kcal/mole) (kJ/mole)	Method	Ref	Remarks
232-41	505-14	Acceleratory	25.33	67.86 283.9	Isothermal DTA	D-14	Sample size 0.4 mg
232-41	505-14	Intermediate	25.43	66.42 277.9	Isothermal DTA	D-14	Sample size 0.4 mg
232-41	505-41	Decay	23.69	63.09 264.0	Isothermal DTA	D-14	Sample size 0.4 mg
243.5-76	516.5-49	Intermediate	19.16	52.67 220.4	Isothermal DTA	D-14	Sample size 0.4 mg
200-33	473-506		15.21	44.20 184.9	DTA	D-14, D-15	Sample size 0.4 mg Calculated by Kissinger Method.
233-41	506-14		22.89	63.23 264.6	DTA	D-14, D-15	Sample size 0.4 mg Calculated by Kissinger Method.
>241	>514		18.67	52.65 220.3	DTA	D-14, D-15	Sample size 0.4 mg Calculated by Kissinger Method.
245-80	518-53			62 259	Isothermal TGA	D-16	20 mg sample. Isolated by Jacobs-Kureshy Method. Flowing He atmosphere.
251-65	524-38			59 247	Isothermal TGA	D-16	20 mg sample over pressure of 760 torr He.
280-95	553-68			65.0 272	DTA	D-16	Calculated by Kissinger Method.
227-59	500-32	Induction		47 197	Pressure rise Plot log t vs 1/T	D-17	For NO formation only; 50 mg sample; 40 mm Argon.
227-59	500-32	Induction		46 192	Pressure rise Plot log t vs 1/T	D-17	For N ₂ O, N ₂ , CO, CO ₂ formation only; 50 mg sample, 40 mm Argon.

TABLE D-2. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF HMX AT AND BELOW ITS MELTING POINT (Cont'd)

Temperature Interval (°C)	Type of Kinetics or Region	Log ₁₀ A (sec ⁻¹)	Activation Energy (kcal/mole) (kJ/mole)	Method	Ref	Remarks	
227-59	500-32 Induction		46	192	Pressure rise log t vs 1/T	D-17	For H ₂ C=O formation only; 50 mg sample; 40 mm Argon.
226-45	499-518 Constant Rate	13	38	159	Pressure rise	D-17	For H ₂ C=O formation only; 50 mg sample; 40 mm Argon.
226-45	499-518 Constant Rate	23	63	264	Pressure rise, log (const. rate) vs 1/T	D-17	For NO formation only; 50 mg sample; 40 mm Argon.
>245	>518 Constant Rate	2.5	13	54	Pressure rise, log (const. rate) vs 1/T	D-17	For NO formation only; 50 mg sample; 40mm Argon.
226-45	499-518 Constant Rate	16	46	192	Pressure rise, log (const. rate) vs 1/T	D-17	For N ₂ , N ₂ O, CO, CO ₂ formation only; 50 mg sample; 40 mm Argon.
>245	>518 Constant Rate	5	18.5	77	Pressure rise, log (const rate) vs 1/T	D-17	For N ₂ , N ₂ O, CO, CO ₂ formation only; 50 mg sample; 40 mm Argon.
226-45	499-518		45	188	Pressure rise	D-18	For β-HMX; other Polymorphs gave different values below 245° (no numbers given except for β-form)
245-68	518-41		10-15	41.8-62.8	Pressure rise	D-18	
268-80	541-53		52	218	Pressure rise	D-18	
220-45	493-518		46	192		D-18	Full discussion not given - Authors state it will be presented in a future paper.
245-70	518-543		18.5	77.4		D-19	
200-33	473-506		44.20	184.9	DTA	D-20	

TABLE D-2. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF HMX AT AND BELOW ITS MELTING POINT (Con't)

Temperature Interval (°C) (°K)	Type of Kinetics or Region	$\log_{10} A$ (sec ⁻¹)	Activation Energy (kcal/mole)(kJ/mole)	Method	Ref	Remarks
233-41 506-14			63.23 264.6	DTA	D-20	
>241 >514			52.65 220.3	DTA	D-20	
			220 ± 24	DSC	D-21	
150-70 423-43	Initial (up to 0.12)	25	67 280	Pressure rise	D-22	" β -Modification" (δ -form?)
180-210 453-83	Initial (up to 0.12)	12.6	41 172	Pressure rise	D-22	" α -Modification" (δ -form?)
Below melting point	Order=0-9	24.079	66.4 278	Thermogravimetry	D-23	Fraction reacted <0.2
Below melting point	Order=0	7.40	22.9 95.8	Thermogravimetry	D-23	0.2 < Fraction reacted <0.55
Below melting point	Order=1	23.58	61.8 259	Thermogravimetry	D-23	Fraction reacted >0.55
240-75 513-48			38.0 159	Thermogravimetry	D-23	Fraction reacted 0.1-0.4
258-70 531-43			58.0 243	Thermogravimetry	D-23	Fraction reacted 0.6
275-80 548-53			256 1071	DSC	D-23	
276-83 549-56			177 741	Thermogravimetry	D-23	
280-300 553-73	Order=1 (assumed)		146 611	DSC	D-24	
200-40 473-513	Order=1 (assumed)		29.9 ^e 125	Mass Spec. Study of decomposition products		
240-60 513-533	Order=1 (assumed)		67.4 282		D-25	
222-42 495-515			42 175	Mass Spec. Study of decomposition products		
251-64 524-37			42±2 176±8	Isothermal DSC	D-27	

TABLE D-2. ARRHENIUS PARAMETERS FOR THERMAL DECOMPOSITION OF HMX AT AND BELOW ITS MELTING POINT (Cont'd)

Temperature Interval (°C) (°K)	Type of Kinetics or Region	$\text{Lg}10\dot{A}$ (sec ⁻¹)	Activation Energy (kcal/mole)(LJ/mole)	Method	Ref	Remarks
252-63 525-36			44±2 181±8 46±10 192±42	Isothermal DSC DSC	D-27 D-27	Scanning (4°-32° C/min)
250-60 523-33		35.760	140 586	Used data of Reference D16	D-28	Obtained from data of Reference D-16, using equation 6.4.2 of Reference D-29.
177-272 450-95		9.08	33.24 139	Manometric (corr for gas reaction)	D-22	Cvetanovic-Singleton Analysis of Data in Figure 3, line 4 of Reference D-22. Are these values and those in the following line half-way-decent estimates of true solid-state HMX decomposition? Sample size 200 mg.
177-222 450-95		9.14	33.4 140		D-22	Ordinary least-squares analysis of data on preceding line.

TABLE D-3. RATE DATA FROM REFERENCE D-22 USED IN STATISTICAL ANALYSIS OF CONDENSED-PHASE DECOMPOSITION OF RDX

Temperature (°C)	1000/T	k(sec ⁻¹)	log ₁₀ k	Remarks
198	2.122	6.40x10 ⁻⁶	-5.194	Data read with an expandable ruler from Figure 3 of Reference D-22. Least-squares analysis gave log A (sec ⁻¹) = 13.51 and Ea = 40.31 Kcal/Mole (Cvetanovic-Singleton) and log A (sec ⁻¹) = 13.50 and Ea = 40.30 Kcal/Mole (ordinary least squares)
188	2.169	2.51x10 ⁻⁶	-5.600	
177	2.235	8.91x10 ⁻⁷	-6.050	
167	2.275	2.82x10 ⁻⁷	-6.550	

TABLE D-4. RATE DATA FROM REFERENCE D-22 IN STATISTICAL ANALYSIS OF CONDENSED PHASE DECOMPOSITION OF HMX

Temperature (°C)	1000/T	k(sec ⁻¹)	log ₁₀ k	Remarks
222	2.022	2.75x10 ⁻⁶	-5.560	Data read with an expandable ruler from Figure 3 of Reference D-22. Least-squares analyses gave log A (sec ⁻¹) = 9.084 and Ea = 33.24 Kcal/Mole. (Cvetanovic-Singleton) and log A (sec ⁻¹) = 9.14 and Ea = 33.36 Kcal/Mole (ordinary least squares)
211	2.065	1.12x10 ⁻⁶	-5.950	
199	2.120	4.68x10 ⁻⁷	-6.330	
177	2.222	9.12x10 ⁻⁸	-7.040	

APPENDIX E.

COMPUTER PROGRAM USED FOR LEAST-SQUARES FIT OF ORIGINAL
DATA

APPENDIX E.

COMPUTER PROGRAM USED FOR LEAST-SQUARES FIT OF ORIGINAL DATA

PROGRAM ACTEN

DIMENSION TITLE(80)

DO 30 I=1,10

READ(5,2001,END=5000,ERR=5000)TITLE

2001 FORMAT(80A1)

WRITE(6,2002)TITLE

2002 FORMAT(80A1, /)

II=0

SX=0.

SX2=0.

SY=0.

SY2=0.

SXY=0.

DO 10 I=1,1000

READ(5,*,END=5000,ERR=5000)X,Y

2000 FORMAT(2F10.4)

IF(X.EQ.999.)GO TO 20

WRITE(6,2000)X,Y

N=N+1

SX=SX+X

SX2=SX2+X**2

SY=SY+Y

SY2=SY2+Y**2

SXY=SXY+X*Y

10 CONTINUE

20 CONTINUE

F1=SX2-((SX**2)/FLOAT(N))

F2=(SXY-((SX*SY)/FLOAT(N)))/F1

F3=(-SX*F2+SY)/FLOAT(N)

F4=((F2**2*SX2)-(SXY*2*F2)+SY2-FLOAT(N)*F3**2)/FLOAT(N)

F5=F4/F1

SB=SQRT(SX2*F5/FLOAT(N))

B=F3

SXM=SQRT(F5)

XM=F2

WRITE(6,400)

WRITE(6,200)XM,SXM,B,SB

ACTFAC=2.3026*1.9872

AXM=(-1.)*XM*ACTFAC

ASXM=SXM*ACTFAC

WRITE(6,502)AXM,ASXM

30 CONTINUE

200 FORMAT(4F11.4)

300 FORMAT(/)

400 FORMAT(/, 'SLOPE, SIG SLOPE, INTERCEPT, SIG INTERCEPT',/)

502 FORMAT(/, 'ACT EN SIG ACT EN',//,2F10.4,//)

5000 CONTINUE

END

APPENDIX F.

COMPUTER PROGRAM USED FOR LEAST SQUARES FIT OF LOGARITHMS
OF DATA

COMPUTER PROGRAM USED LEAST SQUARES FIT OF LOGARITHMS OF DATA

114

C COMPARE THE NEW VALUES OF A AND C WITH THE VALUES FROM THE PREVIOUS
C ITERATION. IF THEY ARE CLOSE ENOUGH, END THE ITERATION.

60

O1=ABS(A-A)/ABS(A)
O2=ABS(C-C)/ABS(C)

IF (O1.LT.1.0E-5.AND.O2.LT.1.0E-5) GO TO 1000

C OTHERWISE, REDEFINE THE TRANSFORMED HEIGHTS AND ITERATE AGAIN.

A=A

C=C

DO 70 K=1,M

70 A(K)=YP(K)*(Y(K)-YP(K))+R(K)/ALOG(Y(K)/YP(K))

500 CONTINUE

1000 CONTINUE

C FIND THE RELATIVE ERROR.

ERR=0.0

DO 1050 K=1,M

D=Y(K)-YP(K)

PC=ABS(D/Y(K))

ERR=ERR+PC**2

75

1050 CONTINUE

ERR=SQRT(ERR/FL0AT(M))

120 FORMAT(1P,E12.4)

RETURN

END

80

59 SQAC

60 SQAC

61 SQAC

62 SQAC

63 SQAC

64 SQAC

65 SQAC

66 SQAC

67 SQAC

68 SQAC

69 SQAC

70 SQAC

71 SQAC

72 SQAC

73 SQAC

74 SQAC

75 SQAC

76 SQAC

77 SQAC

78 SQAC

79 SQAC

80 SQAC

91 SQAC

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1  SUBROUTINE DECOMP(M,N,MUL,SCALE,IPS)
2  DIMENSION UL(M,N),MUL,SCALE(1:M,N),IPS(1:M,N)
3  C THIS IS A STANDARD ALGORITHM FOR SOLVING A SET OF LINEAR
4  C ALGEBRAIC EQUATIONS USING AN LU DECOMPOSITION AND
5  C BACK SUBSTITUTION.
6  C REFERENCE.
7  C FORSYTHE AND WOLF. COMPUTER SOLUTION OF LINEAR ALGEBRAIC SYSTEMS.
8  DO 5 I=1,N
9  IPS(I)=1
10 ROWNR=0.0
11 DO 2 J=1,M
12 IF (ROWNR-ABS(UL(I,J)))>2.0
13 ROWNR=ABS(UL(I,J))
14 CONTINUE
15 IF (ROWNR<1.0E-10)
16 GO TO 5
17 CALL SING(I)
18 SING(I)=0.0
19 CONTINUE
20 M-1=M-1
21 DO 17 K=1,M-1
22 IF (UL(I,K))>0.0
23 DO 11 L=K+1,M
24 IP=IPS(L)
25 SIZE=ABS(UL(I,K))*SCALE(IP)
26 IF (SIZE<SCALE(IP))
27 IF (SIZE<SCALE(IP))
28 IF (SIZE<SCALE(IP))
29 IF (SIZE<SCALE(IP))
30 IF (SIZE<SCALE(IP))
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