THERMAL DECOMPOSITION OF ENERGETIC MATERIALS.
3. TEMPORAL BEHAVIORS OF THE RATES OF FORMATION OF
THE GASEOUS PYROLYSIS PRODUCTS FROM CONDENSED-
PHASE DECOMPOSITION OF 1,3,5-TRINITROHEXAHYDRO-S-
TRIAZINE

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Through the use of simultaneous thermogravimetry modulated beam mass spectrometry (STM/BMS) measurements, time-of-flight (TOF) velocity-spectra analysis, and 2H, 13C, 15N, and 18O labeled analogues of 1,3,5-trinitrohexahydro-s-triazine (RDX), the thermal decomposition products of RDX have been identified as H2O, HCN, CO, CH2O, NO, N2O, NH2CHO, NO2, N2O3, (CH3)NHCHO, oxy-s-triazine (OST), and 1-nitroso-3,5-dinitrohexahydro-s-triazine (ONDNTA) and all of their gas formation rates have been measured as a function of time. From these results the primary reaction pathways that control the decomposition of RDX in both the solid and liquid phases have been discovered. Four primary reaction pathways control the decomposition of RDX in the solid phase on the time scales of 200 and 215°C. Two pathways are first-order reactions solely in RDX. One produces predominantly OST, NO, and H2O and accounts for approximately 30% of the decomposed RDX, and the other produces predominantly N2O and CH2O with smaller amounts of NO2, CO, and NH2CHO and accounts for 10% of the decomposed RDX. The third pathway consists of formation of ONDNTA by reaction between NO and RDX, followed by the decomposition of ONDNTA to predominantly CH2O and N2O. The fourth reaction pathway consists of decomposition of RDX through reaction with a catalyst that is formed from the decomposition products of previously decomposed RDX. ONDNTA is the only product that appears to be formed during the early stages of decomposition of RDX in the solid phase.

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Introduction

The two similar cyclic nitramines, 1,3,5-trinitrohexahydro-s-triazine (RDX, I) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX, II) are energetic ingredients that are used in various propellants and explosives. Understanding the complex physicochemical processes that underlie the combustion of these materials can lead to methods for modifying the propellant and explosive formulations in which they are used to obtain better ignition, combustion, or sensitivity properties. Since the processes that occur in the condensed phase of these materials ultimately lead to the reactants that are consumed in the gas-phase combustion reactions, it is important to understand these condensed-phase processes. Consequently, our work is aimed at obtaining a better understanding of physical processes and reaction mechanisms that occur in the condensed phase of nitramine compounds so that the identity and rate of release of the pyrolysis products can be predicted, as a function of pressure and heating rate, based on the physical properties and molecular conformation of the materials. The present study examines the thermal decomposition of RDX and compares it to our recent studies on the condensed-phase decomposition of HMX.1,2

Reviews3-5 of the literature on RDX and HMX have discussed the roles of unimolecular decomposition and autocatalysis on the thermal decomposition of these compounds. The work on RDX has included slow-heating rate thermal decomposition studies,6-10 mass spectrometry mass spectrometry studies,11-15 high-heating rate thermal decomposition studies,16,17 and studies of shock initiated decomposition.18,19 Much of the controversy about the reaction mechanism that controls the decomposition of RDX and HMX centers around the fact that results from these experiments, using different thermal decomposition measurement techniques, have identified different sets of decomposition products. In general, two different sets of products are formed in these experiments

\[ \text{RDX} \rightarrow \text{N}_2\text{O} + \text{CH}_2\text{O} \quad (\text{R1}) \]

\[ \text{RDX} \rightarrow \text{HCN} + \text{NO}_2 + \text{other products} \quad (\text{R2}) \]

To explain the appearance of these different groups of products, reaction mechanisms based on C-N bond breaking were suggested for \( \text{N}_2\text{O} \) and \( \text{CH}_2\text{O} \) in reaction R1 and N-N bond breaking or four- and five-center HONO elimination reactions for the formation of products in reaction R2. The reasons for why products from reaction R1 were seen in certain types of experiments, whereas products from reaction R2 were seen in other types of experiments, were unclear. Furthermore, simple bond-breaking mechanisms could not explain the apparent "autocatalytic" behavior observed in several thermal decomposition experiments. Arguments, such as the occurrence of a phase change from a solid to a liquid (or molten) state, were put forth to explain the autocatalytic behavior and still allow interpretation of the product identities in terms of unimolecular RDX or HMX bond-breaking sequences. In retrospect, it appears that much of the controversy in interpreting the results of the work carried out by various experimenters stems from the fact that the decompositions of RDX and HMX are complex and consist of several competing reaction pathways that depend on the physical state of the material, as well as its molecular conformation, as it undergoes decomposition. Ultimately, these competing channels produce different thermal decomposition products. Almost all conventional thermal decomposition experiments (i.e., TGA, DTA, DSC, and mass spectrometry analysis) have not been able either to measure the
products larger than those illustrated by reactions R1 and R2 or to monitor the variations in the relative amounts of the products as the chemical composition of the reacting sample changed due to the ongoing decomposition of the initial sample of RDX or HMX.

To circumvent these problems and in an effort to obtain more detailed information on the reaction mechanisms, experiments have been carried out with simpler nitramines, such as dimethylnitramine \((\text{CH}_3)_2\text{N}-\text{NO}_2\) (DMNA), which are more amenable to conventional gas-phase decomposition studies. In addition, photodecomposition experiments on RDX under collisionless conditions have provided detailed information on its unimolecular decomposition by using infrared multiphoton dissociation (IRMPD) to fragment RDX molecules in a molecular beam and determine the identity and translational energy of the resulting fragments using mass spectrometry and time-of-flight (TOF) velocity analysis techniques. These two types of experiments have provided valuable insights into how these nitramines decompose. The question that one poses is whether the mechanisms derived from these experiments also control the decomposition of RDX and HMX in the condensed phase. To answer this question, more detailed information is required than has been obtained in the conventional thermal decomposition experiments. Our experiments collect two additional types of data that will aid the understanding of the decomposition of RDX and HMX in the condensed phase. First, important reaction pathways are uncovered by identifying the more complex molecules that may act as intermediates leading to the formation of lower molecular weight species. Second, since reactions between RDX and its decomposition products can lead to changes in the composition of the sample being studied during the course of an experiment, it is important to determine how the gas formation rates of all the products change as a function of time during the experiment. Reactions that may control the decomposition of RDX by itself may not control its decomposition in the presence of its decomposition products. Obtaining this information on the decomposition products should further our understanding of the decomposition of these materials and hopefully unravel some of the conflicting results that have been observed using more conventional experimental techniques.

Previously, we have used a combination of simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS), TOF velocity-spectra analysis, and isotopic analogues of HMX to study the thermal decomposition mechanisms of HMX in the condensed phase below its melting point. From this work we have identified and measured the rates of formation of all the major thermal decomposition products formed during the decomposition of HMX. We have found that HMX decomposes via several parallel reaction pathways and that trapping of the HMX decomposition products within gas bubbles in the HMX particles plays a significant role in its decomposition mechanism. The reaction pathways that are consistent with both our measured rates of gas product formation\(^1\) and our deuterium kinetic isotope effect (DKIE) and isotopic scrambling experiments\(^2\) are as follows: (1) breaking of the N-N bond to form NO\(_2\), followed by the elimination of the two remaining methylenenitramine \((\text{CH}_3)_2\text{N}-\text{NO}_2\) groups that subsequently decompose to CH\(_3\)O and NO\(_2\), (2) a reaction mechanism that involves the transfer of a hydrogen atom during the rate-limiting step \((\text{H}_2\text{O} \text{trapped within the particle is one possible hydrogen containing species that may be involved in this reaction path}), and (3) the formation of the mononitroso analogue of HMX (ONTNTA, III) within the solid HMX that particles for long periods prior to their release. In contrast, the results on RDX that we present in this paper for the most part occur in the liquid phase, and the release of the decomposition products from the sample is more rapid than in the experiments with solid-phase HMX. The results of the thermal decomposition of RDX in the liquid phase will be shown to indicate that four different primary reaction pathways control its decomposition, and there are significant differences between its decomposition pathways and those of HMX in the solid phase.

In this paper and the following paper,\(^4\) we examine the thermal decomposition reactions and the concomitant effect of physical state (i.e., solid vs liquid) that control the decomposition pathways of RDX and compare the results to those found for the decomposition of HMX. We present in this paper the results from experiments with RDX that are used to identify the decomposition products from the mass spectrometry data, provide the temporal dependence of the rates of formation of the various decomposition products formed in solid, liquid, and mixed-melt phases of RDX, and discuss the primary reaction pathways that control the thermal decomposition of RDX. The following paper contains data on the probable rate-limiting steps and important bond-breaking processes derived from the DKIE and isotopic scrambling results from decomposition of isotopic analogues of RDX and discusses the implications of these results on the reactions that occur in each of the primary reaction pathways.

Experimental Section

Instrument Description. The STMBMS apparatus and the basic data analysis procedures have been described previously.\(^\text{25, 26}\) Briefly, this instrument allows the concentration and rate of formation of each gas-phase species in a reaction cell to be measured as a function of time by correlating the ion signals at different \(m/z\) values measured with a mass spectrometer with the force measured by a microbalance at any instant. In the experimental procedure, a small sample (~10 mg) is placed in an alumina reaction cell that is then mounted on a thermocouple probe that is seated in a microbalance. The reaction cell is enclosed in a high vacuum environment (<10\(^{-6}\) Torr) and is radiatively heated by a bifilar-wound tungsten wire on an alumina tube. The molecules from the gaseous mixture in the reaction cell exit through a small diameter (~25 \(\mu\)m in these experiments) orifice in the cap of the reaction cell, traverse two beam-defining orifices before entering the electron-bombardment ionizer of the mass spectrometer where the ions are created by collisions of electrons with the different molecules in the gas flow. The background pressures in the vacuum chambers are sufficiently low to eliminate significant scattering between molecules from the reaction cell and background molecules in the vacuum chambers. The different \(m/z\)-value ions are scanned with a quadrupole mass filter and counted with an ion counter. The gas flow is modulated with a chopping wheel, and only the modulated ion signal is recorded.

The containment time of gas in the reaction cell is a function of the area of the orifice, the free volume within the reaction cell, and the characteristics of the flow of gas through the orifice. For the reaction cell used in the experiments with RDX, the time constant for exhausting gas from the cell (i.e., the time it takes after its formation, for a gaseous product to exit the reaction cell) is short (~3.2\(\tau\)) compared to the duration of the experiments (>1000\(\tau\)). Since the evaporation rate of the reactant is controlled by the size of the reaction cell orifice, the relative rates of reactant evaporation and reactant decomposition are controlled by adjusting the size of the reaction cell orifice.

Two different types of reaction cells are used in the experiments. Both types are constructed from high density alumina. A new design has been developed to reduce the rate of evaporation of RDX and also to prevent the clogging of the exit orifice by the splattering of molten RDX, as experienced with the previous design.\(^2\) A cross section of the new reaction cell design is shown in Figure 1. The orifice assembly consists of a hole located in the center of a 25.4 \(\mu\)m thick gold foil disk that is sandwiched between two alumina containment plates. The orifice assembly is sealed to the reaction cell with a ground cone fit. A hollow
The cylindrical baffle with four holes in the top plate and constructed The results from the isotopically labeled RDX show that the solubilities in the condensed phase, the rates of release from the density, partial pressure or the rate of molar gaseous product and the ion signal at are determined, the results are expressed as either the number ion signal measured with the mass spectrometer to rates of mass spectrometer from thermal decomposition products (e.g. 

The free volume within the cell is 0.256 cm

The mass range of the mass spectrometer is calibrated using perfluorotributylamine, and the resolution is set so that the peak widths in the 20-300 amu region are approximately 0.7 amu full width at 10% maximum. The ionizer is operated in the linear electron-emission range at 1.0 mA. The electron energy is calibrated using the appearance potentials of N-methyformamide. The ion signals from unlabeled RDX using isotopically labeled analogues TOF spectra in Figure 2 show that ion signals at some of the values measured during one thermal decomposition experiment and separating the different m/z values into temporally correlated groups that represent the major ion signals in the mass spectra of each product, and (3) measuring TOF velocity spectra of ion signals at m/z values representing each decomposition product to determine the molecular weight of the respective thermal decomposition product. Explicit details of this procedure have been described previously for the case of HMX decomposition.

Identification of Decomposition Products. The decomposition products are identified by (1) using isotopically labeled analogues of RDX to determine the formulas of the m/z values measured with the mass spectrometer, (2) performing an autocorrelation analysis on all of the ion signals measured during one thermal decomposition experiment and separating the different m/z values into temporally correlated groups that represent the major ion signals in the mass spectra of each product, and (3) measuring TOF velocity spectra of ion signals at m/z values representing each decomposition product to determine the molecular weight of the respective thermal decomposition product. Explicit details of this procedure have been described previously for the case of HMX decomposition.

Quantification Procedure. The procedures used to convert the ion signals measured with the mass spectrometer to rates of gaseous decomposition product formation have also been described previously. After the mass spectrometer sensitivity factors are determined, the results are expressed as either the number density, partial pressure or the rate of molar gaseous product formation of each species as a function of time. For decomposition products that are present only in the gas phase and have low solubilities in the condensed phase, the rates of release from the reaction cell are equal to the rates of formation of these decomposition products. For products that are present in both the gas and condensed phases, the rate of release from the reaction cell is determined by the equilibrium vapor pressure of the species in the reaction cell.

Sample Preparation. The pure RDX and deuterium labeled analogue of RDX (RDX-d4) are prepared by oxidation of 1,3,5-trinitrosohexahydro-s-triazine following the procedure described in the accompanying paper. The mean particle diameter of RDX used in these experiments is 130 μm. The lower purity RDX sample is prepared according to military specification MIL-R-398C Type B and contains approximately 4% HMX.

Results

Identification of Decomposition Products. The m/z values associated with the various thermal decomposition products formed from unlabeled and 1H, 13C, and 15N labeled RDX are shown in Table II. The formulas for the ion signals of m/z values associated with the lower molecular weight products are as expected from the unlabeled and isotopically labeled RDX analogues. These products include H2O, HCN, CO, CH4O, NO, N2O, and NO2. The results from the isotopically labeled RDX show that the formula for the ion signal at m/z = 45 is H2NCHO and is probably formamide. Likewise, the results also show that the formula that corresponds to m/z = 59 is CH3NHCHO and is most likely N-methylformamide. The ion signals from unlabeled RDX at m/z values of 70 and 97 are temporally correlated and originate from the same product. The results from experiments with the isotopic analogues of RDX show that the formula of the m/z = 70 ion is C4H2N2O and the formula of the m/z = 97 ion is C3H4N3O. Finally, the ion signals at m/z values of 42 and 132 are temporally correlated. The results from the experiments with the isotopic analogues of RDX show that the ion formula for m/z = 132 is C4H2N2(ONO)2. TOF spectra in Figure 2 show that ion signals at some of the m/z values arise solely from the thermal decomposition products. These products include HCN (m/z = 27), N2O (m/z = 44), methylformamide H2NCHO (m/z = 45), HONO (m/z = 47), and C3H4N2O (m/z = 97). On the other hand, TOF velocity spectra of ion signals at several other m/z values show that the ion signals at these m/z values arise from a decomposition product in addition to RDX that evaporates from the reaction cell without undergoing decomposition. Contributions from both RDX and its decomposition products are found at m/z values associated with CO (m/z = 28), CH4O (m/z = 29, 30), NO (m/z = 30), and NO2 (m/z = 46). Finally, the TOF velocity spectra show that ion signals at several m/z values are daughter ions formed in the mass spectrometer from thermal decomposition products (e.g. m/z = 58 that probably originates from the N-methylformamide dimer (MW = 118), the ion signal at m/z = 70 that originates from the C4H2N2O product, and the ion signal at m/z = 132 that originates from 1-nitroso-3,5-dinitrohexahydro-s-triazine (ONDNTA) (MW = 206). Several of the TOF velocity spectra displayed in Figure 3 show that the major ion signals recorded at several m/z values are formed solely from evaporating RDX. These spectra were collected during the isothermal decomposition of RDX under the conditions listed for experiment VI in Table I. The TOF velocity

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<td>ionizer electron energy (eV)</td>
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* RDX denoted as pure or RDX-d4 are pure samples of RDX prepared by the method outlined in ref 24. RDX denoted as Mil is prepared according to military standard Mil-R-398C Type B and contains 96% RDX and 4% HMX. * Reaction cells denoted as 1 are constructed completely from alumina and are described in ref 26. Reactions cells denoted as 2 utilize a 25.4 μm thick gold pinhole orifice and are described in this paper. ^ Quant denotes a quantitative experiment to determine reaction rates, ion denotes only ion signals analyzed, and TOFVS denotes a time-of-flight velocity-spectra experiment.

Figure 1. Cross section of the reaction cell used for thermal decomposition experiments. Reaction cell is construction from alumina and is cylindrically symmetric about the vertical axis through the center of the cell. Gas exhausts through the pinhole orifice located in the 25.4 μm thick gold foil.
Table II: Ion Formulas, m/z Values from Isotopically Labeled Analogues, and Pyrolysis Product Molecular Weights and Formulas from the Thermal Decomposition of RDX

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<td>CH₂N₂O₃(NO)(NO₂)</td>
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*The m/z values measured in thermal decomposition experiments with unlabeled (ul), deuterium-labeled (d₆), ¹³C-labeled, and ¹⁵N-labeled analogues of RDX. The experimental parameters used for ¹³C- and ¹⁵N-labeled samples were identical to those used for experiments I–III in Table I.

The molecular weights of the compounds contributing to the ion signal at each m/z value are determined from TOF velocity spectra.

Figure 2. Time-of-flight velocity spectra of ion signals at various m/z values measured with the mass spectrometer. The signals are formed from the mixture of products evolving from the reaction cell during the decomposition of RDX. The symbols represent the measured data, the error bars denote the ± standard deviation, and the solid and dashed curves represent the contribution to the ion signals from the various species (denoted by their molecular weights) that are contained in the mixture of products flowing out of the reaction cell during the decomposition. The details of the deconvolution procedure to fit the data are described in ref 26. TOF velocity spectra at m/z values of 30, 44, 46, 70, 97, and 132 were collected in experiment VI where the sample temperature was 192 °C. The remaining spectra were collected in experiment VII where the reaction cell temperature was 197 °C for m/z values of 27, 28, and 29 and 201 °C for m/z values of 45, 47, and 58.
The temporal behaviors of the gas formation rates of the decomposition products were collected in experiment VI where the sample was melted at a temperature of 195 °C. The gas formation rates of the decomposition products are divided into three groups for each experiment based on differences in the time-to-peak and the temperature at which it occurs.

The ion signals formed from ONDNTA are at \( m/z = 128 \) and \( m/z = 148 \) were collected in experiment VII that decomposed at a temperature of 192 °C and the spectra at \( m/z = 74 \) was collected in experiment VII at a temperature of 193 °C.\(^{30}\)

Another higher molecular weight thermal decomposition product forming the ion signal at \( m/z = 45 \) is consistent with the formamide product. The TOF velocity spectra of the ion signal at \( m/z = 58 \) show that this product has a molecular weight of approximately 118 and together with the formula of the ions as determined from the correlation of the \( m/z \) values in the various isotopic analogues of RDX suggest that this product is N-methylformamide that evolves as a dimer from the reaction cell. The ion signal at \( m/z = 73 \) is small, and TOF velocity spectra were not collected. The structural assignments of these products are consistent with the previous tandem mass spectrometry studies of Snyder et al.\(^{31}\)

Some products that are formed during the decomposition, and not observed with the mass spectrometer, is an orange-brown residue that coats the inner walls of the reaction cell.

**Rates of Formation of Thermal Decomposition Products.** In addition to providing the identities of the decomposition products formed from RDX, the results also provide the rates of release of each individual product from the reaction cell as described above under the “Quantification Procedure.”

The results from four experiments (experiments I–IV) illustrate the effect of melting on the decomposition of RDX and show the presence of several different reaction branches that control the thermal decomposition of RDX. The series of experiments include two thermal ramp experiments with pure RDX experiment I with pure RDX and experiment II with RDX-ONDNTA, one thermal ramp experiment with an RDX/HMX mixture experiment I1 that forms a lower melting eutectic, and two thermal ramp experiments with pure RDX (experiments I and II) held below its melting point. The analysis of the data from experiments I–IV was carried out in the manner described above, and the results are presented in Table III. As shown in Table III, the mass balance for carbon, hydrogen, nitrogen, and oxygen is within 2% of nominal for experiments I–III. Table III also lists the amount of each product formed during each experiment and the ratio of the total amount of each product formed to the amount of RDX that decomposed.

The temporal behaviors of the gas formation rates of the thermal decomposition products from pure RDX (experiment I) and RDX-ONDNTA (experiment II) are shown in Figures 4 and 5, respectively. The gas formation rates of the decomposition products are divided into three groups for each experiment based on differences in their temporal behaviors. The products in the first group are shown in the panel A of Figures 4 and 5 and consist of the OST, H₂O, NO, and HCN thermal decomposition products. The general behaviors exhibited by these products include a very rapid rise from zero in their gas formation rates as the RDX melts, the maximum rate of gas formation immediately after melting, and a decrease in the rate of gas formation of OST, H₂O, and NO as the amount of RDX in the reaction cell diminishes. Furthermore, in these two experiments, and many other experiments with pure RDX, the following general features were observed in the OST, H₂O, and NO gas formation rates: (1) the OST, H₂O, and NO showed a sharp peak after the sample melted; (2) following the sharp peak, the OST gas formation rate gradually declined as the amount of RDX sample remaining diminished; and (3) following the sharp peak, the H₂O and NO gas formation rates rose to form a second broader peak or a shoulder and then also declined as the amount of RDX sample remaining diminished.

The products in the second group are shown in panel B in Figures 4 and 5 and consist of N₂O, CH₃O, CO, NO₂, and NH₂CHO. The general behaviors exhibited by these products include a rapid rise from zero in their rates of gas formation as the sample melts followed by a more gradual rise to a very broad peak or plateau in their gas formation rates as the amount of RDX remaining decreases. The gas formation rates of N₂O and CH₃O remain at high levels even when the amount of RDX has greatly diminished near the end of the experiment. It is clear that the gas formation rates of these products are not simply proportional to the amount of RDX present as is the case with OST, H₂O, and

\[ \text{(CH₃)NHCHO (m/z = 58, 59)} \]

The TOF velocity spectra displayed in Figure 2 show that the molecular weight of the thermal decomposition product forming the ion signal at \( m/z = 45 \) is consistent with the formamide product. The TOF velocity spectra of the ion signal at \( m/z = 58 \) show that this product has a molecular weight of approximately 118 and together with the formula of the ions as determined from the correlation of the \( m/z \) values in the various isotopic analogues of RDX suggest that this product is N-methylformamide that evolves as a dimer from the reaction cell.

**Table III**

<table>
<thead>
<tr>
<th>Product</th>
<th>Time (ms)</th>
<th>Rate of Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>OST</td>
<td>1</td>
<td>High</td>
</tr>
<tr>
<td>H₂O</td>
<td>2</td>
<td>Medium</td>
</tr>
<tr>
<td>NO</td>
<td>3</td>
<td>Low</td>
</tr>
</tbody>
</table>

The TOF velocity spectra displayed in Figure 2 show that the molecular weight of the thermal decomposition product forming the ion signal at \( m/z = 45 \) is consistent with the formamide product. The TOF velocity spectra of the ion signal at \( m/z = 58 \) show that this product has a molecular weight of approximately 118 and together with the formula of the ions as determined from the correlation of the \( m/z \) values in the various isotopic analogues of RDX suggest that this product is N-methylformamide that evolves as a dimer from the reaction cell.
Figure 4. Gas formation rates of the thermal decomposition products formed during experiment I using pure unlabeled RDX and a heating rate of 0.58 °C/min. The gas formation rates of the products are divided into three groups with similar temporal behaviors: Panel A shows products whose gas formation rates peak after the sample melts and then remain approximately proportional to the amount of sample left in the reaction cell. Panel B shows products whose gas formation rates peak between the onset of decomposition and the depletion of the sample, and panel C shows products whose gas formation rates keep increasing throughout the experiment until the sample is depleted. The weight fraction of the original sample (1 - X) remaining in the reaction cell is shown in panel D.

Figure 5. Gas formation rates of the thermal decomposition products formed during experiment II using pure RDX-d₆ and a heating rate of 0.58 °C/min. The gas formation rates of the products are divided into three groups with similar temporal behaviors: Panel A shows products whose gas formation rates peak after the sample melts and then remain approximately proportional to the amount of sample left in the reaction cell. Panel B shows products whose gas formation rates peak between the onset of decomposition and the depletion of the sample, and panel C shows products whose gas formation rates keep increasing throughout the experiment until the sample is depleted. The weight fraction of the original sample (1 - X) remaining in the reaction cell is shown in panel D.

NO. Since products formed from the decomposition of RDX in the gas phase would be proportional to its vapor pressure (3-6 Torr in these experiments), it is possible that N₂O and CH₂O are formed by this route. Results from previous gas-phase decomposition studies of RDX¹⁴ (A = 10¹⁶, Eₚ = 40.4 kcal/mol) indicate that between 5 and 10% of the N₂O formed after the RDX melts may arise from decomposition in the gas phase. However, these same results and the assumption that each gas-phase RDX molecule decomposes to form two N₂O molecules show that the formation rates of N₂O prior to melting are overestimated by at least a factor of 2 when compared to the N₂O gas formation rates prior to melting in our experiments. This is illustrated in Figures 4 and 5 by the relatively low gas formation rates of N₂O prior to melting (panel B) compared to the smaller change in the vapor pressure of RDX as the sample melts (panel A). This is reasonable since the fraction of gas-phase RDX is small (~2 × 10⁻³) in these experiments. Consequently, it appears that the rates of formation of products in this group may be a result of either "autocatalytic" reactions or reactions between RDX and its own decomposition products.

The products in the third group are shown in panel C of Figures 4 and 5 and consist of ONDNTA, HONO, and N-methylformamide. The general behaviors of the products in this group differ from the previous two groups. The products in this group do not exhibit a rapid rise in their rates of gas formation when the sample melts. Instead their rates of gas formation rise slowly from zero to a peak when the sample is almost completely depleted. This suggests that these components may be soluble in, or derived from a product that is soluble in, RDX and that their release rates from the reaction cell may be dependent on their vapor pressures which...
The gas formation rates of the products formed during the decomposition of the RDX/4% HMX sample (experiment III) are shown in Figure 6. In a manner similar to experiments I and II, the results are also divided into the same three groups as in Figures 4 and 5 that depend on the temporal behaviors of the products. The general sequence of release of the products in each group is the same as that for the pure RDX and RDX-d6. The products in the first group are released first, and their gas formation rates are proportional to the amount of RDX remaining in the experiment. The gas formation rate of products in the second group increase later than the first group and gradually increase and remain at a constant gas formation rate until the sample is depleted. The gas formation rates of the third group of products increase constantly until the sample is depleted.

Figure 6. Gas formation rates of the thermal decomposition products formed during experiment III using RDX that contains approximately 4% HMX and a heating rate of 0.54 °C/min. The gas formation rates of the products are divided into three groups with similar temporal behaviors. Panel A shows products whose gas formation rate rises from zero at 193 °C, gradually increases and peaks first during the decomposition, panel B shows products whose gas formation rates peak later than the first group but prior to the depletion of the sample, and panel C shows products whose gas formation rates keep increasing throughout the experiment until the sample is depleted. The weight fraction of the original sample (1 - X) remaining in the reaction cell is shown in panel D.

in turn are dependent on their mole fractions in the solution.

The gas formation rates of the products formed during the decomposition of the RDX/4% HMX sample (experiment III) are shown in Figure 6. In a manner similar to experiments I and II, the results are also divided into the same three groups as in Figures 4 and 5 that depend on the temporal behaviors of the products. The general sequence of release of the products in each group is the same as that for the pure RDX and RDX-d6. The products in the first group are released first, and their gas formation rates are proportional to the amount of RDX remaining in the experiment. The gas formation rate of products in the second group increase later than the first group and gradually increase and remain at a constant gas formation rate until the sample is depleted. The gas formation rates of the third group of products increase constantly until the sample is depleted.

However in contrast to the behaviors of the gas formation rates with the pure RDX and RDX-d6, the temporal behaviors of the products within the groups differ. The first difference is that the evolution of products in all of the groups starts at lower temperatures than those observed in the experiments with pure RDX and RDX-d6. For example, the evolution of OST, H2O, and NO starts at 188 °C and the evolution of CO, CH2O, N2O, NO2, and NH2CHO starts at 193 °C. Another difference between the gas evolution rates is the absence of an abrupt increase in the gas formation rates of the products that coincides with melting of the sample as seen in the experiments with pure RDX and RDX-d6. Since the mixture of RDX/4% HMX is known to form a lower melting eutectic that melts over a wider temperature range, the results are consistent with the thermal decomposition rate of RDX being much higher in the liquid phase than in the solid phase.

Comparison of the behaviors of the gas formation rates of the decomposition products from pure RDX and RDX-d6, with the behaviors of the gas formation rates of the products from RDX/4% HMX in the vicinity of the melting point of RDX (201 °C) raises the question of whether there is significant decomposition of RDX in the solid phase. For example, in the experiment with pure RDX it is possible that RDX undergoes decomposition in the solid but that the products are trapped within the solid and not released at significant rates until the sample melts. To check whether there was decomposition within the solid prior to melting, an isothermal decomposition experiment with pure RDX was conducted at 193 °C (experiment IV) where no significant melting would have occurred. The results from this experiment are summarized in Table III and shown in Figure 7. The only product observed in this experiment is ONDNTA, and it was formed at very low rates. The data from experiment IV were analyzed for all of the other products observed in experiments I-III, and no other products were observed. Thus, these results show that the decomposition rate of RDX is very much lower in the solid phase than it is in the liquid phase. Furthermore, the results of experiment IV do not exhibit the accelerating decomposition rate observed previously with HMX. This is due to the shorter length of time that the RDX sample used in experiment IV had to decompose in comparison to the previous experiments with HMX. To ascertain whether RDX exhibits the same type of decomposition behavior in the solid phase as HMX, larger samples of RDX were used in several experiments. The results of the isothermal decomposition of a 29.2-mg sample of pure RDX at 190 °C are shown in Figure 8. In this experiment only the ion signals at the m/z values representing each decomposition product are shown because as the larger samples start to decompose some of the liquid splatters and blocks the exit orifice making quantification of the results not possible. However, the results clearly show that RDX undergoes an accelerated release of the decomposition products. The products that are released during the induction period are ONDNTA, N2O, and a small amount of formaldehyde. At approximately 20,000 s the decomposition rate accelerates and
the evolution of OST, H₂O, NO, and N₂O commences. Although the data from experiment V is not strictly quantitative, it is clear that the amount of N₂O formed compared to OST is much greater in the solid-phase decomposition than it is in the liquid-phase decomposition (since the relative ion formation probability is smaller for N₂O than OST, the ratio of N₂O to OST will be larger than the ratio of the ion signals of these two products shown in Figure 8).

Discussion

As stated in the Introduction, we discuss here the identity of the decomposition products of RDX above its melting point, their rates of formation, and the temporal correlations among them. Following this, four primary branches of the decomposition mechanism will be identified and discussed. Pyrolytic reactions predominantly occur via free radical pathways, but it should be borne in mind that during the later stages of the decomposition the presence of water produced during the reaction may give rise to contributions from ionic processes. More definitive conclusions about the mechanisms involved in the four primary branches and comparison to the previously published HMX decomposition chemistry will be deferred to the next paper, in which insights into the bond-breaking processes are derived from additional experimental data on isotopic scrambling and deuterium kinetic isotope effects.

Lower Molecular Weight (Gaseous) Products. The nature and distribution of the low molecular weight (up to 47) products (H₂O, CH₃, CH₂, N₂O, NO, CO, and HCN) from RDX decomposition closely parallel those from HMX. In RDX small amounts of three additional ones, namely, NH₂CHO, NO, and HONO were detected. These were probably formed in the decomposition of HMX but were not observed because of secondary reactions within the HMX particle. Among the gaseous products, CH₂O and N₂O are the largest ones in both RDX and HMX but the ratio of N₂O/CH₂O is larger in HMX. The amount of HCN formed is also larger in HMX. However, judging from the general similarities in products and the closely related structures of RDX and HMX, the reaction pathways previously suggested for the gaseous products from HMX should also be valid for RDX. To recall, it has been assumed that CH₂O and N₂O, which are the major products, arise by a concerted process from each methylene nitramine unit in HMX:

\[
\begin{align*}
\text{CH}_2\text{N} = \text{N} &= \text{O} \\
\text{CH}_2\text{N} &= \text{N} \\
\text{CH}_2\text{N} &= \text{N} \\
\end{align*}
\]

In both RDX and HMX the amount of N₂O formed corresponds approximately to the collapse of one less methylene nitramine unit than present in the respective molecules. This is consistent with the conclusion that the decomposition process probably commences with the "least energy" pathway, namely, the cleavage of an NO₂ group after which the rest of the methylene nitramine units collapse mostly to CH₂O and N₂O. This requires that the rates of formation of CH₂O and N₂O should be proportional to the amount of RDX at any given time. However, in Figure 4, panel B, the shapes of the gas formation rate curves are inconsistent with the expected decline in rate with the RDX consumed. This suggests that there are other sources for N₂O and CH₂O formation which will be discussed later (see below). The rates of formation of NO and H₂O, however, do exhibit the expected decline as RDX is consumed (panel A, Figure 4), suggesting that they are products from a different reaction pathway.

Larger Molecular Weight Products. In addition to the gaseous products, RDX forms three larger products, ONDNTA, OST, and methylformamide, discussed briefly in Results. In the next paper, ONDNTA is shown to be formed by N=N bond cleavage followed by the recombinination of the residual radical with NO from another reaction as shown in the following:

\[
\begin{align*}
\text{CH}_2\text{N} &= \text{N} \\
\text{CH}_2\text{N} &= \text{N} \\
\text{CH}_2\text{N} &= \text{N} \\
\end{align*}
\]
it was suggested by the incomplete nitrogen isotope scrambling that ONDNTA formation was the result of N-N bond cleavage followed by reaction of NO to form NO and recombinetion of the NO with the residual amine radical in the HMX lattice cage. However, this does not rule out the contribution from simple N-O bond cleavage in HMX.

Oxy-s-triazine (OST), represented by one of the three structures IV-VI, is a unique and significant (0.38 mol/(mol of RDX decomposed) formed product from RDX with no counterpart characteristic of solid-phase decomposition reactions. This behavior is similar to that found in the decomposition of solid-phase HMX. The temporal behaviors of the gas formation rates of the various products are controlled by condensed-phase decomposition reactions and changes in the physical state of the sample and can be summarized as follows:

**Solid-Phase Decomposition.** The results from the isothermal decomposition of solid-phase RDX (experiment V, Figure 8) exhibit the classic induction and acceleratory features that are characteristic of solid-phase decomposition reactions. This behavior is similar to that found in the decomposition of solid-phase HMX.1 The temporal behaviors of the gas formation rates of the various products are controlled by condensed-phase decomposition reactions and changes in the physical state of the sample and can be summarized as follows:

| Table III: Quantitative Results from the Thermal Decomposition of RDX
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>amount (mg)</td>
<td>molar ratio</td>
<td>amount (mg)</td>
<td>molar ratio</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.054</td>
<td>0.70</td>
<td>0.058</td>
<td>0.74</td>
</tr>
<tr>
<td>HCN</td>
<td>0.008</td>
<td>0.07</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO</td>
<td>0.026</td>
<td>0.22</td>
<td>0.027</td>
<td>0.22</td>
</tr>
<tr>
<td>CH₂O</td>
<td>0.128</td>
<td>0.99</td>
<td>0.127</td>
<td>0.97</td>
</tr>
<tr>
<td>NO</td>
<td>0.1</td>
<td>0.77</td>
<td>0.082</td>
<td>0.63</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.221</td>
<td>1.17</td>
<td>0.206</td>
<td>1.07</td>
</tr>
<tr>
<td>H₂NCHO</td>
<td>0.057</td>
<td>0.29</td>
<td>0.095</td>
<td>0.48</td>
</tr>
<tr>
<td>HONO</td>
<td>0.037</td>
<td>0.19</td>
<td>0.144</td>
<td>0.72</td>
</tr>
<tr>
<td>CH₂NHCHO</td>
<td>0.007</td>
<td>0.03</td>
<td>0.006</td>
<td>0.02</td>
</tr>
<tr>
<td>OST</td>
<td>0.157</td>
<td>0.38</td>
<td>0.201</td>
<td>0.48</td>
</tr>
<tr>
<td>ONDNTA</td>
<td>0.118</td>
<td>0.13</td>
<td>0.079</td>
<td>0.09</td>
</tr>
<tr>
<td>RDX</td>
<td>2.993</td>
<td>3.13</td>
<td>6.302</td>
<td>6.51</td>
</tr>
</tbody>
</table>

*a The conditions for each experiment are given in Table I. *The species refer to either the listed species or its deuterium-labeled analogue where appropriate. *These relatively minor species are masked by overlap of ion signals from CO and H₂NCHO that occur at the same m/z values as the deuterium-labeled analogues of these products.

The results clearly show that the rate of decomposition is much higher in the liquid phase than in the solid phase. For example, in the experiments with both pure and RDX-d₆, essentially no products appear until the sample starts to melt, at which time there is a rapid increase in the rate of formation of the decomposition products. The rate of increase in the gas formation rates of several of the products is determined by the increasing amount of liquid RDX present as the sample melts over a temperature range of approximately 1 °C. Further evidence for the rate of decomposition being proportional to the amount of liquid is observed in the decomposition of the RDX/4% HMX sample. In this case the sample starts to melt at a lower temperature (188 °C) and melts over a broader temperature range. The more gradual increase in the amount of liquid RDX present as the sample is heated manifests itself in a more gradual increase in the rate of formation (and release) of the decomposition products (Figure 6).

**Liquid as Solid-Phase Decomposition.** The results show that the rate of decomposition is much higher in the liquid phase than in the solid phase. For example, in the experiments with both pure and RDX-d₆, essentially no products appear until the sample starts to melt, at which time there is a rapid increase in the rate of formation of the decomposition products. The rate of increase in the gas formation rates of several of the products is determined by the increasing amount of liquid RDX present as the sample melts over a temperature range of approximately 1 °C. Further evidence for the rate of decomposition being proportional to the amount of liquid is observed in the decomposition of the RDX/4% HMX sample. In this case the sample starts to melt at a lower temperature (188 °C) and melts over a broader temperature range. The more gradual increase in the amount of liquid RDX present as the sample is heated manifests itself in a more gradual increase in the rate of formation (and release) of the decomposition products (Figure 6).

**Solid-Phase Decomposition.** The results from the isothermal decomposition of solid-phase RDX (experiment V, Figure 8) exhibit the classic induction and acceleratory features that are characteristic of solid-phase decomposition reactions. This behavior is similar to that found in the decomposition of solid-phase HMX. The temporal behaviors of the gas formation rates of the various products are controlled by condensed-phase decomposition reactions and changes in the physical state of the sample and can be summarized as follows:

```
RDX (s) → ONDNTA (molten) Products associated with liquid-phrase decomposition (see below)
N₂O (g) + CH₂O (g)
```

The solid-phase RDX forms ONDNTA that subsequently decomposes predominantly to N₂O and CH₂O that remain trapped in the solid. As the build up of CH₂O and N₂O continues, N₂O is released from the sample and CH₂O disperses in the solid RDX causing the lattice structure of RDX to weaken, leading to the formation of molten RDX and the more rapid reactions associated with the liquid-phase decomposition. This decomposition pathway is consistent with the appearance of only ONDNTA, N₂O, and CH₂O prior to the start of the acceleratory stage. In addition, the fact that the release rate of N₂O is greater than that of CH₂O during the induction stage (see Figure 8) is consistent with the dispersion of CH₂O in the RDX lattice. The formation of
The decomposition of RDX in the liquid phase exhibit a complex further reactions prior to their measurement, it is not possible at gas formation rates of the decomposition products formed during occur in the liquid phase and generate products that can undergo in the conventional sense.

Change from solid to liquid and not from catalysis of the reaction the products in pathway P1 may in the solid-phase decomposition most likely arises from a phase pathway may be formed by a series of reactions. For example. our results it appears that a large part of the acceleratory effect sociated with each channel. The products associated with each effect has been described as "autocatalysis". However, from The reaction pathways, P1 - P4 denote the products that are as-

Studies with solid HMX. has been observed in many previous

- analogue, ONDNTA, in the crystal lattice.
- and those of HMX, it appears that RDX also forms a mononitroso HMX. Thus, from similarity of the results from experiment V
- scrambling in HMX contrasts with the complete scrambling group that replaced the ONTNTA product formed participated in scrambling of the NO
- work with solid-phase decomposition of HMX. In isotopic scrambling the main features of the temporal behaviors of the gas formation
- of ONDNTA in liquid RDX and was ascribed to the formation of ONNTA in the crystal lattice of HMX. Thus, from similarity of the results from experiment V and those of HMX, it appears that RDX also forms a mononitroso analogue, ONDNTA, in the crystal lattice.
- The acceleratory behavior of RDX, like that observed in the experiments with solid HMX, has been observed in many previous studies on HMX and RDX decomposition. In much of this work the effect has been described as "autocatalysis". However, from our results it appears that a large part of the acceleratory effect in the solid-phase decomposition most likely arises from a phase change from solid to liquid and not from catalysis of the reaction in the conventional sense.

Liquid-Phase Decomposition. The temporal behaviors of the gas formation rates of the decomposition products formed during the decomposition of RDX in the liquid phase exhibit a complex behavior that is determined by the formation of products from several different parallel reaction channels. The temporal behaviors of the data have been examined in light of the various reaction channels (reactions R1 - R12) that were developed on the basis of the identity of the decomposition products. This effort has led to the development of a simple decomposition model that requires the following four primary reaction channels to predict the main features of the temporal behaviors of the gas formation rates of the decomposition products.

\[
\text{OST} + H_2O + NO + NO_2 \quad (P1)
\]

\[
RDX \quad \text{[NO]} \quad \text{ONDNTA} \rightarrow N_2O + CH_2O + \text{other} \quad (P3)
\]

\[
N_2O + CH_2O + NO_2 + NH_2CHO \quad (P4)
\]

The reaction pathways, P1 - P4 denote the products that are associated with each channel. The products associated with each pathway may be formed by a series of reactions. For example, the products in pathway P1 may be formed via reaction R8 followed by the reaction of HONO by either reaction R6 or R7. Since the reactions that comprise these four reaction pathways occur in the liquid phase and generate products that can undergo further reactions prior to their measurement, it is not possible at this time to determine their exact details. However, the data do establish these pathways as major decomposition routes that control the decomposition of RDX in the liquid phase.

Simple Model for the Four Primary Reaction Pathways. The contribution of each of these reaction pathways to the various decomposition products is shown in Figure 9 for pure RDX.
decomposition pathways. The bold line (-) in all of the graphs represents the total contribution from all of the reaction channels. The square-dot portion to the amount of RDX remaining in the reaction cell. This reaction cell as the quantity of RDX decreases seems contrary to the rates of formation of more than one reaction channel. Appro- priate expression to account for its decomposition has not been developed.

The difference between the calculated and measured gas formation rates for OST, depicted in Figures 9 and 10, it can be seen that OST and ONDNTA exhibit relatively simple temporal behaviors and are representative of reaction pathways P1 and P3, respectively, whereas the other products have temporal behaviors that are determined by more than one reaction channel.

OST. The rate of formation of OST and, to a certain extent, the rates of formation of NOx and NO decrease in direct proportion to the amount of RDX remaining in the reaction cell. This behavior indicates that the decomposition reaction is first order in the amount of RDX and supports a possible unimolecular decomposition mechanism. The rates of formation of NOx and NO are similar to OST except for the presence of a shoulder on the curve that originates from reaction pathway P3. The calculated rate of formation of OST, shown in Figures 9 and 10, is based on the simple first-order rate expression

\[ \frac{dn_{OST}}{dt} = k_1 n_{RDX} \]  

(1)

where \( n_{OST} \) is the amount of OST, \( k_1 \) is the rate constant, and \( n_{RDX} \) is the amount of liquid RDX present. The amount of liquid RDX present during melting is assumed to be a linear function of time between the onset and completion of melting, and it is determined by optimizing the fit to the data. The fits to the OST data shown in Figures 9 and 10 predict the general trend in the formation of OST quite well. However, the fits overpredict the amount of OST present as the sample is heated, and they also assume that the rate constant is independent of temperature. This behavior indicates that eq 1 does not adequately represent all of the reactions that involve OST. For example, it is quite possible that OST also decomposes in the reaction cell and eq 1 should contain a term to represent the decomposition of OST. Unfortunately, although the decomposition of OST to HCN is likely, it is not readily apparent from the data what fraction of the HCN products have temporal behaviors that are determined by more than one reaction channel.

ONDNTA. The increasing rate of ONDNTA release from the reaction cell as the quantity of RDX decreases seems contrary to initial expectations. However, since ONDNTA is very similar to RDX, we assume that it will form an ideal solution with RDX. Furthermore, if we assume that its vapor pressure is approximately equal to that of RDX, then we may express its release from the reaction cell as

\[ \frac{dn_{ONDNTA}}{dt} = \frac{dn_{RDX}}{dt} = \frac{n_{ONDNTA}}{n_{ONDNTA} + n_{RDX}} \]  

(2)

where \( \frac{dn_{RDX}}{dt} \) is the rate of release of RDX from the reaction cell and \( n_{ONDNTA} \) is the amount of ONDNTA in solution. The amount of ONDNTA present in the reaction cell at any time during the experiment may be expressed as

\[ \frac{dn_{ONDNTA}}{dt} = k_{ps} n_{RDX} [NO] - k_{pd} n_{ONDNTA} - \frac{dn_{RDX}}{dt} x_{ONDNTA} \]  

(3)

where \( k_{ps} \) is the pseudo-rate constant for formation of ONDNTA, \( k_{pd} \) is the rate constant for decomposition of ONDNTA. \([NO]\) is the concentration of NO in the reaction cell, and \( x_{ONDNTA} \) is...
the mole fraction of ONDNTA in the liquid. The first term on the right side of eq 3 represents the rate of formation of ONDNTA, and since the isotopic scrambling results (see next paper) indicate that it is formed via reactions P2 and P3, it has been made first order in both RDX and NO. Since the reactions occur within the liquid RDX, the rate of formation of ONDNTA is actually proportional to the amount of NO in the liquid. \( \alpha_{NO} \).

Therefore, \( k_1 \) includes a term that relates the amount of NO in the liquid to its concentration in the gas phase in the reaction cell in addition to the rate constant for the reaction. The second term represents the decomposition of ONDNTA. Our preliminary studies of the decomposition of ONDNTA show that its major decomposition products are \( NO \) and \( CH_2O \). Since specifics of the decomposition mechanism of ONDNTA are presently unknown, it is assumed a priori that the decomposition is first order in ONDNTA.

The third term represents the loss of ONDNTA from the reaction cell through the orifice. The constants \( k_2 \) and \( k_4 \) are varied to give the best fits to the ONDNTA data shown in Figures 9 and 10.

It is interesting to note that even though the isotopic scrambling experiments with pure RDX and RDX-\( d_6 \) do not exhibit a DKIE in the formation of ONDNTA, the rate of formation of ONDNTA is significantly higher for unlabeled RDX (Figure 9) than it is for RDX-\( d_6 \) (Figure 10). The maximum rate of formation of ONDNTA for unlabeled RDX is \( 4.5 \times 10^{-5} \) mol/s per mole of RDX present at the start of the experiment compared to a maximum rate of \( 1.4 \times 10^{-5} \) mol/s for RDX-\( d_6 \). This large difference is most likely due to the lower rate of formation of NO from pathway P1, which exhibits a primary DKIE, resulting in the formation of less ONDNTA in the experiment with RDX-\( d_6 \). In contrast, since the isotopic scrambling experiments were conducted with solutions of unlabeled RDX and RDX-\( d_6 \), the concentration of NO available for reaction R3 was the same for both the unlabeled RDX and RDX-\( d_6 \), and hence a DKIE was not observed for the formation of ONDNTA. This behavior further illustrates the complexity of the thermal decomposition of RDX, since not only are there several parallel reaction pathways that lead to the products, but the reaction pathways are also coupled.

\( H_2O \), \( NO \). The gas formation rates of water and NO, shown in Figures 9 and 10, also exhibit temporal behaviors that indicate that their rates of formation are first order in RDX. This behavior is consistent with their formation via pathway P1 in which RDX decomposes via reaction R8 to \( H_2O \) and \( NO \), and then via reaction R7 to form \( H_2O \) and \( NO \). The gas formation rates for this reaction pathway are simply expressed as:

\[
\frac{dn_{NO}}{dt} = \alpha_{NO} \frac{dn_{H2O}}{dt} = \alpha_{H2O} \frac{dn_{H2O}}{dt} = \alpha_{NO} \frac{dn_{H2O}}{dt} (4)
\]

where \( \alpha_{H2O} \) and \( \alpha_{NO} \) are stoichiometric factors, and the results are shown as the square-dot lines in Figures 9 and 10.

The results for \( H_2O \) and NO also indicate that a portion of these products originate from reaction pathway P3. Since the mechanism for the decomposition of ONDNTA is unknown at present, the gas formation rates of the products formed from reaction pathway P3 are simply expressed as:

\[
\frac{dn_{prod.}}{dt} = c_3 k_4 \alpha_{NO,ONDNTA} (5)
\]

where \( c_3 \) represents the product formed from reaction pathway P3 and \( c_3 \) is an empirical constant. The contributions of \( H_2O \) and NO formed by reaction pathway P3 to the total gas formation rates of \( H_2O \) and NO are shown in Figures 9 and 10. Note that the contribution to the \( H_2O \) and NO gas formation rates from pathway P3 is greater for the unlabeled RDX than for RDX-\( d_6 \). As was the case for ONDNTA, this is consistent with reaction pathway P1 exhibiting a DKIE and thus producing less NO that one would expect a decreasing amount of products formed via the natural gas decomposition of RDX according to the reaction shown as pathway P2. The more gradual increase in these products is attributed to the decomposition of ONDNTA, by reaction pathway P3. However, these two decomposition pathways alone cannot account for the large amounts of these products that are formed at the end of the experiment when little RDX remains. Therefore, three other reaction pathways were considered to explain this behavior. First, gas-phase decomposition of RDX was considered since its vapor pressure within the reaction cell is independent of the amount of pure liquid-phase RDX present in the cell and its decomposition would explain the observed temporal behaviors of these products. However, this pathway was rejected because gas-phase decomposition does not play a significant role in our experiments as discussed above. Also considered was the decomposition of ONDNTA in the gas phase. With this pathway it was not possible to obtain a fit to the data that matched even the general features of their temporal behaviors. The third path considered, and finally used, was a catalytic channel. Since the decomposition of RDX in the reaction cell produced a small amount of brownish residue on the walls of the reaction cell, it was assumed that this coating may catalyze the decomposition of the liquid- or gas-phase RDX as it comes in contact with the walls of the reaction cell. The following simple expression was used to characterize the rate of gas formation of the various products from the catalytic reaction pathway P4:

\[
dn_{prod.} / dt = d \cdot k_4(t) \cdot [RDX(t)] (6)
\]

where \( d \) represents the product formed from reaction pathway P4, \( d \) is the stoichiometric factor that relates the number of molecules of product formed per molecule of RDX decomposed by pathway P4, \( k_4(t) \) is the time-dependent rate constant that characterizes both the growth in the amount of catalyst present in the reaction cell and its rate of reaction with RDX, and \([RDX(t)]\) is the concentration of RDX in contact with the catalyst at time \( t \). For the fits to the data shown in Figures 9 and 10, \( k_4(t) \) was assumed to have a linear growth rate starting at zero when the sample melted. The value of the growth rate was determined from the best fit to the data. This simple treatment of the catalytic pathway is used since it seems reasonable that the amount of catalyst present in the reaction cell may accumulate as it is formed by reaction of the RDX decomposition products. The reaction between the RDX and the catalyst may very well not be characterized by the linear rate assumed here, but there is not sufficient evidence to warrant any more sophisticated treatment. The main point of invoking the catalytic channel is that this type of behavior is able to account for the formation of the \( N_2O \), \( CH_2O \), \( NO_2 \), CO, HCN, and \( NH_2CHO \) products during the later stages of the decomposition. Reaction pathway P4 is the least well-defined, and further studies would be required to determine more details. The fits to the data using reaction pathways P2-P4 are shown in Figures 9 and 10.

It is interesting to note that, unlike HMX in which it was postulated that \( H_2O \) may act as a catalyst in its solid-phase decomposition, water does not appear to catalyze the decomposition of RDX in the liquid phase. If water catalyzes the decomposition of liquid-phase RDX, then one would expect the rate of gas formation of the products formed from this channel to be dependent on the amount of water present in the reaction cell. From the data in Figures 9 and 10, it is clear that the water present in the reaction cell decreases as the experiment progresses and one would expect a decreasing amount of products formed via the catalytic pathway if water was the catalyst. However, this does not rule out the possibility that water acts as a catalyst of HMX because in the solid phase the concentration of the water in contact with HMX will be much higher than in the liquid-phase RDX since it is trapped within the HMX particles.
The gas formation rate of CH₃NHCHO gradually grows during the experiment and peaks as the sample nears complete depletion in a manner similar to ONDNTA. This behavior may arise from either the decomposition of a polyamide that is formed during the decomposition or from an increasing concentration of the amide in the solution in the reaction cell. Since the vapor pressure of N-methylformamide (NMFA) is relatively high, this suggests that little NMFA will remain in solution. However, the results from the TOF velocity spectra measurements indicate that the molecular weight of the species that evolves from the reaction cell and produces the ion signals associated with the NMFA product has a molecular weight that is approximately twice that of NMFA, suggesting that NMFA is present in the form of a dimer. The vapor pressure of this species may be sufficiently low that its release rate may be determined by its mole fraction in the solution. Since neither of these sources of NMFA can be ruled out, it is not possible to determine whether NMFA originates from reaction R9 or the decomposition of the polyamide that leads to the formation of the residue.

The relative amounts of RDX that decompose by each of these different reaction pathways, as estimated from the fits to the data shown in Figures 9 and 10 using the simple model, are given in Table IV. These results illustrate that the lower molecular weight products formed during the thermal decomposition of RDX originate from four different primary reaction channels. The reaction channels involving unimolecular decomposition of RDX appear to account for only 40% of the total amount of RDX that decomposes. The other 60% decomposes either through the ONDNTA intermediate or by the catalytic decomposition of RDX.

Comparison with Other Earlier Work. The results of this study are consistent with previous TGA²² and DSC²¹ measurements that have shown, through the use of DKIE studies with RDX, that hydrogen is involved in the rate-limiting step. However, due to the limited amount of information obtained in TGA and DSC experiments, these studies were unable to identify the products associated with the rate-limiting step, the presence of concurrent decomposition pathways that do not involve hydrogen in the rate-limiting step, nor where the rate-limiting step occurs in the reaction pathway. The first-order reaction behavior observed in the DSC experiments is consistent with reaction pathway P1 observed in the present study. Unfortunately, the DSC and TGA experiments cannot account for a concurrent reaction pathway P2 that does not exhibit a DKIE since the extent of the DKIE for a given reaction is dependent on several different parameters. Furthermore, the very subtle manner in which the DKIE manifests itself in reaction pathway P3 is not typically considered in interpretation of results from DKIE experiments. In the case of pathway P3, the DKIE expresses itself by limiting the amount of ONDNTA that is formed by controlling the amount of NO that is produced by reaction channel P1. As discussed in the following paper, neither the formation of ONDNTA nor its decomposition to CH₂O and N₂O exhibit a DKIE. Consequently, reaction pathway P3, which produces a large fraction of the CH₂O and N₂O in thermal decomposition experiments with RDX, is overlooked in interpreting the DKIE results from conventional DKIE and TGA experiments.

A comparison of the decomposition of RDX with that of di-methylnitramine (DMNA) illuminates the contrasting features of their decomposition reactions. The studies with DMNA²⁶⁻²⁸ have found that the major product formed in the decomposition of DMNA is N,N-dimethylnitrosoamine (DMNO) [(CH₃)₂N-O]. The studies by Flannery²⁹ and Lin³⁰ explained this product by the reaction of NO with the dimethylnitramine radical whereas Nigenda et al.³¹ invoked additional channels including nitro-nitrate rearrangement and displacement of the nitrite by NO to explain their results. Melus and Binkley³² on the other hand suggest that radical addition to one of the nitro group oxygens leads to the formation of ONDNTA. In our experiments the reaction of NO with the amino radical left after the N-NO; bond scission to form ONDNTA is similar to the decomposition of DMNA and is consistent with the complete isotopic scrambling of the N–NO nitrogen observed (see next paper) in the ONDNTA product. The isotopic scrambling also precludes the formation of ONDNTA via radical addition to one of the nitro group oxygens followed by the direct abstraction of the oxygen atom. Since reaction pathway P1 produces NO during the decomposition of RDX, the source of NO that participates in the recombinations reaction with the amino radical is not in question as it is for the formation of DMNO from DMNA.

Further comparison of the decomposition of RDX with that of DMNA shows that the primary first-order reaction pathway for RDX that produces OST and exhibits a DKIE does not have an analogous pathway in the decomposition of DMNA. Consequently, although the study of the simpler DMNA molecule provides insight into certain aspects of nitramine decomposition that are applicable to the more complicated RDX molecule, our results on RDX show that DMNA does not mimic all of the reaction pathways that occur during the decomposition of RDX and that it is necessary to study RDX itself to fully understand its decomposition.

Comparison of our results on the thermal decomposition of RDX in the bulk with the results from the unimolecular IRMPD of RDX under collision-free conditions in a molecular beam provides intriguing contrasts and raises the question of how molecules that surround a decomposing RDX molecule affect its decomposition. The most dramatic difference between these two types of experiments is the decomposition of approximately 30% of the RDX (70-75% of the RDX whose decomposition is solely first order in RDX) in the liquid phase via pathway P1 to form OST and the apparent absence of this decomposition pathway in the IRMPD experiments. This difference could readily be explained by the occurrence of secondary reactions between the decomposition RDX and its decomposition products if it were not for several important aspects of its formation. First, the rate of formation of OST is first order in RDX and independent of the concentration of any other species. Second, as discussed in the following paper, OST does not undergo isotopic scrambling of any of its elements (i.e., all of the atoms in one OST molecule originate from one RDX molecule). These results imply that the ring from the RDX molecule remains intact and the oxygen atom and three hydrogen atoms on the ring all remain from the original molecule. The ion representing OST (m/z = 97) was not reported in the IRMPD results. Possible explanations for this discrepancy are: (1) the reaction “temperatures” in the IRMPD experiments are between 200 and 300 °C higher than the thermal decomposition temperatures used in our experiments thus precluding this channel in the IRMPD experiments; (2) the analysis of the IRMPD data may not have considered the formation of OST by reaction R8 which is somewhat similar to reactions A and B in ref 23; or (3) the close proximity of adjacent RDX molecules in the liquid phase may alter the unimolecular decomposition mechanism due to effects such as hydrogen bonding. At this time it is not clear which of these three explanations are more likely.

Another difference between our results and those from the IRMPD experiments is the large fraction (0.67) of RDX that decomposed through the concerted symmetric triple fission (CSTF) to form three methylenenitramine fragments that subsequently decomposed in secondary reactions to HCN, HONO, N₂O, and CH₂O in the IRMPD experiments. In our thermal decomposition experiments only about 10% of the RDX that decomposes (25% of the RDX whose decomposition is solely first order in RDX) produces products (N₂O and CH₂O) that may
be formed through the CSTF mechanism. The CSTF mechanism may be responsible for this 10% of the RDX that decomposes. However, our results are also consistent with reaction

\[
\text{RDX} \rightarrow \text{H}_2\text{CN} + \text{NO}_2 + 2\text{CH}_2 = \text{N} = \text{NO}_2
\]

followed by the decomposition of the two methylenenitramine fragments. H\(_2\)CN is a species that is likely to form the NMFA observed in the decomposition. The NO\(_2\) that originates from unimolecular RDX decomposition may be formed by either pathways P1 or P2. Thus it is not clear whether N—NO\(_2\) bond breaking or the CSTF mechanism leads to the N\(_2\)O and CH\(_2\)O products formed in reaction pathway P2.

It is clear from the results that neither experiments with simpler nitramines such as DMNA nor elegant unimolecular decomposition experiments fully address the reaction mechanisms that control the decomposition of RDX in the solid and liquid phases. It is evident that the formation of ONDNTA and its subsequent decomposition to final products and the catalytic decomposition of RDX both play important roles in determining the identities and rates of formation of the products from the thermal decomposition of RDX. Controlling these decomposition pathways through the use of additives or the synthesis of nitramines with slightly different molecular configurations may provide avenues for developing propellants with better combustive properties.

From our results showing the presence of four primary pathways that control the thermal decomposition of RDX in the liquid phase, it is readily apparent why there have been so many conflicting results on both the identities of its decomposition products and its rate of decomposition. When this is combined with the diversity of the decomposition behavior observed in the solid phase, the interpretation of the results from experiments that either identify reaction intermediates, measure the distribution of final products, or measure thermochemical behaviors, in terms of various simple bond-breaking sequences, provides an inadequate framework for understanding the very complex mechanisms that control the decomposition of RDX and HMX. The changing nature of the sample of RDX, due to its interaction with its decomposition procedure for analyzing the TOF data, and J. R. Autera for assistance in running the experiments and collection of data. Schaeffer for assistance in developing the sample itself, and the necessity of correlating the identities and rates of formation of the various products with the composition of the sample at any given time during its decomposition. If this is not done, the products that are detected cannot be correlated with the individual reaction pathways, thus making the interpretation of their appearance ambiguous.

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