the v' = 2 level, which has very small partial cross sections, shows a larger discrepancy between quantum mechanics and the QCT-QSS method. For the higher final vibrational levels when reaction begins in a j = 0 state of the v = 0, 1, or 2 vibrational level, the quantal calculations show much more structure than the QCT-QSS ones, even though we have summed over three total angular momenta; some of the peaks in the quantum distributions are missing in the QCT-QSS ones. This effect is especially clear in v' = 1 levels, and it also occurs for HD v' = 1 produced by the reaction H + D₂(v=1, j=6), where we have summed over five total angular momentum/parity blocks. Acknowledgment. We are grateful to Richard N. Zare, Dahv Kliner, and Klaus Rinnen for stimulating discussions and to David Chatfield for checking some of the calculations. This work was supported in part by the National Science Foundation and the Minnesota Supercomputer Institute.

Supplementary Material Available: Four tables of reaction probabilities and convergence checks for all initial states in each of four total angular momentum/parity blocks at total energy 1.49 eV (8 pages). Ordering information is given on any current masthead page.

Thermal Decomposition of Energetic Materials: Temporal Behaviors of the Rates of Formation of the Gaseous Pyrolysis Products from Condensed-Phase Decomposition of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

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The temporal behaviors of the rates of formation of the gaseous products from the pyrolysis of HMX (octahydro-1,3,5,7tetranitro-1,3,5,7-tetrazocine) are determined by simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS). The gaseous products formed from the pyrolysis of HMX, and its deuterium- and ¹⁵NO₂-labeled analogues, between 210 and 235 °C are H₂O, HCN, CO, CH₂O, NO, N₂O, CH₃NHCHO, (CH₃)₂NNO, 1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine (ONTNTA), and their isotopic analogues. In addition, a nonvolatile residue (NVR) is formed. The NVR is a polyamide that decomposes between 250 and 780 °C producing NH₃, HCN, HNCO, H₂NCHO, CH₃NHCHO, and products that include long-chain hydrocarbons. The temporal behaviors of the rates of gas formation of the pyrolysis products along with the macroscopic and microscopic structure of the NVR indicate that complex physical processes and chemical mechanisms within the condensed phase of HMX control the decomposition. The temporal behaviors of the rates of gas formation show induction, acceleratory, and decay stages that are characteristic of either condensed-phase or autocatalytic decomposition. The NVR is composed of broken ellipsoidal shells whose diameters range from 0.3 to 5 μ m. The shells appear to be remnants of gas-filled bubbles that are formed within the HMX particles during the pyrolysis. The pressures within the gas bubbles may exceed 7 MPa. The major portion of the pyrolysis products observed in the experiments comes from gases that have been contained within the bubbles. Gases released earlier in the decomposition are contained in smaller bubbles and therefore are formed under higher pressure conditions. This results in the variation of the relative rates of formation of the gas products. For example, the ratio of the rates of formation of CH_2O to N_2O is between 0.7 and 0.8 during the induction stage, decreases to a minimum of 0.36 during the acceleratory stage, and increases to ~ 1 at the end of the decay stage. Variations in the relative rates of formation of the other products are also observed. The changes in the rates of release of products from the initial to final stages of the decomposition indicate that different species are formed when the pyrolysis products are contained at different pressures. The effects of these different physical processes on the relation between the observed pyrolysis products and the underlying chemical decomposition mechanisms are discussed.

Introduction

The cyclic nitramines octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX, I) and hexahydro-1,3,5-trinitro-*s*-triazine (RDX, 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 provide a link between the physical properties and molecular structure of these molecules and their combustive behavior which, in turn, may lead to methods for modifying propellant and explosive formulations in order to obtain better control of their ignition, combustion, or sensitivity.

The overall goal of our work is to understand the relationship between the physical properties and molecular structures of different nitramines and their combustive behavior. This requires understanding the reaction kinetics and transport processes in both the gas and condensed phases. The gas-phase reaction kinetics and transport properties of the various gaseous pyrolysis products of the nitramines are relatively well understood.^{1,2} On the other hand, the reaction kinetics and transport properties associated with the reactions occurring in the condensed phase are not well understood. The thrust of our work is to obtain a better understanding of the physical processes and reaction mechanisms that occur during the decomposition of nitramines in the condensed phase so that the identity and rate of release of the pyrolysis products can be predicted based on the physical properties and molecular structure of the material. This information can then be used along with the gas-phase reaction models to correlate

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modifications of the nitramine ingredients with variations in the overall combustive behavior. To obtain data on the decomposition of nitramines in the condensed phase, we make accurate measurements³⁻⁵ of the identity and rate of release of all the major, and most of the minor, gaseous products formed during the pyrolysis of the nitramine compounds as a function of time under well-controlled temperature conditions.

Over the past 40 years many studies have been conducted on the decomposition of HMX and RDX under various conditions. Recent reviews of the decomposition and combustion,^{6,7} thermal decomposition,⁸ and summaries of possible decomposition mechanisms^{8a,9} have been published for these materials. Based on many of these results and structural similarities of HMX and RDX, the same decomposition mechanisms have been proposed for both materials.

Robertson's¹⁰ results on the decomposition of RDX show that in solutions of dicyclohexyl phthalate and trinitrotoluene (TNT) the decomposition exhibits unimolecular behavior, whereas neat RDX and HMX show an effect of neighboring molecules. Postanalysis of the gases evolved in his experiments shows the presence of NO, N₂O, N₂, CO, CO₂, CH₂O, and H₂O. This work provides the initial evidence that the decomposition of HMX and RDX occurs by transfer of an oxygen atom from the NO₂ group to the CH₂ group.

Subsequent mass spectral analysis of the decomposition products from HMX below its melting point, by Bulusu and Graybush,¹¹ shows the same products as those observed by Robertson.¹⁰ In addition, they found that the rate of formation of the products varied during isothermal decomposition experiments in a way that can be explained either by the characteristic induction, acceleratory, and decay stages associated with solid-phase decompositions or by invoking autocatalytic behavior. Furthermore, ¹⁵N-tracer studies¹² indicate that the N₂O is formed without N–N bond breaking, thus suggesting that oxygen atom transfer to the CH₂ group and C–N bond rupture is an important step in the decomposition in agreement with Robertson. However, since the total nitrogen is not accounted for in these experiments, N–N bond breaking cannot be ruled out as the initial step in the decomposition.

A deviation from the oxygen atom transfer mechanism suggested above comes from the RDX experiments of Rauch and Fanelli¹³ in which they observe the formation of NO₂ in addition to the products observed by Robertson¹⁰ and Bulusu.¹¹ They indicate that the NO₂ is formed in the gas-phase decomposition of RDX.

More recent works on the decomposition of RDX¹⁴ and HMX¹⁵ report additional decomposition products. These products include

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HCOOH, NH₃, and hydroxymethylformamide from RDX¹⁴ and HMX.¹⁵ Observations of these products suggest that the decomposition mechanism leading to the formation of the pyrolysis products is more complicated than simple unimolecular decomposition. Several studies of autocatalytic effects^{16,17} on RDX decomposition find that formaldehyde and hydroxymethylformamide both have a catalytic-like effect on the decomposition. It is not clear whether this is due to catalysis of the RDX decomposition or from liquefaction of the RDX that, in turn, increases the release rate of the products from the condensed phase.

Experiments¹⁸ conducted at atmospheric pressure and at nominal temperatures of 300, 600, and 800 °C, which are higher than used in previous experiments¹⁰⁻¹⁷ on HMX and RDX, show that the relative amounts of HCN and NO produced, compared to N₂O and CH₂O, are greater at 600 and 800 °C than they are at 300 °C. In light of previous work,13 this implies that evaporation and subsequent gas-phase decomposition of the RDX and HMX are favored over condensed-phase decomposition at atmospheric pressure and higher heating rates. This effect is also observed in planar laser-induced fluorescence (PLIF) measurements on HMX¹⁹ and coherent anti-Stokes Raman spectroscopy (CARS) measurements on RDX²⁰ low-pressure flames in which NO₂ and HCN are measured close to the surface of the burning propellant. In addition, mass spectrometric measurements on low-pressure flames of RDX²¹ and HMX²² also show substantial fractions of HCN in the gas above the burning propellant surface. The steps leading to the pyrolysis products under these low-pressure highheating-rate conditions appear to be different than those in the slow-heating-rate thermal decomposition experiments.

Several studies to determine the initial steps in the decomposition of HMX and RDX have been conducted using Langmuir and Knudsen cell evaporation with appearance energy mass spectrometric measurements²³ and infrared multiphoton dissociation (IRMPD) in a molecular beam.²⁴ The appearance energy mass spectrometric measurements indicate that the stoichiometry of the initial gaseous products from the pyrolysis of RDX and HMX is the same as several of the daughter ions found in the mass spectra of these materials. However, subsequent mass spectrometric work on HMX⁴ shows that HMX fragmentizes in the mass spectrometer at low electron energies. Therefore, appearance energy measurements cannot differentiate between daughter ions from the HMX molecule and molecular ions from its pyrolysis products. Hence, these experiments²³ did not determine the initial products from the pyrolysis of HMX. The collision-free IRMPD experiments show that RDX molecules dissociate via both concerted symmetric triple fission and N-N bond scission channels.

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These primary products dissociate further to form HCN, HONO, N_2O , and CH_2O . Whether these reactions control the decomposition of RDX and HMX in the condensed phase and whether reactions between adjacent molecules are important, as originally suggested by Robertson, are still in question.

A number of studies show that decomposition reactions occur in the condensed phase of these materials. High-pressure studies of the β -HMX to δ -HMX phase transition²⁵ between 190 and 240 °C show evidence of formation of decomposition products within the 175- μ m-diameter particles used in the experiments. In experiments with deuterium-labeled analogues of HMX.²⁶ a primary deuterium kinetic isotope effect (DKIE) is observed in the rate of decomposition of the solid phase and is attributed to C-H bond breaking in the rate-controlling step. In the liquid phase, a secondary kinetic isotope effect is observed, suggesting that breaking the C-N bond that is adjacent to the C-H bond is important. This work emphasizes the importance of the state of the material in which the reactions occur and suggests that the decomposition mechanism is linked to the physical processes occurring in the material. This linkage has been suggested previously, by Oyumi and Brill,²⁷ in their high heating rate experiments on RDX and HMX in which they found larger fractions of N₂O and CH₂O in experiments under higher pressure conditions where evaporation of the reactant is reduced. Thermogravimetric analysis (TGA) and shock sensitivity experiments on deuteriumlabeled HMX and RDX²⁸ both show a DKIE. The large A factors found in these TGA experiments rule out a cyclic transition state and suggest that chain reactions are important in the condensed-phase decomposition. The lower shock sensitivities of the deuterium-labeled analogues of HMX and RDX in the exploding foil experiments suggest that hydrogen also plays a role in the shock-initiated decomposition chemistry of these materials.

Two studies^{29,30} on the products formed during shock-initiated decomposition of RDX have shown the formation of products not previously observed in thermal decomposition experiments. The presence of the nitroso derivatives of RDX (1,3,5-trinitroso-1,3,5-triazacyclohexane, 1,3-dinitroso-5-nitro-1,3,5-triazacyclohexane, and 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane) were found in residues formed during drop weight impact experiments.²⁹ The presence of nitroso derivatives of RDX as well as compounds with a melamine functionality was found with X-ray photoelectron spectroscopy (XPS) measurements on RDX subjected to drop weight impact and underwater shocks at levels close to ignition.³⁰ If similar products can be identified in thermal decomposition experiments and the mechanisms leading to their formation explained, then a connection between shock-initiated decomposition chemistry and processes that occur during thermal decomposition may be established.

From all of the studies on HMX and RDX decomposition, it is still not possible to predict the identity and rate of formation of the pyrolysis products under different heating and pressure conditions. The underlying reason is that in all experiments (with

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the exception of the MPD molecular beam experiments) many different physicochemical processes occur simultaneously, and it has not been possible to associate any set of products with the processes leading to their formation. For example, when gas-phase and condensed-phase decompositions occur simultaneously, it has not been possible to quantitatively associate the measured products with the phase in which they were formed. Although experiments such as the IRMPD of RDX provide valuable mechanistic information on the decomposition of the isolated molecules, the behavior of the nitramines in a combustive environment may involve more complicated processes. Such processes may include follow-up bimolecular reactions of the initial decomposition products, autocatalytic reactions between decomposition products and the reactant, stress-induced reactions between molecules along slip planes, and preferential reactions at the reactant surfaces. A key to understanding how the nitramines decompose lies in relating the observed species and their rate of formation to these different processes that lead to their formation.

This paper will present results on the condensed-phase decomposition of HMX. Using unlabeled and deuterium- and $^{15}NO_2$ -labeled HMX, we determined the identity and rate of release of the gaseous products from solid HMX particles as a function of time during their decomposition. This is correlated with microscopic evidence of physical processes occurring within the particles. The effects of temperature, sample size, and deuterium labeling on the decomposition of HMX, 50–80 °C below its melting point, are used to construct a qualitative model of the decomposition process and to propose possible reactions that lead to the observed products.

Experimental Section

Instruments Description. The STMBMS apparatus and basic data analysis procedure have been described previously.^{3,4} 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 (<10⁶ Torr) and is radiatively heated by a bifilarwound tungsten wire on an alumina tube. The molecules from the gaseous mixture in the reaction cell exit through a small diameter orifice (~ 0.01 cm in these experiments) in the cap of the reaction cell and traverse two beam-defining orifices before entering the electron-bombardment ionizer of the mass spectrometer where the ions are created from 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 selected with a quadrupole mass filter and counted with an ion counter. The gas flow from the reaction cell 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 orifice area, 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 HMX, the time constant for exhausting gas from the cell is small (~ 0.2 s) compared to the duration of the experiments (> \sim 1000 s). Note that the containment time of gas within the reaction cell is short once the gas molecules are in the free volume of the cell, but it may be much longer if the gas is trapped in the condensed phase of the material within the cell. For study of reactions that occur within the condensed phase, the reaction cell allows the surface regression rate of the particles due to evaporation to be controlled by adjusting the area of the exhaust orifice. In this way a balance is achieved between the rate of product formation within the particles and the rate of release of gaseous products from the particles.

The gaseous products from the pyrolysis are identified in two steps. First, an autocorrelation analysis of all the ion signals

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Figure 1. Transmission electron micrograph of the residue that remains after an isothermal decomposition of HMX at 224 °C. The residue consists of broken ellipsoidal shells.

measured during one thermal decomposition experiment is used to separate the different m/z values into temporally correlated groups. The different m/z values in these groups may be formed from either one or several pyrolysis products. Second, TOF velocity spectra for each of the m/z values are measured. These are used to determine the molecular weight of each different gaseous product leading to a signal at each m/z value, thus determining the molecular weight of each gaseous product formed during the pyrolysis.

Sample Preparation. The HMX powder used in these experiments is >99.5% pure and has an approximate median particle diameter of 150 μ m. The HMX- d_8 and HMX-*nitro*-¹⁵N (HMX-¹⁵NO₂) samples were supplied by Dr. S. Bulusu of the U.S. Army Armaments Research, Development, and Engineering Center. The nonvolatile residue, formed during the isothermal decomposition experiments, is prepared for the transmission electron microscopy (TEM) by dispersing it in methanol and depositing it on a copper grid.

Results

The experimental conditions for the six isothermal decomposition experiments with HMX presented in this paper are listed in Table. I.

Pyrolysis Product Identities. The formulas of the pyrolysis products along with the m/z values of the ions formed in the mass spectrometer that are representative of the pyrolysis products for the different isotopic analogues are listed in Table II. The products from the experiments with unlabeled HMX are identical. The products formed from HMX-d₈ and HMX-¹⁵NO₂ are isotopic analogues of the pyrolysis products formed from the unlabeled HMX. H₂O and CH₂O have the expected deuterium-substituted analogues. DCN was not observed because of the much larger signal at m/z = 28 from CO. The HCN from the HMX-¹⁵NO₂ is present at m/z = 27, indicating that it is formed from the ring nitrogen, but since the CO contribution to the signal at m/z =28 is large, it does not preclude some HCN arising from the NO2 group. The results from the HMX-15NO2 also indicate that the NO arises from the NO₂ group, the N₂O maintains the original mix of one ¹⁴N and one ¹⁵N, the amide product does not incorporate nitrogen from the NO2 group, and one nitrogen from the NO2 group is incorporated into the dimethylnitrosamine (DMNA) product, (CH₃)₂NNO. The HMX-d₈ results show that the DMNA product, represented by m/z = 74 in the unlabeled experiments, contains six hydrogens, and the HMX-15NO2 results show that it contains two nitrogens and not CO, which remains a possibility if one relies on just the results from unlabeled HMX.

TABLE I: Experimental Parameters

expt	material	mass, mg	mean particle diam, μm	orifice diam, cm	t _{iso} , ^a s	T _{iso} , ^b °C
I	HMX	9.956	150	0.0137	1110	210.5
II	HMX	8.600	150	0.0149	2995	235.2
111	HMX-d ₈	7.932	35	0.0105	2870	234.8
IV	HMX-15NO2	8.210	35	0.0105	2835	235.0
V	HMX	27.94	150	0.0105	2815	234.4
VI	HMX	8.58	150	0.0149	3960	226.5

 ${}^{a}t_{iso}$ = time from the start of experiment to when the sample first reaches the isothermal temperature. ${}^{b}T_{iso}$ = isothermal temperature.

The heavier molecular weight products formed during the decomposition are 1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine (ONTNTA, III), a compound with amide functional groups,



DMNA, and the nonvolatile residue. The ONTNTA product, represented by the m/z = 132 ion signal, is consistent with the expected m/z values from the experiments with HMX- d_8 and HMX- $^{15}NO_2$. The molecular structure of the amide product is limited to several possibilities. The m/z values of 58 and 59 for the ions are consistent with methylformamide (MFA) as the product. However, as indicated in Table II, the TOF velocity spectra indicate that the molecular weight of the pyrolysis product is approximately 116. Several products that may produce ion signals at m/z values of 58 and 59, contain four and five hydrogen atoms, respectively, and have a molecular weight of ~116 include the MFA dimer, 1-acetyl-3-methylurea (IV), succinamide (VI), or a product such as 1,2-di-N-formamidoethane (VI) that may



be formed from primary decomposition products, such as H₂CN

TABLE II: Gaseous Products from the Pyrolysis of HMX and Their Associated Mass Spectrometer Ion Signal m/z Values^a

ion mol w							
			HMX-	pyrolysis products			
formula	HMX-h ₈	HMX-d ₈	¹⁵ NO ₂	mol wt ^b	formula		
H ₂ O	18	20	18	18	H ₂ O		
HCN	27	с	27	27	HČN		
со	28	28	28	28	CO		
нсо	29	30	29	30	CH ₂ O		
NO	30	30	31	30	NO		
N ₂ O	44	44	45	44	N ₂ O		
C₂H₄NO	58	62	58	~116	(CH ₃ NHCHO) ₂		
C ₂ H ₅ NO	59	64	59	d	(CH ₃ NHCHO) ₂		
$C_2H_6N_2O$	74	80	75	74	$H_6C_2N_2O$		
$CH_3N_2O_2$	75	78	76	296	HMX		
$C_2H_4N_4O_3$	132	136	134	280	H ₈ C ₄ N ₈ O ₇		
$C_2H_4N_4O_4$	148	152	150	296	HMX		

^aA detailed presentation of the correlation between all of the different m/z values measured in the mass spectra of each isotopomer of HMX is given in ref 4. ^bThe approximate molecular weights of the gaseous products from the pyrolysis of HMX was determined by the time-of-flight velocity spectra method described in ref 4. ^cNot observed. ^dNot measured.



Figure 2. Weight loss from the decomposition of the nonvolatile residue formed during experiments I, III, and IV. The residues from experiments III and IV were heated to only 500 $^{\circ}$ C.

and CH_2O . The elemental analysis of a typical NVR shows that the mole percent composition is 33.9% carbon, 27.5% hydrogen, 18.6% nitrogen, and 20.0% oxygen. Thus, the NVR is enriched in carbon and hydrogen relative to HMX. The NVR that remains after an isothermal decomposition is orange-brown and has a structure similar to the original sample (i.e., the shape of the original HMX particles is still discernible). A TEM of the residue that remains after an isothermal decomposition at 224 °C and has been dispersed in methanol during the TEM sample preparation is shown in Figure 1. The residue consists of fractured ellipsoidal shells whose diameters range from 0.3 to 5 μ m and whose wall thicknesses are about 0.1 μ m. At the end of the isothermal decomposition, these shells are agglomerated in the shape of the original particles. The sizes and structures of these shells suggest that as the sample decomposes the gaseous products are contained in bubbles within the solid particles.

The TGA of the NVR formed in experiments I, III, and IV are shown in Figure 2. The NVR decomposes gradually as it is heated to 780 °C. The temporal behaviors of the ion signals at m/z values representing the products formed during the decomposition of the NVR that was created in experiments with both unlabeled HMX and HMX- d_8 are shown in Figure 3. The m/z values that have correlated temporal behaviors between the two experiments are listed in Table III along with the decomposition products that they represent. The results indicate that the NVR is characteristic of a polyamide since the products contain the HNCO moiety. The ion signal at m/z = 136 is characteristic of a large group of different m/z values that appear to represent a pyrolysis product (or products) that contains a long-chain hydrocarbon moiety. The products with amide or long-chain hydrocarbon groups evolve between 275 and 400 °C. Between 400 and 780 °C the products that evolve are NH₃, HCN,



Figure 3. Ion signals at different m/z values from the decomposition of the nonvolatile residue that was formed during experiments I and III. The ion signals are representative of the different pyrolysis products formed during the decomposition of the NVR. The temporal correlation between the ion signals at the different m/z values for each experiment is used to determine the identity of the products. The stoichiometries of the products associated with the different m/z values are NH₃ (17, 20), HCN (27, 28), HNCO (43, 44), H₂NCHO (45, 48), and (CH₃)NHC-HO (59, 64). The temperature ramp for experiment III was terminated at 530 °C due to experimental limitations while the sample was still decomposing.

TABLE III: Correlated Ion Signals at Different m/z Values from the Decomposition of the Nonvolatile Residue Formed during the Decomposition of HMX and HMX- $d_{e^{\alpha}}$

,	m/z	
HMX, exp VI	HMX-d ₈ , exp III	product ^b
17	20	NH ₁
27	28	HCN
43	44	HNCO
45	48	H ₂ NCHO
59	64	CH ₃ NHCHO
136		c

^a The correlations are based on the curves shown in Figure 3. ^b These are the products assuming the signals detected with the mass spectrometer at the values listed are molecular ions. ^c The ion signal m/z =136 is representative of a group of ion signals at different m/z values that have the same temporal behavior. This group is consistent with long-chain hydrocarbons containing different functional groups.

and HNCO. The residue left after the NVR is heated to 780 °C is a black carbonaceous material.

Vapor-Pressure Measurements. The vapor pressure of HMX, measured in this work, from 191 to 234 °C using a 0.098-cm orifice diameter is represented by log p = 14.74 - 8395/T where p is in Torr and T is in kelvin. The heat of vaporization based on these data is 158.6 \pm 2.9 kJ/mol. This work extends the temperature range of the vapor pressure data up to 234 °C. Previous effusion cell measurements determined the heat of vaporization of β -HMX to be 175.3 kJ/mol in the 97-129 °C range³¹ and 161.5 \pm 4.2 kJ/mol in the 188-213 °C range.³² Taylor and Crookes³² found that at constant temperature the vapor pressure appeared to increase as the orifice size was decreased. On the basis of previous work,³³ they assumed that the HMX did not

 ⁽³¹⁾ Rosen, J. M.; Dickinson, C. J. Chem. Eng. Data 1969, 14, 120.
 (32) Taylor, J. W.; Crookes, R. J. J. Chem. Soc., Faraday Trans. 1 1976, 72, 723.

TABLE IV: Quantitative Results from Experiments with Unlabeled HMX^a

		exp I				exp II			exp V			exp VI		
ion mass	neutral product	RIFP	amount, mg	molar ratio	RIFP	amount, mg	molar ratio	RIFP	amount, mg	molar ratio	RIFP	amount, mg	molar ratio	
18	H ₂ O	0.40	0.553	1.15	0.45	0.356	0.94	0.44	1.412	0.92	0.42	0.306	0.80	
27	HCN	0.38	0.256	0.36	0.80	0.212	0.37	0.85	0.365	0.16	0.35	0.168	0.29	
28	CO	0.40	0.641	0.86	0.99	0.220	0.37	0.56	1.513	0.63	0.80	0.278	0.47	
29	H ₂ CO	0.50	1.485	1.85	0.67	0.999	1.58	0.53	5.325	2.07	0.50	1.044	1.64	
30	NÖ	1.83	0.498	0.62	1.49	0.554	0.88	1.49	2.580	1.00	0.73	0.738	1.16	
44	N ₂ O	0.94(R)	3.485	2.97	0.94(R)	2.399	2.59	0.94(R)	11.141	2.96	0.85	2.283	2.45	
74	C ₂ H ₆ N ₂ O	1.46	0.148	0.07	0.90	0.147	0.09	0.48	0.822	0.13	0.57	0.195	0.12	
58	(CH ₁ NHCHO) ₂	1.20	0.082	0.03	0.90	0.131	0.05	1.10	0.339	0.03	0.35	0.132	0.05	
132	C ₄ H ₈ N ₈ O ₇	0.67	0.399	0.05	0.61	0.564	0.10	1.00	0.470	0.02	0.40	0.665	0.11	
148	HMX	0.69	2.058		0.70	2.365		0.60	1.960		0.8(R)	2.301		
	residue		0.351	0.13		0.652	0.31		1.724	0.20		0.470	0.22	
	total		9.956			8.599			27.651			8.580		
	Euclidean norm		1.27E-05 ^b			2.47E-05			1.35E-04			1.65E-05		
mass	% Н		98.6			100.9			99.7			99.5		
balance	% C		99.5			102.6			97.5			100.9		
	% N		97.9			100.5			100.1			100		
	% O		102.1			98.6			100.9			99.7		
	temp, °C		210.5			235.2			234.4			226.5		

^a The conditions for each experiment are given in Table I. RIFP is the relative ion formation probability and is described in ref 5, the molar ratio is the number of moles of product produced per mole of decomposed HMX, and the stoichiometry of the residue is as follows: C, 3.3; H, 2.7; N, 1.8; O, 2. The RIFP marked with an R was used as the reference for constraining the fit. ^bRead as 1.27×10^{-5} .

IABLE V: Quantitative Results from Experiments with isotopically Labeled	I HMX ^a
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exp III					exp IV				
ion mass	neutral product	RIFP	amount, mg	molar ratio	ion mass	neutral product	RIFP	amount, mg	molar ratio
20	D ₂ O	0.68	0.242	0.63	18	H ₂ O	0.43	0.463	1.26
	-				27	HCN	0.35	0.300	0.55
28	CO	0.35	0.214	0.40	28	CO	0.70	0.249	0.44
30	NO	1.20	0.321	0.56	29	H ₂ CO	0.84	1.009	1.65
32	D ₂ CO	1.41	1.543	2.51	31	¹⁵ NO	1.20	0.418	0.66
44	N ₂ O	0.94(R)	2.673	3.17	45	N ¹⁵ NO	0.94(R)	2.686	2.92
80	$C_2D_6N_2O$	1.46	0.133	0.09	75	C ₂ H ₆ N ¹⁵ NO	0.43	0.264	0.17
62	$C_4 D_{10} N_2 O_2$	1.20	0.125	0.05	59	$C_4H_{10}N_2O_2$	0.60	0.106	0.05
136	$C_4D_8N_8O_7$	1.46	0.339	0.06	134	C ₄ H ₈ N ₄ ¹⁵ N ₄ O ₇	1.50	0.220	0.04
152	HMX-d ₈	0.57	2.099		150	HMX- ¹⁵ NO ₂	0.59	2.092	
	residue		0.243	0.12				0.403	0.20
	total		7.932					8.210	
	Euclidean norm		1.68E-05 ^b					3.83E-05	
mass balance	% H							106.3	
	% D		101.2						
	% C		99					99.3	
	% N		98.9					101.2	
	% O		101.2					98.6	
	% ¹⁵ N							101.5	

^a The conditions for each experiment are given in Table I. RIFP is the relative ion formation probability and is described in ref 5, the molar ratio is the number of moles of product formed per mole of decomposed HMX. The RIFP marked with an R was used as a reference for constraining the fit. ^bRead as 1.68×10^{-5} .

decompose in the temperature range of their investigations and suggested that either lower condensation coefficients or surface diffusion on the cell walls may account for the increased vapor pressure. Our results clearly show that as the net rate of vaporization from the HMX is decreased, a greater amount of decomposition takes place. Therefore, the decomposition products account for the apparent increase in the HMX vapor pressure in the Knudsen effusion cell experiments of Taylor and Crookes.

Quantitative Results. The rates of gas formation or gas release from the solid of each of the pyrolysis products identified in the previous section, the mass loss from the sample due to each pyrolysis product, the fraction of the original sample remaining in the reaction cell, (1-X), and the stoichiometry of the sample remaining in the reaction cell for each of the experiments listed in Table I are shown as functions of time in Figure 4. The parameters used in the fitting procedure to obtain the results shown in Figure 4 along with the total product formation results for each experiment are listed in Tables IV and V. The Euclidean norms of the calculated and the measured rate of force change⁵ along with an elemental mass balance which gives the expected total to within 2% for each of the elements indicate that the results are good fits to the data.

Parameters that were varied in the experiments included the isothermal temperature, the sample size, and the effect of isotopic substitution. In all six experiments the major products are N₂O, CH₂O, H₂O, NO, and CO and the minor products are HCN, the amide product, DMNA, ONTNTA, and the NVR. For the experiments with unlabeled HMX and HMX-¹⁵NO₂, the molar ratios (moles of product per mole of decomposed HMX) show the same general behavior. The molar ratios are 2.5–3.0 for N₂O, 1.6–2.2 for CH₂O, and approximately 1 for H₂O and NO. (Note that a simple decomposition of HMX to N₂O and CH₂O would have molar ratios of 4 for these products.) The molar ratios for

⁽³³⁾ Bawn, C. E. H.; Rotter, G. The Science of Explosives; M.O.S.; H.M.S.O.: 1956; Vol. II, p 713.

⁽³⁴⁾ See: (a) Budnikov, P. P.; Ginstling, A. M. Principles of Solid State Chemistry Reactions in Solids; MacLaren and Sons Ltd.: London, 1968; p 155. (b) Bamford, C. H.; Tipper, C. F. H. Comprehensive Chemical Kinetics: Reactions in the Solid State; Elsevier Scientific: New York, 1980; Vol. 22, p 41.



Figure 4. Results from the isothermal decomposition of HMX using the experimental parameters in Table I and the fitting parameters in Tables IV and V for experiments (A) I, (B) II, (C) III, (D) IV, (E) V, and (F) VI. The top panels show the rate of formation of each of the different gaseous products from the pyrolysis of HMX in the reaction cell. The middle panels show the mass loss for each pyrolysis product and the fraction of the original sample remaining, (1 - X), in the reaction cell. The lower panels show the stoichiometry of the sample remaining in the reaction cell. The solid lines in the lower panels represent the stoichiometry based on the fit parameters in Tables IV and V, and the dashed lines represent the stoichiometry when the fits are modified to account for 100% of each element.

Thermal Decomposition of Energetic Materials

HCN and CO fall between 0.2 and 0.5. The molar ratios of the gaseous products from the pyrolysis of HMX- d_8 differ from the experiments with the other HMX samples in that the molar ratios for D₂O and NO are smaller and the molar ratio for CD₂O is higher. These products clearly take part in reactions in which there is a DKIE.

The magnitude and source of errors associated with the STMBMS measurements have been described previously.⁵ The errors in the results are smaller for the decomposition products with a larger relative abundance (i.e., N_2O , CH_2O , H_2O , CO, and NO). Possible variations in the results for the major products should be less than 10%, whereas the variation in the results for the minor products could be as high as a factor of 2. These errors are for the possible variation in the total amount of each product formed and not temporal variations for each individual species, which is less.

Temporal Behaviors. Although the molar ratios of the decomposition products determined from experiments I-VI are similar to many of the previous results,8 the temporal behaviors (i.e., the characteristic induction, acceleratory, and decay stages) of these products as the sample decomposes are more intriguing. The rates of gas formation, shown in Figure 4, are actually the rates of appearance of the gases in the free volume of the reaction cell. Once the gas is in the free volume of the cell, the time constant for release from the cell is approximately 0.2 s. The possible sources of the gases are gas-phase reactions within the reaction cell, reactions on the walls of the cell, or reactions on, or within, the condensed-phase material followed by subsequent release to the free volume of the cell. To test the effects of the alumina walls of the reaction cell on the HMX decomposition, the alumina surface area was increased 60% by placing an alumina tube within the cell. This produced no change in the product identity or rate of gas formation in the reaction cell.

The temporal variation in the rates of gas formation is typical of both condensed-phase³⁴ and autocatalytic reactions.¹⁶ The data show that the rate of gas formation of the different species vary by up to a factor of 40 during the decomposition at constant temperature. In addition, the rates of gas formation of each species, relative to each other, vary significantly during the decomposition. For example, during the acceleratory period, the ratio of the rates of H₂O to N₂O formation is \sim 1, whereas later in the decomposition the ratio falls to 0.5 and continues to decrease as more of the sample evaporates and decomposes. These variations in the rates of formation of the different products affect the stoichiometry of the sample remaining in the reaction cell as illustrated in Figure 4. In all of the experiments, the nitrogen and oxygen content decreases relative to the carbon and hydrogen content. This tends to separate the fuel and oxidizer segments of the molecule into the solid and gas phase, respectively. More specific details of the temporal behaviors of the rates of formation of the gaseous products are presented in the next section.

The initial stage of the decomposition is illustrated in Figure 5 by the behaviors of the gas formation rates of H₂O, CH₂O, N₂O, and HMX during the induction periods. For each experiment the rates of formation of CH₂O and N₂O are proportional to the gas formation rate of HMX. (This is essentially proportional to the vapor pressure of HMX within the cell with some variations in the exhaust rate due to flow conditions through the orifice that are sensitive to the number density within the cell.⁵) The ratio of the gas formation rates of CH_2O to N_2O during the induction stage varies between 0.7 and 0.8 for protonated HMX and is 1.2 for HMX- d_8 . Furthermore, water is clearly formed and released from the HMX starting at the transition from the induction stage to the acceleratory stage of the decomposition. This is clear from all four experiments. However, the results from the HMX- d_8 sample show this most clearly because there is no source of D₂O other than the HMX. The temporal behavior of the release of H_2O during the induction stage of the decomposition is less clear due to the signal from adsorbed water in the apparatus. Some H_2O appears to be released during the induction stage in the other three experiments. The two experiments with the 150-µm-diameter HMX particles, experiments II and VI, show evidence of



Figure 5. Gas formation rates for H_2O , CH_2O , N_2O , and HMX during the induction periods of experiments (a) II, (B) IV, (C) III, and (D) VI. The HMX gas formation rate is determined by the equilibrium vapor pressure and the exhaust rate from the reaction cell, and it is indicative of the sample temperature.

water formation during the induction stage. The water that evolves in experiment VI may be due to water adsorbed on the HMX since it peaks before the HMX attains its constant gas release rate as the sample reaches its constant temperature. The higher relative gas formation rates of the N₂O and CH₂O compared to the HMX formation rate in the vicinity of the H₂O peak in experiment VI suggest that water may catalyze the decomposition.

The induction periods decrease with increasing temperature (comparing experiments II and VI) and increased by a factor of 3 with HMX- d_8 (comparing experiments II and III). The fact that the induction periods of experiments II and IV differ, although they were conducted at the same temperature and the induction periods are expected to be similar, suggests that other parameters may also influence the decomposition behavior during the induction

period. Two possible causes may be adsorbed water or the larger particle size of the material used in experiment II.

Rates of Gas Formation/Release vs Extent of Reactant Depletion. A better comparison between the different experiments can be made if the rate of gas formation is examined as a function of the fraction of sample remaining in the reaction cell, X. The results are presented in this manner for the major and minor products in Figure 6.

The general features of the rates of gas formation of each pyrolysis product in all six experiments are the following: (1) The fraction of sample that leaves the reaction cell prior to reaching a constant temperature is less than 1%. (The HMX gas formation rate is determined by the sample temperature and is indicative of the temperature of the sample.) (2) All of the experiments have an induction period during which time the products formed are CH_2O and N_2O . (3) During the acceleratory stage all of the products, except for the evaporating HMX, show an increased rate of formation. The most rapid rates of increase are for H_2O , N₂O, and the amide compound. Slower increases in the rates of gas release are observed for CO, NO, CH₂O, HCN, DMNA, and ONTNTA. (4) The most rapid rates of decrease in the gas formation rates during the decay stage of the decompositon are for H_2O , followed by the amide, and then the N_2O . (5) The most rapid rate of decrease in the H₂O formation rate occurs when the rate of increase in the CH_2O formation rate is a maximum. (6) The rates of decrease of the gas release rates of CH₂O, CO, and NO are smaller than the other products. (7) The rates of formation of H₂O and DMNA fall to zero as the amount of HMX remaining in the sample goes to zero. (8) The rates of formation of all of the other products approach a nonzero gas formation rate as the amount of HMX remaining in the sample goes to zero.

The differing rates of change in the gas formation rates of the gaseous products indicate a variation in the processes controlling the identity and the rates of formation of the different products during the course of the decomposition of the sample. This is supported by the following features of the decomposition: (1) The ratios of the CH₂O to N₂O gas formation rates vary from 0.7 to 0.8 during the induction stage, decrease to a minimum of 0.35 during the acceleratory stage, and increase to ~ 1 near the end of the decay stage. (2) The ratio of the H₂O to N₂O gas formation rates is zero during the induction stage, increases to a maximum of ~ 1 during the acceleratory stage, and decreases to zero at the end of the decay stage. (3) The gas formation rate of ONTNTA increases during the acceleratory stage of the decomposition and decreases to a nonzero value near the end of the decay stage.

The temperature dependence of the rate of gas formation of the products is shown in Figure 6a-c. As the temperature increases, the maximum rates of release of H_2O and N_2O occur at smaller sample depletion fractions. In addition, the relative rate of NO gas release to CO gas release increases with temperature. Otherwise, the temporal behaviors of the gas release rates do not change appreciably in the temperature range of the experiments.

The rates of gas formation are greater for a larger sample size (experiment V) as illustrated in Figure 6, c and f, for the data from experiments II and V. Furthermore, the rates of formation of H_2O and N_2O are equal for a smaller fraction of the sample depletion of the larger sample. The fraction of water produced in the larger sample is also less. The relative amount of ONTNTA formed is also less in the larger sample than in the smaller sample.

Comparison of the data from the unlabeled HMX (experiment II) to the deuterium-labeled HMX (experiment III) shows a clear deuterium kinetic isotope effect. The ratio of the maximum rates of gas formation of H_2O , CH_2O , and N_2O from unlabeled HMX compared to HMX- d_8 are 3.3, 1.2, and 1.65, respectively. The deuterium isotope effect is larger in the H_2O and N_2O formation than in the CH₂O formation.

Discussion

The temporal behaviors of the rates of gas formation of the pyrolysis products during the isothermal decomposition of an HMX sample are consistent with either an autocatalytic reaction mechanism or a condensed-phase decomposition, in which release of the gas products is controlled by both chemical and physical processes, or a combination of both. However, since the transmission electron micrographs of the NVR remaining after the thermal decomposition show evidence that bubbles form within the HMX particles during decomposition, autocatalysis alone is not responsible for the temporal behaviors of the measured gas formation rates.

A model for the decomposition of HMX that is consistent with the features of the decomposition observed in our experiments has at least three main physical processes. These processes include net evaporation of the HMX from the surface of the particles, nucleation of bubbles within the particles, and growth and coalescence of the bubbles within the particles. This is supported by the structure of the residue that remains after the isothermal decomposition. The macroscopic structure of the NVR shows that the NVR is formed in individual particles, and the microscopic structure shows that it is the remnant from gas bubbles. A model of this simple physical picture is shown in Figure 7. The gas bubbles are located within the HMX particles, and the NVR is located at the interface between the gas within the bubbles and the unreacted HMX.

In the experiments, the gaseous products are measured when the regressing surface of the particles intersect the bubbles that have formed within the particle. When the bubbles intersect the receding surface of the particle, the gas within the bubble breaks the shell of residue and escapes; the fragment of the shell is left behind. During the initial stages of the decomposition, the bubbles are smaller and occupy only a small fraction of the volume of the particle. Therefore, the products that are released during the early stages are representative of the physical and chemical process occurring in small individual bubbles. Furthermore, the release rate is controlled by the evaporation of HMX from the surface of the particle. During the later stages of the decomposition, growth and subsequent coalescence of the bubbles can provide pathways for gas release from the particles. Consequently, predicting the rate of gas release from the sample will be more complicated during the later stages of the decomposition. Other possible mechanisms for gas release from the particle include migration of gas along grain boundaries within the particle and fracture of the particle followed by gas flow through cracks. These effects will alter the details of the gas release from the particle, but the general features of the decomposition of the HMX within the particle, followed by subsequent reactions of the gas products within the particle, and finally release of the gaseous products, still describe the general temporal behavior of the rates of gas formation and release from HMX. This qualitative model of the decomposition is strongly supported by the observations in our experiments.

The transition from the release of products controlled by evaporation of HMX to that controlled by coalescence of the bubbles occurs in the early portion of the weight loss. By assuming that the release due to coalescence of the bubbles will occur when between 50% and 67% of the sample has decomposed to products and then by determining when the ratio of rates of release of HMX to all of the HMX decomposition products falls within this range, one can determine the time of the transition to release due to coalescence. For experiment II this corresponds to a transition time between 4600 and 5200 s, and release due to coalescence starts when the sample has lost only between 9% and 13% of its original weight. This implies that the release rate during the acceleratory stage is determined predominantly by the rate of coalescence of the products and the formation of exit channels to the surface of the particles. It also suggests that previous kinetic studies based on either pressure-time 10,16 or TGA²⁸ data are reporting rate constants that are significantly influenced by the physical processes of product coalescence and release from the particle and not the chemical decomposition kinetics of the nitramine. These same physical processes controlling the release in the solid will also influence the rate constants determined for the liquid-phase decomposition of HMX.¹⁰ To determine even global rate constants for the decomposition of HMX, it is necessary to understand and properly characterize the physical processes



Figure 6. Gas formation rates of the products formed during the pyrolysis of HMX as a function of the fraction of the original sample that has left the reaction cell, X. The results are for experiments (A) I, (B) VI, (C) II, (D) III, (E) IV, and (F) V whose experimental conditions are listed in Table I.



Figure 7. Processes occurring during the decomposition of an HMX particle. The processes transforming an HMX particle into a NVR with the same shape are HMX evaporation, bubble nucleation and growth, reactions within the bubbles, and release of gaseous products from the bubbles.

occurring during the decomposition. The data in this paper provide the basis for this modeling.

An estimate of the range of pressures that is expected within the bubbles can be made based on the size of the shells of residue. Using the heat of vaporization of HMX, we estimate that the surface free energy of HMX is 600 erg/cm². If we use this value and assume no external forces are exerted from the particle, the pressure of the gas within the bubbles will range from 0.5 MPa for bubbles with a 5- μ m diameter to 9 MPa for bubbles with a 0.3-µm diameter. On the other hand, if each molecule of HMX is assumed to produce eight gas molecules and the volume that the gas molecules occupy is that originally occupied by the HMX molecule, then gas pressures within the bubble may range up to 240 MPa. Although the exact gas pressures within the gas bubbles are not known, it is clear that the pressures under which the gaseous pyrolysis products react are many orders of magnitude greater than is expected for a thermal decomposition experiment under Knudsen cell conditions.

If the pressure within the bubbles is inversely proportional to the bubble diameter, then during the early stages of the decomposition the bubbles that rupture will be smaller and the pressure of the gas within the bubbles will be higher than later in the decomposition. If this assumption is correct, then the products that are observed early in the decomposition would be characteristic of a higher pressure environment than those observed later in the decomposition.

With this model for the decomposition of HMX below its melting point, it is clear that secondary reactions and transport processes are important in determining the identity and rates of evolution of the products from the HMX particles. The reactions at a bubble site must account for at least the following processes: reaction of the HMX at the bubble surface, reactions of the gases contained within the bubble, and formation of the residue at the surface of the bubbles. Clearly, this involves an even more complicated reaction scheme than many of the decomposition schemes already proposed.^{8,9,26} However, it allows other plausible reactions to account for many of the different products and features observed during the decomposition.

The results show that it is important to account for the reaction environment in which the individual products are created when decomposition mechanisms are proposed based on the observation of gaseous products from the pyrolysis of HMX. It is therefore necessary to determine the location of the reactions in addition to the identity of the products before reaction mechanisms are postulated.

The reaction locations that may be important in our experiments (and most other experiments on HMX and other related nitramines) are the low-density environment of the free volume in the reaction cell, the bulk of the solid, on the surfaces, and in the high-density gas environment created within the solid particles.

The reactions in the bulk may occur at defects and grain boundaries or be induced by stresses created within the particles. Surfaces that may play a role in the decomposition are located at the surface-vacuum interface, the gas-surface interface, and the NVR-surface interface. Reactions between the starting material and its decomposition products in the gas phase at both low and high densities must also be considered.

The reactions that must be considered include the unimolecular decomposition of HMX, secondary reactions between the decomposition products, reactions between the decomposition products and HMX, and the thermal decomposition of the more stable products (e.g., the NVR) that are formed during the decomposition of HMX.

As a starting point for interpreting the results of our experiments, we consider the decomposition steps observed in the IRMPD experiments with RDX.²⁴ By analogy with the IRMPD results for RDX, the HMX may undergo a quadruple fission to four methylenenitramine molecules that may undergo further decomposition to either HCN and HONO or N₂O and CH₂O. The facts that 3 mol of N₂O is measured for each mole of decomposed HMX and no mixing is observed in nitrogen-15 scrambling experiments^{12,35} can be explained by either a branching ratio of the methylenenitramine of 3:1 for the N2O/CH2O and HCN/HONO channels or, more likely, the domination of the N-N bond dissociation pathway for the first step in the decomposition, followed by ring fragmentation and decomposition to N2O and CH₂O of the remaining molecule.

$$O_2 N \qquad NO_2 \qquad H_2 C N + NO_2 + 3H_2 C = N - NO_2$$

$$O_2 N \qquad NO_2 \qquad (2)$$

$$H_2C == N - NO_2 \rightarrow N_2O + CH_2O \qquad (3)$$

This mechanism (2 and 3) is similar to that proposed by Melius³⁶ based on the BAC-MP4 quantum chemical method. The formation of methylenenitramine after the rupture of the initial N-N bond is consistent with, but not proved by, our results. However, reaction 2 is a likely decomposition pathway based on the BAC-MP4 calculations,³⁶ which show that once the NO₂ is removed the adjacent C-N bond strength falls from 350 to 75 kJ/mol. Since neither H₂CN nor NO₂ is observed in the HMX experiments and the numbers of moles of N2O and CH2O produced are not equal, the role of secondary reactions in determining the identity and rates of release of the gases from the particles is important.

Secondary reactions that can explain the lack of NO₂, a smaller than expected amount of CH2O, and H2O, CO, and NO as products are37

$$CH_2O + NO_2 \rightarrow H_2O + CO + NO$$
 (4)

and

$$2HONO \rightarrow H_2O + NO + NO_2$$
(5)

These reactions alone cannot account for the ratio of the amount of N₂O to CH₂O formed in our experiments or the even higher ratio of release rates of these two products during the acceleratory stage of the decomposition. In addition, they alone cannot account for either the equal rates of release of N2O and H2O during the acceleratory stage or the differences in temporal behaviors of the release rates of the H2O, CO, and NO. The release rates of water from our experiments are higher than can be produced by reactions 4 and 5. Other reactions that can explain the higher rate of release of water during the acceleratory stage is the formation of amide polymers by condensation reactions. One route for formation of the amide is by reaction of the H₂CN radical formed during the first decomposition step with the excess of CH₂O in the bubbles

$$H_2CN + CH_2O \rightarrow H_2CNHCHO$$
 (6)

followed by subsequent polymerization to the polyamide that can

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then undergo a cross-linking reaction with formaldehyde to form water.



These types of reactions can account for several of the products we observe. The N-methylformamide can be formed after hydrogen abstraction by the radical generated in reaction 6. The fact that the molecular weight of the species producing the ion in the mass spectrometer that has the (CH₃)NHCHO stoichiometry is approximately 116 suggests that either the (CH_3) -NHCHO forms a dimer or possibly two of the radicals formed in (6) combine to form the product. The temporal behavior of this product peaks at the same time as the N₂O and water, suggesting that it is formed during the portion of the decomposition associated with the higher pressure bubbles. However, the amide has a nonzero rate of release at the end of the decomposition and is also a product from the decomposition of the NVR at higher temperatures. This suggests that the amide products are also formed from the thermal decomposition of the NVR while the isothermal decomposition of HMX is still in progress. The products formed during the higher temperature decomposition of the NVR are HNCO, H₂NCHO, (CH₃)NHCHO, NH₃, and HCN. These products are expected from the decomposition of a polymer such as formed in reaction 7. Furthermore, since this polymer contains $H_2C-N-CH_2$ structures, it is possible that the dimethylnitrosamine is formed by the reaction of NO₂ or NO with the polymer. This is consistent with the bubble model and the temporal behavior of the rate of release of the DMNA.

The final product that may be formed in this relatively simple decomposition scheme is ONTNTA. If the N-N bond-breaking step in reaction 2 is fast compared to the subsequent decomposition of the rest of the ring, then, since the NO concentration within the bubbles is high, NO may add to the N radical on the ring to form ONTNTA. Whether this mechanism is responsible for the formation of the nitroso compounds in shock-initiated decomposition in RDX^{29,30} or in our experiments is not clear. Isotope scrambling experiments with ¹⁵N-labeled HMX will further the understanding of the mechanism leading to the formation of ONTNTA by determining whether the N-N bond breaks during the formation of ONTNTA.

The reaction scheme considered so far is relatively simple in that the HMX decomposition is assumed to be unimolecular and secondary reactions of the initial products formed during the unimolecular decomposition lead to the observed products. More complicated reaction schemes between decomposition products and the remaining HMX are also likely and may even control the rate of decomposition after the initial stages of the decomposition of the sample.

Bimolecular reactions between the decomposition products and the HMX may be important. Quantum chemical calculations³⁶ indicate that after a hydrogen atom is abstracted from the CH₂ group the bond strength of the adjacent N-N bond drops to 8kJ/mol, thus causing the NO₂ group to leave. Hydrogen atoms may be abstracted either by radicals present in the gas phase, such as OH, or by radicals involved in the formation of the amide polymer. Water is another species that is present within the HMX particles, and it may initiate the decomposition of HMX. During the early stages of the decomposition, water and N_2O are the most abundant species released from the particles. The combination of the high concentration of water, the high pressure within the bubbles, and the basicity of the amides suggests that OH⁻ may initiate the decomposition of the HMX. The presence of water may also cause any methylenenitramine that is formed to decompose to N_2O and CH_2O , rather than HCN and HONO. These bimolecular reactions are consistent with previous studies^{26,28} using deuterium analogues of HMX that show that hydrogen plays a role in the decomposition of HMX. Our results with HMX- d_8 also show a DKIE. However, our results also show that there are a number of possible reaction pathways and not all of them are expected to exhibit a DKIE. Determination of the particular reaction channels that exhibit a DKIE and the extent of the effect requires detailed reaction modeling of our results and will be presented in another paper.

The amount of HMX available for reaction in our experiments is greater in the bulk and on the surface than in the gas phase. For example, under the conditions used in experiment II, the amount of HMX available for reaction at the start of the experiment is approximately 2×10^{-10} , 4×10^{-10} , and 3×10^{-5} mol in the gas, surface, and bulk, respectively. As the sample decomposes, the surface area of HMX will increase due to the new surface formed around the bubbles and decrease due to the regression of the particle surface. These features may be related to the observed products. The rates of formation of N₂O and CH_2O during the induction stage may be due to reactions either in the gas phase or on the surface. Products from the decomposition within the bulk probably do not contribute to the measured products during the induction stage and should have little contribution near the end of the decomposition. However, the rates of formation of N₂O and CH₂O are 5 times higher at the end of the decomposition than during the induction stage of the decomposition. Since the vapor pressure of HMX is the same during these stages of the decomposition, it suggests that the decomposition occurs on the surface of either the HMX or the NVR. Unfortunately, since the surface area of the HMX is not known during most of the decomposition, the different rates of formation of these products only suggest this as a possibility. Another explanation for the difference in the rates of formation of N₂O and CH₂O during these stages may be catalytic activity of the NVR accelerating the decomposition rate of HMX that is transported to its surface. Further experiments investigating the decomposition rates of HMX with NVR formed during previous experiments may answer this question.

Since the containment time and density of the gas-phase species are many orders of magnitude higher within the bubbles than in the free volume of our reaction cell, the products that are observed are dominated by the reactions that occur in the bubbles. The bubble model is consistent with the temporal behaviors of the release rates of the gases, the formation of the polymeric NVR, the macroscopic and microscopic structure of the NVR, the observed DKIE, and the sample size dependence of the decomposition. What controls the nucleation and growth of the bubbles is not known and requires further experimentation and analysis. The nucleation may occur at defects within the crystals or along grain boundaries. It is also possible that the formation of ONTNTA is associated with the formation of defects within the lattice as suggested by the results from the shock-induced decomposition studies.²⁹ These defects, in turn, may be the nucleation centers for bubble growth.

Our results also suggest that the interface region between the gases within the bubbles and the HMX may be important in the decomposition of HMX. Several different scenarios can be envisioned. If unimolecular decay of HMX occurs at the bubble interface, the products must traverse the NVR film to enter the interior of the bubble. Diffusion of the products through the film could affect the decomposition rate. The film may also react with the HMX at the interface. As the film polymerizes the active sites formed during the polymerization reactions may also react with the HMX at the interface. This would also affect the rate of decomposition. The presence of the film as a barrier between the gas-phase products and the unreacted HMX may also change the manner in which the gaseous products interact with the HMX. This suggests that testing the catalytic effects of different gas products by measuring the decomposition rate in the presence of various concentrations of the different gas products^{14,16,17} may not simulate the actual environment during the decomposition of HMX by itself. Similarly, combining the NVR with the HMX, as was done previously with RDX,16c also may not have the same effect as when it is created within the particles because gas pressure

within the bubbles is no longer present to maintain contact between the NVR and the HMX.

Summary and Conclusions

The temporal behaviors of the rates of gas formation and gas release of the pyrolysis products from HMX show that the mechanisms controlling the identity and release of gas products from the particles are due to complex physicochemical mechanisms. The formation of bubbles within the solid HMX particles is apparent from both the temporal behaviors of the rate of gas release of the different pyrolysis products and the macroscopic and microscopic morphology of the polymeric nonvolatile residue formed during the decomposition. The TEM of the NVR shows that the NVR consists of broken ellipsoidal shells that are probably the remnants of bubbles that had formed within the HMX particles. Simple arguments indicate that the pressure of the gases within the bubbles ranges up to 9 MPa and may range up to 240 MPa depending on the strength of the solid HMX at the decomposition temperature. Comparison of the rate of vaporization of HMX and the rate of release of HMX decomposition products suggests that the decomposition products may be retained in the solid for long periods of time after they are formed and that their rate of release is substantially controlled by the coalescence of the products and the creation of exit channels from within the particles. This implies that previous studies used to determine reaction rate constants by either pressure-time or TGA methods were measuring rates that were substantially controlled by the gas release process and not the decomposition reaction kinetics.

The identity of the pyrolysis products and their temporal behaviors indicate that at least two different general reaction schemes are producing products. The first one, which is operational by itself during the induction stage of the decomposition and concurrently during the other stages, produces N_2O and CH_2O at approximately equal rates and appears to depend on the surface area of the HMX. The second scheme, whose products first appear at the start of the acceleratory stage, produces a wider range of products with varying ratios of gas release rates during the decomposition. The second reaction scheme is associated with the formation of the bubbles and produces N_2O , H_2O , CH_2O , NO, and CO in larger quantities and HCN, $(CH_3)NHCHO$, $(C-H_3)_2NNO$, ONTNTA, and the NVR in lesser quantities. Thermal decomposition of the NVR indicates that it is a form of a polyamide. The formation of the relatively high concentration of water and the polyamide film early in the acceleratory stage of the decomposition is consistent with the reactions of the second scheme occurring in the high-pressure bubbles.

The second reaction scheme emphasizes the complex nature of the physical processes occurring during the decomposition. Most of the products observed during the decomposition are formed in this reaction scheme. Under the high-pressure conditions in which the products are formed, a reaction environment is created that can affect, and perhaps control, the HMX decomposition. This environment consists of a polyamide film at the interface of HMX and high-pressure gaseous products. The relatively large concentration of water indicates that the reactions occur in a hightemperature aqueous environment.

Further insight into the decomposition mechanisms requires more studies on which bonds in the products have been formed during the decomposition and which remain from the original molecules. Isotope scrambling experiments may answer some of these questions. In addition, the development of a model to predict the formation and subsequent release of gas products from the particles will allow more conclusive statements about the mechanism and the determination of the temperature dependence of the controlling reactions.

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Photoionization Mass Spectroscopic Studies of Ethylene and Acetylene Clusters: Intracluster Excess Energy Dissipation

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The intact cluster ions of ethylene, $(C_2H_4)_n^+$ (n = 2-6), and acetylene, $(C_2H_2)_n^+$ (n = 2-4), have been found in addition to normally observed fragmented ions by using the near-threshold photoionization method. These intact ions have either not been observed or detected only very weakly in the (full-collision type) conventional ion-molecule reactions of ethylene and acetylene. The intact ions are produced by photoionization (11.83 and 11.62 eV) of the mixed neutral clusters with argon, $(Ar)_n(C_2H_4)_m$ and $(Ar)_n(C_2H_2)_m$, in the ionization threshold. The excess energies on ionization are randomized within the ionized clusters $[(Ar)_n(C_2H_4)_m^+]_{vip}^*$ and $[(Ar)_n(C_2H_2)_m^+]_{vip}^*$ ("intracluster excess energy dissipation") and finally converted to the decomposition of argon atoms, giving rise to the observed intact cluster ions, where vip represents vertically ionized points. The evidence of some especially stable cluster ions of ethylene and acetylene is also presented.

Introduction

A recent important progress in the cluster ion chemistry is the finding of the so-called intracluster ion-molecule reactions.¹⁻¹² The intracluster ion-molecule reactions that have been reported

so far are unique as compared with the conventional (full-collision type) ion-molecule reactions. Several distinct features of the

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