Mechanisms of Nitramine Thermolysis[1]

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The thermal decomposition of a number of nitramines was studied in dilute solution and in the melt. The nitramines included acyclic mononitramines [dimethylnitramine (DMN), diethylnitramine (DEN), dipropylnitramine (DPN), and diisopropylnitramine (DIPN)], cyclic mononitramines [*N*-nitropiperidine (NPIP) and *N*-nitropyrrolidine (NPyr)], cyclic dinitramines [*N*-dinitropiperazine (pDNP), 1,3-dinitro-1,3-diazacyclopentane (DNI), and 1,3-dinitro-1,3-diazacyclohexane (mDNP)], and 1,3,5-trinitro-1,3,5-triazocyclohexane (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexanitrohexaazaisowurtzitane (HNIW), and 1,3,3-trinitroazetidine (TNAZ). For the acyclic and cyclic mono- and dinitramines, the corresponding nitrosamines were the only or major condensed-phase product. Kinetics and activation parameters were determined for the thermolysis of dilute solutions (0.01–1.0 wt %) over the range 200–300 °C. The thermolyses were found to be first-order with the rate constants unaffected by the use of deuterated solvent. As the nitramines became more complex than dimethylnitramine (DMN), the rate of decomposition increased and the product distribution became more complex. As the length of the aliphatic chain increased (DMN < DEN < DPN), the rate of thermolysis increased, yet nitrosamine remained the only observed condensed-phase product. When a secondary carbon was attached to the *N*-nitramine (DIPN) rather than the primary (DPN), the rate of decomposition increased and a new condensed-phase product was observed. Among the cyclic nitramines, the rate of decomposition increased as the number of NNO_2 groups increased (NPIP < pDNP; NPyr < DNI; mDMP < RDX). The position of the nitramine groups affected the decomposition: meta NNO_2 groups (mDNP) decomposed faster than para (pDNP). Ring strain decreased stability: mDNP < DNI; HMX < RDX. In complex nitramines, the increase in decomposition rate, the appearance of new products, and the change in the relative importance of nitrosamine and of N_2 and N_2O are attributed to new decomposition routes available to them. However, since complex nitramines (e.g. RDX) maintain first-order kinetics and since most have activation energies in the range of 40–50 kcal/mol, it is believed that the triggering mechanism remains N–NO_2 homolysis. Intramolecular hydrogen transfer is also considered an important mode of nitramine decomposition.

Introduction

Before we attempted to understand the mechanisms operating in species containing multiple nitramine functionalities, we examined the simple nitramine dimethylnitramine (DMN).[2] To avoid complications resulting from multiphase decomposition and autocatalysis,[3,4] we studied the thermolysis in dilute solution. Two different ^{15}N-labeling studies were performed. In both, complete label scrambling was observed in the N_2 and N_2O gases and in the dimethylnitrosamine. Only partial scrambling of the ^{15}N-label was observed in the reactant DMN.[2] Kinetic studies of DMN, diisopropylnitramine (DIPN), and *N*-nitropiperidine (NPIP) showed that as the viscosity of the solvent increased, the rate of decomposition decreased. This solvent cage effect and the observations of a large positive activation volume ($V^* = +30$) for DMN suggested that the rate-determining step was homolysis, the N–NO_2 bond being the most obvious point. A deuterium kinetic isotope effect (DKIE) was observed in the decomposition of DMN and its deuterated analog, implying that internal hydrogen transfer was involved in the rate-determining step. Acidic and basic species and free-radical scavengers appeared to have no effect on the rate of DMN decomposition, either in the neat melt or in solution. From the above results, two decomposition routes were postulated for DMN: hydrogen transfer from the methyl group in the nitramine to its NO_2 group resulting in loss of HONO, and N–NO_2 homolysis.[2] The first route would be first-order and would explain the ^{15}N-label scrambling in the nitrogen gases and the internal DKIE. The second would be a first-order route to nitrosamine and would explain the solvent cage effect and positive activation volume.

In the present studies, we compare the thermal decomposition of dimethylnitramine to a number of more complex nitramines—acyclic, cyclic, and polycyclic. Primarily thermolyses have been performed in solution, using the solvent as a possible radical trap for intermediates and also as a diluent to discourage autocatalysis. The mechanism of decomposition was deduced from observed reaction kinetics and decomposition products.

Experimental Section

Dimethylnitramine (DMN), ^{15}N-labeled DMN, and N-nitropyrrolidine were prepared by dehydration of the corresponding dialkylammonium nitrate salt.[5] Perdeuterodimethylnitramine was prepared from perdeuterodimethylformamide by the method of Robson.[6] Diisopropyl-, diethyl-, and dipropylnitramine, *N*-nitropiperidine, and dinitropiperazine were formed by treatment of the corresponding amine with dinitrogen pentoxide.[7,8] 1,3-Dinitro-1,3-diazacyclopentane and 1,3-dinitro-1,3-diazacyclohexane were formed by condensation of the appropriate dinitramine with formaldehyde.[9] RDX, HMX, TNAZ, and HNIW were supplied by various government laboratories. Dimethylnitrosamine and diisopropylnitrosamine were prepared by adding the corresponding amines to a cold aqueous solution of sodium nitrate, which had been acidified with hydrochloric acid.[10] The mononitroso analogue of RDX was prepared by the method of Bell and Dunstan and recrystallized by published procedures.[11,12] The di- and trinitroso analogues of RDX were synthesized by the procedure outlined by Hoffsommer and references therein.[13]

Isothermal decompositions of the nitramines were conducted in sealed glass tubes as previously discussed.[2] Typically samples were benzene, isooctane, or acetone solutions containing 0.1–1.0 wt % nitramine (*N*-nitropiperidine was 10 wt % in benzene).

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TABLE 1: Kinetic Parameters of Nitramine Decomposition

sample	no. data	temp range (°C)	E_a kcal/mol	E_a kJ/mol	A (1/s)	solvent	concn (%)	rate const at 240 °C
DMN	6	200–300	46.7	195	6.72E+17	isooctane	0.1	9.0E-04
	6	200–280	38.0	159	1.72E+13	neat		1.0E-03
DEN	6	200–300	45.1	189	1.81E+16	isooctane	0.1	1.2E-03
DPN	3	220–260	48.0	201	4.40E+17	isooctane	0.1	2.0E-03
DIPN	6	200–300	42.6	178	8.80E+15	isooctane	0.1	6.2E-03
	3	220–250	43.9	184	1.38E+16	acetone	0.7	2.9E-03
NPIP	5	220–300	48.2	202	4.42E+16	benzene	10	6.5E-04
	5	240–290	47.5	199	2.07E+16	acetone	0.7	1.2E-04
NP	5	240–290	51.5	215	2.87E+18	acetone	0.7	3.0E-04
pDNP	5	220–280	52.6	220	1.23E+19	acetone	0.9	5.4E-04
mDNP	5	200–280	49.1	205	9.40E+17	acetone	0.9	4.7E-03
	6	200–300	40.0	167	4.00E+14	ethanol		
	3	240–260	41.9	175	2.53E+15	neat		3.5E-03
TNAZ	4	189–263	43.6	182	2.80E+16	acetone	0.7	8.3E-03
	3	220–250	43.7	183	1.85E+16	neat		4.6E-03
HMX	6	189–289	50.2	210	8.28E+18	acetone	1	2.5E-03
	4	230–270	52.9	221	2.46E+18	neat		
DNI	5	200–240	47.8	200	1.27E+19	acetone	0.9	2.7E-02
	4	200–250	47.2	197	4.92E+18	neat		3.4E-02
RDX	3	200–240	45.4	190	7.40E+17	acetone	0.7	3.2E-02
	6	206–256	38.5	161	1.39E+14	benzene	0.9	
	4	200–250	37.8	158	1.99E+14	neat		1.7E-02
HNIW	6	146–226	42.4	177	4.0E+17	acetone	1	8.8E-02 (at 226 °C)

Rate Constants at 240 °C

	benzene	benzene-d_6		benzene	benzene-d_6
DMN	2.7E-04	2.8E-04	mDNP	4.1E-03	3.0E-03
DEN	4.8E-04	4.6E-04	RDX	1.1E-03	9.7E-04
DIPN	4.1E-03	4.3E-03			

Thermolyses were performed isothermally in the temperature range 200–300 °C, with the bath temperature maintained within 1 °C of the desired temperature. To examine the condensed and vapor phase thermolyses, about 0.2 mg of the desired nitramine was sealed into the glass thermolysis tube. To promote vapor phase decomposition, the tubes were evacuated. To determine the energy of activation (Table 1), solution rate constants were determined for at least five temperatures. Rate constants at as few as three temperatures were used for condensed-phase activation energy calculations. For comparative purposes, only the rate constants at 240 °C are listed in Table 1.

The thermolysis products were analyzed by a Hewlett-Packard 5890A gas chromatograph (GC) equipped with a 5970B quadrupole mass-selective detector (MS) and a narrow-bore HP-1 (cross-linked methylsilicone) capillary column (25 m × .20 mm i.d.). Identification of a mass spectrum was achieved by comparing the mass spectrum to that of an authentic sample or by interpretation of the fragmentation pattern. Gaseous products were separated and quantitatively identified using a Varian 3600 gas chromatograph equipped with a thermal conductivity detector (GC-TCD).[2] The GC was configured with a PORAPAK-Q column in series across the TCD detector with a molecular sieve (MS13X) column. Identification and quantification of the gases were achieved by comparing the retention times and areas to calibration curves of known gases.

The method in which the fraction of unreacted nitramine was quantified depended on the properties of each species. For many, a gas chromatograph (GC, Varian 3600) equipped with capillary column (DB-05) and flame ionization detector was used (helium flow rate, 30 mL/min). For others, a high-performance liquid chromatograph equipped (HPLC) with a 20-uL sample loop and UV detector was employed. Individual chromatographic conditions are shown in Table 2. FT-NMR spectra were recorded on a JEOL GSX400 spectrometer with a 5-mm broadband probe at ambient temperature. ^{13}C spectra were ^{1}H-decoupled. Resonances reported are relative to the solvent benzene-d_6.

Results and Discussion

Like dimethylnitramine (DMN) and diisopropylnitramine (DIPN), all the nitramines in solution or in the neat melt decomposed with first-order kinetics. Rate constants at 240 °C, as well as activation energies, are given in Table 1. For three nitramines, diethylnitramine (DEN), 1,3-dinitro-1,3-diazacyclohexane (mDNP), and RDX, thermolysis rates were compared in benzene and in benzene-d_6. As was the case for DMN and DIPN,[2] no solvent deuterium kinetic isotope effect (DKIE) was observed, supporting the hypothesis that in the decomposition of these nitramines intermolecular hydrogen transfer is not important. However, it should be noted that, in the case of RDX, this result disagrees with a previous report.[13] Although deuterated analogues were not prepared for each of the nitramines in this study, we observed a primary DKIE in DMN-d_6 (1.56), and a primary DKIE has been reported for both RDX and HMX.[14,15] From these kinetic results, we postulated that, like DMN, other nitramines have a decomposition mode involving intramolecular hydrogen transfer. However, in the case of DMN decomposition, hydrogen transfer produced only gaseous products; this result would not be expected in more complex nitramines.

In the thermal decomposition of dimethylnitramine, about half a mole of gas was formed per mole of nitramine; this was attributed primarily to products arising from the intramolecular hydrogen-transfer route. The only condensed-phase product was dimethylnitrosamine, formed in over 80% yield.[2] The nitrosamine was assumed to arise from $N-NO_2$ homolysis. Examining the condensed-phase species remaining from the thermolysis of mixed $^{15}N-^{15}N$-labeled dimethylnitramine with unlabeled dimethylnitramine, we observed complete label scrambling in dimethylnitrosamine, in agreement with similar results of Suryanarayana and Bulusu.[16] However, in contrast to their findings, we also observed a limited amount of label scrambling in the reactant nitramine.[2]

To determine if the mechanism suggested for DMN applied to more complex nitramines, the thermal decomposition products of a series of acyclic nitramines [diethylnitramine (DEN),

TABLE 2: Chromatographic Conditions for Nitramine Detection

Gas Chromatography

sample	column	temp (°C)	hold time (min)	heat ramp (°C/min)	ret time (min)	sample	column	temp (°C)	hold time (min)	heat ramp (°C/min)	ret time (min)
DMN	DB-05	50–180	1	15	1.4	DNI	DB-05	80–180	0	15	3.8
DIPN	DB-05	60–180	2	15	4.4	NPyr	DB-05	80–180	0	15	1.9
NPIP	DB-05	60–180	2	15	3.7	RDX	DB-05	50–180	2	15	10.1

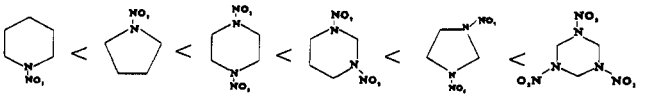
High-Pressure Liquid Chromatography

sample	column	eluent	flow rate (mL/min)	detection UV (μm)	ret time (min)
pDNP	Econosphere C18, 5u (25 cm × 4.6 mm)	$CH_3OH/THF/H_2O$ (32/4.8/63.2)	0.75	229	6.2
mDNP			0.75	229	9.8
DNI			0.75	229	
RDX			0.75	229	20.0
HMX			0.75	229	12.3
TNAZ			0.75	254	11.6
HMX	Adsorbosphere CN, 5u at 50 °C (25 cm × 4.6 mm)	CH_3CN/H_2O (40/60)	0.8	229	10.0
HNIW			1.2	229	11.0
DMN	Lichrosorb SI-60 (25 cm × 4.6 mm)	ethanol/isooctane (7/93)	1.5	254	6.3
DEN			1.5	254	4.6
DIPN			1.5	254	3.5
DPN		ethanol/isooctane (2.5/97.5)	1.5	254	3.8
HNIW		ethanol/hexane (10/90)	1.5	229	12.2

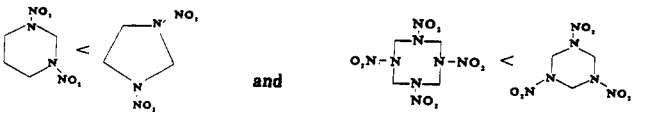
dipropylnitramine (DPN), and diisopropylnitramine (DIPN)] were examined. All formed about a half a mole of gas per mole of nitramine, and for all, except DIPN, the only condensed-phase product was the corresponding nitrosamine. For DIPN, the proposed hydrogen-transfer decomposition route should have produced nitrogen gas, isopropanol, and acetone. Thermolysis of DIPN produced N_2, diisopropylnitrosamine, and acetone in roughly a 1:1:2 ratio. Although no isopropanol was detected in DIPN thermolysis, it was argued that under the reaction conditions isopropanol would be oxidized to acetone. Therefore, this additional condensed-phase product (acetone) found in DIPN thermolysis is accounted for by intramolecular hydrogen transfer.[2] However, it should be noted that the decomposition of DIPN produced some propane and other unaccounted for condensed-phase species; furthermore, the thermolysis of diisopropylnitramine was significantly faster than that of the other acyclic nitramines. We interpret these results as an indication that as the hydrocarbon substituent on the nitramine becomes more complex, the number of available reaction paths increases. In fact, among the acyclic nitramines, the rate of decomposition increased as the carbon chain length increased, indicating the importance of the degree of substitution on the carbon attached to the amine nitrogen.

GC/MS analysis was used to identify the condensed-phase products of cyclic mononitramines [*N*-nitropiperidine (NPIP) and *N*-nitropyrrolidine (NPyr)], cyclic dinitramines [*N*-dinitropiperazine (pDNP), 1,3-dinitro-1,3-diazacyclopentane (DNI), and 1,3-dinitro-1,3-diazacyclohexane (mDNP)], and 1,3,5-trinitro-1,3,5-triazocyclohexane (RDX) and 1,3,3-trinitroazetidine (TNAZ). All these nitramines produced nitrosamines; in fact only in the case of RDX were they not the principal products. Those compounds with more than one nitramine functionality showed evidence of sequential conversion of nitro to nitroso; for NPIP, NPyr, and mDNP nitroso compounds were the only condensed-phase products. For dinitropiperazine (pDNP), piperazine itself was also identified by comparison to an authentic sample. Thermolysis products of TNAZ, other than the *N*-nitroso, will be discussed elsewhere.[17] For 1,3-dinitro-1,3-diazacyclopentane (DNI) the fragmentation pattern was not definitive for the nitrosamines, but they were inferred from the large peak at *m/e* 30 and from their retention times; the ^{13}C NMR suggested there may be at least one other condensed-phase product. RDX thermolyzed in benzene to about 40% decomposition produced GC peaks identified by comparison with the GC/MS patterns of authentic samples as the mono-, di-, and trinitroso species. At higher levels of conversion, these species disappeared, leaving numerous uncharacterized species. Nitrosamines have also been observed in the residue of drop-weight impact studies on RDX[18] and in the residue of burned RDX propellant.[19] In a label scrambling test similar to that which we conducted with DMN,[2] RDX was heated under an $^{15}NO_2$ atmosphere. The time of heating had to be shortened to prevent complete decomposition of the RDX since NO_2 accelerated its decomposition, as it did the decomposition of DMN. Although the GC/MS spectrum was unclear as to whether any nitrosamine products were produced, the lack of incorporation of the ^{15}N label in the starting material is in line with what was observed for DMN.

Among the cyclic nitramines, it was observed that the presence of more than one nitramine functionality in the ring enhanced decomposition (Table 1). The two mononitramines *N*-nitropiperidine (NPIP) and *N*-nitropyrrolidine (NPyr) decomposed more slowly than the dinitramines, dinitropiperazine (mDNP) and 1,3-dinitro-1,3-diazacyclohexane (pDNP). A dramatic increase in decomposition rate was observed when the dinitramine functionalities were meta to each other, as in 1,3-dinitro-1,3-diazacyclopentane (DNI) and 1,3-dinitro-1,3-diazacyclohexane (pDNP), rather than para, as in dinitropiperazine. Therefore, it



is not surprising that RDX, HMX, and HNIW are among the least thermally stable nitramines studied. Ring strain or perhaps bonding angle around the amine nitrogen[20] appears to play a role in increasing the rate of thermal decomposition since 1,3-dinitro-1,3-diazacyclohexane (mDNP) decomposes much more slowly than 1,3-dinitro-1,3-diazacyclopentane (DNI) and HMX decomposes more slowly than RDX.



Although the 240 °C decomposition rate constants differ considerably for acyclic, cyclic, and multifunctional nitramines, all the observed decompositions, in solution or neat, were first-

TABLE 3: Moles of Gas per Mole of Nitramine Heated at 240 °C for 10 Half-Lives

	condensed-phase neat						1% in acetone				
	N_2	N_2O	CO_2	CO	NO	total	N_2	N_2O	CO_2	CO	total
DMN	0.15	0.01	0.26	0.07		0.49	0.02	0.00	0.07	0.07	0.15
DEN	0.31	0.01	0.08	0.08		0.48					
DPN	0.29	0.03	0.06	0.08		0.45					
DIPN[a]	0.35	0.04	0.04	0.02		0.45	0.15	0.01	0.02	0.04	0.23
NPIP							0.07	0.02	0.06	0.04	0.19
NPyr	0.19	0.07	0.17	0.04		0.47	0.07	0.03	0.06	0.03	0.19
pDNP	0.37	0.07	0.48	0.12		1.04	0.26	0.05	0.12	0.17	0.60
mDNP	1.13	0.25	0.98	0.43		2.79	0.63	0.08	0.20	0.26	1.17
HMX	0.82	2.81	1.2	0.61		5.44	0.99	0.26	0.60	0.48	2.33
DNI	1.18	0.15	0.77	0.27		2.37	0.41	0.05	0.21	0.22	0.89
RDX	1.37	1.24	0.86	0.88		4.35	0.49	0.04	0.15	0.26	0.94
HNIW	4.29	0.82	3.30	1.20		9.61	0.97	0.07	0.20	0.19	1.43
TNAZ	0.86	0.11	1.55	0.61	0.9	4.03	0.15	0.03	0.31	0.38	0.87

[a] Plus 0.1 mol/mol propane.

TABLE 4: RDX Thermolsyis. Maximum Moles of Mononitroso Derivative Formed per Mole RDX

	240 °C				220 °C			
	NO–RDX (mol/mol)	k (s^{-1})	t (s)	% decomp	NO–RDX (mol/mol)	k (s^{-1})	t (s)	% decomp
acetone	0.238	0.033	40	71	0.237	0.0071	180	73
neat	0.059	0.014	40	44	0.046	0.0021	120	18
vapor	0.061	0.017	70	71				

TABLE 5: Moles of Gas Formed per Mole RDX Heated at 240 °C

	1% in acetone		neat			vapor		
% decompsn	100	70	100	70	30	100	70	30
t, s	211	37	481	83	25	397	69	21
N_2	0.90	0.43	1.31	1.07	0.39	1.33	0.52	0.19
N_2O	0.09	0.03	1.18	0.81	0.13	1.09	0.59	0.08
CO_2	0.26	0.08	0.72	0.44	0.13	0.60	0.21	0.03
CO	0.28	0.03	0.74	0.58	0.22	0.53	0.21	0.30
total	1.53	0.57	3.95	2.90	0.87	3.55	1.53	0.60

order with activation energies in the range of 40–50 kcal/mol. Furthermore, these activation energies differ little from the corresponding ones measured in the neat condensed-phase decomposition (Table 1). Since the presence or absence of solvent had little effect of the activation energy and deuteration of the solvent had no effect on the rate constant, the decomposition mechanism being probed must be unimolecular. The retarding effect of increased solvent viscosity,[2] the positive activation volume,[2,21] the common observation of nitrosamines, and the fact that this diverse group of nitramines all exhibited activation energies similar in magnitude to the N–NO_2 bond energy suggest a common rate-determining step in the decomposition. The most logical common step is N–NO_2 bond scission.

Having focused on the similarities in the decomposition of various nitramines, we must also acknowledge the differences. Although the activation energies among the nitramines are of similar magnitude, the rates of decomposition vary over a 100-fold range (compared at 240 °C, Table 1). RDX, DNI (1,3-dinitro-1,3-diazacyclopentane), and HNIW (hexanitrohexaaza-isowurzitane) were the most thermally unstable nitramines. HNIW was so unstable that the highest temperature that could be studied readily was 226 °C rather than 240 °C. This difference in thermal stability undoubtedly arises from the decomposition pathways available subsequent to N–N bond homolysis. The number and accessibility of these subsequent routes to decomposition depend on the other structural features in the molecule.

Thermolysis of mixed ^{15}N–^{15}N-labeled dimethylnitramine with unlabeled dimethylnitramine yielded nitrogen with complete label scrambling. This is in line with the proposed intramolecular hydrogen transfer, which is the source of the internal DKIE. However, this result is in contrast to those observed when $^{15}NO_2$-labeled HMX was examined: all N_2 and N_2O contained one labeled and one unlabeled nitrogen, and NO was exclusively ^{15}N-labeled.[22] The composition of the gaseous decomposition products for all the examined nitramines is shown in Table 3. RDX and HMX are unique among the nitramines studied in the large quantities of nitrous oxide produced. However, in solution-phase decomposition, they behaved more like the other nitramines, with N_2 by far the major nitrogen-containing gas. Probing for the source of this difference, we examined the decomposition products of RDX. Upon complete decomposition, neat RDX produced primarily gases, but some unidentified condensed products were also formed. In contrast, when the solution-phase thermolysis of RDX was about 40% complete, it was possible to identify the mono-, di- and trinitrosamine decomposition products by comparison of their GC/MS patterns with those of authentic samples.

Curious about possible differences in solution-, vapor-, and condensed-phase thermolyses, we examined the decomposition of RDX at 240 °C in each phase. Table 4 compares the rate constants and the maximum amount of mononitroso RDX derivative formed, and Table 5, the decomposition gases under each condition. The solution-phase reaction accentuates the nitrosamine intermediate (Table 4). At about 71% decomposition, RDX in solution showed about 24% of the mononitroso product; at the same point in the decomposition in vapor phase, only about 6% of the mononitroso product was detected. At the same time, Table 5 indicates that substantially less gas but more N_2 has been formed in the solution decomposition than in the vapor. Both the vapor and neat decomposition yielded about equal amounts of N_2 and N_2O, while the solution decomposition produced almost no N_2O. Decomposition rate constants vary slightly in the various phases, but the variation in rate constants is minor compared to the variations in the products.

Understanding the difference in product distribution in the vapor- and solution-phase decompositions of RDX facilitates our understanding of other differences in their decomposition schemes.

In all nitramines, the trigger linkage appears to be N–N homolysis. In solution decomposition, the amine radical is stabilized sufficiently so that it resists further decomposition and instead reacts with NO to form nitrosamine. However, in vapor- or condensed-phase decomposition, the amine radical undergoes further breakdown before the lost NO_2 can return as the reduced NO; therefore, little nitrosamine is formed. In the case of RDX and HMX, the loss of only one NO_2 group triggers the breakdown of the entire heterocycle. In monofunctional nitramines, N–N scission means the most likely fate of each nitrogen atom is formation of nitrogen gas. In RDX and HMX, once the first N–N bond is broken, the rest of the heterocycle can unravel, the extra nitramine functionalities forming nitrous oxide rather than nitrogen gas.

$$HMX \rightarrow NO_2 + HCN + 3\ H_2C{=}N{-}NO_2$$

$$H_2C{=}N{-}NO_2 \rightarrow NNO + H_2CO$$

In solution, the decomposition gases are predominately dinitrogen, and more nitrosamine is observed because the amine radical remaining after initial NO_2 loss is stabilized by the solvent, preventing further unraveling of the ring. This explains why previous labeling experiments with neat HMX[22,23] and RDX[24] showed no scrambling of the label in N_2O, while we observed label scrambling in all the nitrogen-containing decomposition gases of DMN. In DMN decomposition, nitrous oxide is a minor product. In the decomposition of RDX or HMX, it is a major product, but the production of nitrous oxide in these species is by an entirely different route than it is in DMN. It arises from the decomposition of $H_2C{=}N{-}NO_2$, resulting from the unraveling of the heterocyclic ring.

Conclusions

For dimethylnitramine (DMN), two decomposition routes are postulated: hydrogen transfer from the methyl group of the nitramine to the NO_2 group resulting in loss of HONO, and N–NO_2 homolysis. The first route would be first-order and would explain the ^{15}N-label scrambling in the nitrogen gases and the internal DKIE. The second would be a first-order route to nitrosamine and would explain the solvent cage effect and positive activation volume.[2]

As the nitramines become more complex than DMN, the rate of decomposition increases and the product distribution is more complex. As the length of the aliphatic chain increases in acyclic nitramines, the rate of thermolysis increases, yet nitrosamine remains the only condensed-phase product. When a secondary carbon is attached to the *N*-nitramine (DIPN) rather than the primary (DPN), the rate of decomposition increases and a new condensed-phase product is formed. Among the cyclic nitramines, the rate of decomposition increases as the number of NNO_2 groups increases. The position of the nitramine groups affects the decomposition: meta NNO_2 groups decompose faster than para. An increase in ring strain or a decrease in the bond angle around nitrogen also accelerates decomposition.

The increase in decomposition rate, the appearance of new products, and the change in the relative importance of nitrosamine and of N_2 and N_2O are due to new decomposition routes available to complex nitramines. However, since complex nitramines (e.g. RDX) maintain first-order kinetics and an internal DKIE and produce nitrosamines and since most have activation energies in the range of 40–50 kcal/mol, it is believed that the triggering mechanism remains N–NO_2 homolysis. In solution thermolyses of the reactant nitramines, the intermediate amine radical is stabilized, thus promoting nitrosamine formation and suppressing autocatalytic behavior. In the condensed- or vapor-phase thermolysis of nitramines with alternating nitramine functionalities, such as RDX and HMX, initial loss of NO_2 triggers the unraveling of the heterocyclic ring. Furthermore, there is evidence that intramolecular hydrogen transfer, postulated for DMN, is also important in more complex nitramines and could act as an alternate trigger for ring dissociation.

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References and Notes

(1) Taken in part from the theses work of Rick Szeckeres and Weiyi Zheng, New Mexico Institute of Mining & Technology.
(2) Oxley, J. C.; Hiskey, M. A.; Naud, D.; Szekeres, R. *J. Phys. Chem.* **1992**, *96*, 2505–2509.
(3) Cosgrove, J. D.; Owens, A. J. *Combust. Flame* **1974**, *22*, 13. Cosgrove, J. D.; Owens, A. J. *Combust. Flame* **1974**, *22*, 19.
(4) Batten, J. J. *Aust. J. Chem.* **1970**, *24*, 945; **1971**, *24*, 2025.
(5) Chute, W. J.; Herring, K. G.; Toombs, L. E.; Wright, G. F. *Can. J. Res.* **1947**, *26*, 89–103.
(6) Robson, J. H.; Reinhart, J. *J. Am. Chem. Soc.* **1955**, *77*, 2453–2457. Robson, J. H. *J. Am. Chem. Soc.* **1955**, *77*, 107–108.
(7) Emmons, W. D.; Pagano, A. S.; Stevens, T. E. *J. Org. Chem.* **1958**, *23*, 311–313.
(8) Gruenhut, N. S.; Goldfrank, M.; Cushing, M. L.; Caesar. 20. *Nitrogen Oxide. Inorg. Synth. Ed.*, 78–81.
(9) Goodman, L. *J. Am. Chem. Soc.* **1953**, *75*, 3019.
(10) Blatt, H. H. In *Organic Synthesis*; Blatt, A. H., Ed.; Wiley: New York, 1943; p 211.
(11) Bell, J. A.; Dunstan, I. *J. Chem. Soc. (C)* **1969**, 1556 and 1559.
(12) Bonner, T. G.; Hancock, R. A.; Roberts, J. C. *J. Chem. Soc. Perkin Trans. 2* **1974**, 653. Brockman, F. J.; Downing, D. C.; Wright, G. F. *Can. J. Res.* **1949**, *27(B)*, 469.
(13) Hoffsommer, J. C.; Glover, D. J. *Combust. Flame* **1985**, *59*, 303.
(14) Hoffsommer, J. C.; Glover, D. J.; Kubose, D. A. *J. Phys. Chem.* **1977**, *81*, 380. Hoffsommer, J. C.; Carlson, D. W. *Combust. Flame* **1987**.
(15) Bulusu, S.; Weinstein, D. I.; Autera, J. R.; Velicky, R. W. *J. Phys. Chem.* **1986**, *90*, 4121. Shackelford, S. A.; Coolidge, M. B.; Goshgarian, B. B.; Loving, B. A.; Rogers, R. N.; Janney, J. L.; Ebinger, M. H. *J. Phys. Chem.* **1985**, *89*, 3118.
(16) Suryanarayanan, K.; Bulusu, S. *J. Phys. Chem.* **1972**, *76*, 496.
(17) TNAZ manuscript in preparation.
(18) Hoffsommer, J. C.; Glover, D. J.; Elban, W. L. *J. Energ. Mater.* **1985**, *3*, 149–167.
(19) Schroeder, M. A.; Fifer, R. A.; Miller, M. S.; Pesce-Rodriguez, R. A.; Singh, G. Condensed-Phase Processes During Solid Propellant Combustion. Part II: Chemical and Microscopic Examination of Conductivity Quenched Samples of RDX, XM39, JA2, M30, and HMX-Binder Compositions. BRL-TR-3337, May 1992.
(20) Burov, Yu. M.; Nazin, G. M. *Kinet. Katal.* **1982**, *23*, 12; translation pages 5–10.
(21) Piermarini, G. J.; Block, S.; Miller, P. J. *J. Phys. Chem.* **1989**, *93*, 462–466; *J. Phys. Chem.* **1987**, *91*, 3872–3878.
(22) Suryanarayana, B.; Graybush, R. J.; Autera, J. R. *Chem. Ind.* **1967**, 2177.
(23) Behrens, R. *J. Phys. Chem.* **1990**, *94*, 6706. Behrens, R.; Bulusu, S. *J. Phys. Chem.* **1991**, *95*, 5838–5845.
(24) Behrens, R.; Bulusu, S. *J. Phys. Chem.* **1992**, *96*, 8877–8891. Behrens, R.; Bulusu, S. *J. Phys. Chem.* **1992**, *96*, 8891–8897.