JOURNAL OF PROPULSION AND POWER
Vol. 17, No. 2, March–April 2001

Thermal Decomposition of RDX in the Presence of Added $K_2B_{12}H_{12}$

Michael A. Schroeder,* Robert A. Fifer,* Pamela J. Kaste,* and Shirley A. Liebman*
U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005-5069

In an effort to understand the enhancement effect of boron hydride salts on the burning rates of nitramine gun propellants, the thermal decomposition of RDX has been studied, in the presence and absence of added $K_2B_{12}H_{12}$, by two methods: 1) The samples are decomposed in an adapter attached to the inlet of a gas chromatograph, and the less-volatile products are examined by gas chromatography–mass spectrometry (GCMS). 2) The decomposition is quenched short of completion, and the nonvolatile residue is analyzed by high-pressure liquid chromatography. The pyrolysis-GCMS studies resulted in the chromatographic detection of the mechanistically significant 1,3,5-triazine as a product of RDX thermal decomposition; they also indicated that added $K_2B_{12}H_{12}$ changes the product distribution obtained from RDX decomposition. The residue-analysis studies confirmed the formation of MRDX and related nitrosoamines in RDX decomposition and also produced evidence for chemical acceleration, by added $K_2B_{12}H_{12}$, of the thermal decomposition of RDX. Some possible mechanisms for formation and breakdown of 1,3,5-triazine during RDX thermal decomposition are discussed.

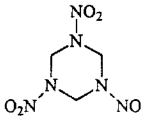
Introduction

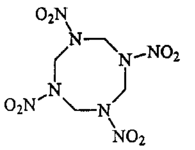
BORON hydrides, especially certain alkali-metal and ammonium salts of the $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ anions, have been of interest[1–10] for a number of years as burning rate accelerants for nitramine propellants in applications requiring propellants with very high burning rates (see previous work cited in Ref. 8 and especially pages 1914 and 1915 in Ref. 10). The work described here is intended to elucidate the chemical mechanisms responsible for the burning rate acceleration, with the ultimate goal of optimizing propellant formulations for maximum burning rate and minimum sensitivity. It might seem that thermal effects might be important here because reaction of the borohydride salt with nitro-group-containing oxidizing agents to form oxides or nitrides of boron would be an exothermic reaction. However, this factor is apparently not too important because thermochemical calculations using the BLAKE code indicate that calculated impetus and flame temperature both decrease with increasing boron hydride salt content.[9] Possibly, this is due to reaction of B_2O_3 with the radicals O, H, and OH, and with H_2O, that are present in the reaction zone.[10]

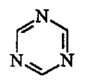
Two approaches were employed in the work described here. The first approach involved partial decomposition of pure RDX and of mixtures of RDX with $K_2B_{12}H_{12}$ followed by high-pressure liquid chromatographic (HPLC) and spectroscopic analysis of the remaining solids. The second approach involved pyroprobe decomposition of similar mixtures, followed by gas chromatographic–mass spectroscopic (GCMS) analysis of the pyrolysis products.

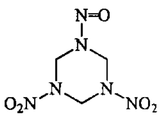
The present paper describes our experimental studies, whereas a previous paper[11] includes a review of the available literature on decomposition of alkali-metal salts of the $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ anions, both alone and in mixtures with HMX and RDX, as well as discussion of possible chemical mechanisms that may be associated with acceleration of decomposition and combustion by these additives. The thermal decomposition of pure HMX and of pure RDX has been previously reviewed.[12–21] In general, it is well known[12–21] that the thermal decomposition of HMX and RDX gives about 80 ± 10% recovery of the highly volatile and permanently gaseous products, such as H_2O, CO, CH_2O, NO, N_2O, etc. In the present work, we concentrated mainly on the less-volatile products, namely, those whose volatilities are intermediate between those of the more commonly studied permanently gaseous products on the one hand and that of unreacted RDX on the other.

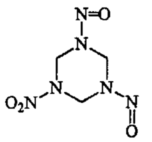
The structures of HMX and of RDX, as well as those of some other compounds mentioned in this paper, are as follows:

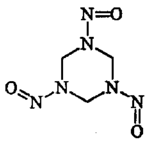

RDX


HMX


1,3,5-triazine


MRDX


DRDX


TRDX

Experimental

Starting Materials

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) was obtained by recrystallizing class A military grade RDX from reagent-grade acetone. HPLC analysis of the recrystallized material showed no noticeable impurities except octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), the amount of which had been reduced from 5–10% to ≤0.3%.

RDX for the residue-analysis runs was obtained in this way. The resulting material consisted of fine crystals that were either used directly or mixed before use with 29% by weight of borohydride. The residue-analysis runs were carried out on RDX from the same recrystallization batch, so that particle size effects should have been similar for all runs. The overall validity of the residue-analysis data (Table 1) is supported by its internal consistency, for example, longer reaction times or higher reaction temperatures led to greater extent of reaction (less RDX remaining and/or more hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine [mononitroso-RDX (MRDX)]). A different procedure was used in making up samples for the GCMS runs. These samples were made from RDX recrystallized from acetone as described earlier, but in an attempt to minimize particle size effects, a portion of RDX was ground in a mortar for several minutes and divided into two portions: One was mixed with the $K_2B_{12}H_{12}$,

---

Received 13 March 1996; revision received 17 March 1999; accepted for publication 28 July 2000.

*Research Chemist, Propulsion Science Branch.

Table 1 Representative pyroprobe/HPLC data: RDX and MRDX decomposition with and without borohydride catalyst

System	Heat rate, °C/min	Temperature, °C	Hold, min	Sample, mg	Residue, mg	Products, mg			Recovery,[a] %
						RDX	MRDX	DRDX	
RDX	300	215	0.1	15.2	15.0	13.5	0.05	——[b]	91
RDX	300	215	1.0	10.7	0.55	0.007	——[c]	——[c]	97
RDX	120	215	0.5	12.7	0.86	——[c]	——[b]	——[b]	74
RDX	300	210	0.1	6.58	6.51	8.8	0.01	——[b]	135
RDX	300	205	0.1	5.63	5.52	4.76	——[c]	——[b]	78
RDX + K[d]	300	205	0.1	4.20	1.90	0.26	0.08	0.02	89

[a] Assuming 5% of the weight of RDX and all of the $K_2B_{12}H_{12}$ weight showed up as nonvolatile residue. [b] Not detected.
[c] Peak shows in chromatogram but was too small to register on integrator. [d] By weight, 29% $K_2B_{12}H_{12}$.

and the other was used in the runs carried out without accelerant. The average particle size was found to be about 100 μm by using a standard set of sieves.

A reference sample of HMX was used as received. A sample of $K_2B_{12}H_{12}$ was obtained from Callery Chemical Company, Callery, Pennsylvania. Unless otherwise specified, all solvents were HPLC grade. Samples of hexahydro-1,3,5-trinitroso-1,3,5-triazine [trinitroso-RDX (TRDX)] were furnished by J. C. Hoffsommer, Naval Surface Warfare Center, and by T. B. Brill, University of Delaware, and a sample of MRDX was also furnished by T. B. Brill. Note that nitrosoamines such as MRDX, DRDX, and TRDX, containing α-hydrogen atoms, are potent carcinogens and require special care in handling.

Pyrolysis-Residue Analysis Studies

For the residue-analysis experiments, the system included a Chemical Data System (CDS) Model 123 Pyroprobe pyrolysis system, including a Model 122 programmable Pyroprobe pyrolyzer interfaced to a CDS model 320 sample concentrator. The thermal desorption chamber of the 320 concentrator acted as a chemical reactor. The RDX sample was heated in a glass capillary tube using the microprocessor-programmed time/temperature controller. Sample size was 3–15 mg, and quartz-wool plugs contained the material during decomposition but allowed a flow of helium over the sample surface. In the final selected series of runs reported here, the sample was heated by the platinum coil probe, operating in pulse-heating mode; pulse heating to about 215°C was used to maximize the amount of nonvolatile residue. Separate calibration experiments were carried out to relate the pyroprobe digital-set temperatures to those actually experienced by the sample. A sample of purified RDX was heated in the quartz tube at 300°C/min to successively increasing set temperatures and held for 0.3–1.0 min. Sample melting was first observed for samples heated to set temperatures of 215–220°C, indicating that the sample temperature was about 15°C lower than the pyroprobe control setting. This corrected value is reflected in the decomposition temperatures given in Table 1.

HPLC Analysis of Residues

The residues from the nitrosoamine analysis runs were analyzed using Perkin-Elmer (PE) Series 4 HPLC equipment, with a liquid chromatography (LC)-85 variable wavelength detector set at 220 nm, an LC autocontroller, and a PE 3600 data station running PE CHROM 2 software. Residues were dissolved in a known volume of acetone, and 5-μl aliquots were injected onto a PE C18 column (2.1 mm × 25 cm) using a 3:1 water-methanol mobile phase.

Infrared Analysis

HPLC runs were carried out with large injections (20–40 μl). Samples corresponding to the peaks in the chromatogram were collected using a Gilson Model 201 programmable fraction collector. For selected fractions, solvent was evaporated under a stream of nitrogen and the residues were dissolved in chloroform and deposited onto a KBr matrix for identification by diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy. Infrared (IR) spectra were obtained using a Barnes DRIFT accessory in the sample compartment of a Digilab Fourier transform IR spectrometer. Spectra were obtained corresponding to each of the HPLC peaks from the nonvolatile residue from RDX decomposition. Spectral identification was accomplished by performing the same HPLC-DRIFT analysis on reference samples of RDX, MRDX (initially containing some hexalydro-1-nitro-3,5-dinitroso-1,3,5-triazine [dinitroso-RDX(DRDX)]), and TRDX, so that component identification was based on both spectral matching and retention time.

GCMS Studies on the Less-Volatile Products

The GCMS experiments on the less-volatile products were carried out using a Hewlett-Packard (HP) Model 5890 gas chromatograph, with an HP 5970 mass-selective detector and a 59970B workstation consisting of a 9133 disk drive, 9100-236 computer, and associated software, including library-search software and a library (National Bureau of Standards) of about 38,000 spectra. The software is capable of producing complete spectra at any point, as well as total ion chromatograms (plots of total ion intensity vs time) or ion chromatograms (plots of intensity vs time for any particular ion or group of ions). Pyrolyses were carried out with a CDS Pyroprobe pyrolyzer with coil probe, which was fitted to the injection port of the gas chromatograph (GC) by means of a heated interface, which was also obtained from CDS. Temperatures given are pyroprobe set temperatures; these represent temperatures reached by the isolated coil under ideal conditions. The temperatures actually reached by the sample are believed to be somewhat lower (at the higher temperatures, possibly as much as 100–200°C).

It was noted that in most of these pyrolysis-GCMS runs, some residual undecomposed RDX escaped from the pyprolyzer and appeared in the GCMS chromatogram. Presumably this residual RDX arose because some of the sample vaporized without decomposition; this often happens in RDX decomposition experiments.[20] Some of the sample could vaporize as the sample is heated, before it reaches the final temperature; however, even at the final temperature, it would not seem surprising if the sample partitioned itself between decomposition and vaporization.

In a typical run, an unweighed sample (approximately 1 mg) was retained in a quartz tube 25 mm long × 2 mm i.d. with a small plug of quartz-wool on each side. The sample was pyrolyzed by heating the probe to the desired temperature at the fastest possible heating rate (approximately 75°C/ms) and holding it there for 20 s. A split inlet was used on the GC, split ratio approximately 30. The GC carrier gas was helium, with a flow rate through the column of approximately 0.5 ml/min. Total flow was 40–45 ml/min, and the inlet purge flow was approximately 6 ml/min. An HP-1 GC column was used (cross-linked methyl silicone gum, 12 m long, 0.2 mm i.d., 0.3-μm film thickness). The temperature program was as follows: initial temperature 70°C, held for 3 min followed by heating at 20°C/min to 210°C, then a final 5-min hold time.

Results and Discussion

The results of this study are summarized in Tables 1–5 and Fig. 1.

Pyroprobe-Residue-Analysis Studies

RDX was pyrolyzed at temperatures between 205 and 215°C in a quartz tube using a pyroprobe pyrolyzer. The solid residue was first analyzed by HPLC; after combining and evaporating effluent from several runs, comparison of the DRIFT spectra of the components with IR spectra from the literature[22,23] allowed identification of unreacted RDX and of MRDX. A third component is believed to be DRDX, based on its mode of formation (from RDX decomposition, sequential to MRDX) and retention time (Table 2) [identical to that of the second component in the MRDX sample from Brill (following paragraph)]. These nitrosoamines have previously been detected among the products of RDX decomposition.[14,16,20,24–29]

As mentioned, a sample of MRDX was furnished by T. B. Brill. HPLC indicated that, in addition to MRDX (identified by comparison of its IR spectrum with that in the literature),[22] this material also contained about 30% of a material believed, on the basis of its DRIFT spectrum (similar to that of MRDX except for greater relative intensity of the nitrosamine[23] peak at 1490–1500 cm^{-1}), to be DRDX. These IR spectra were obtained, as already described, by the DRIFT technique after recovering and evaporating HPLC fractions.

Further pyroprobe decompositions were then carried out, on pure RDX and on RDX–$K_2B_{12}H_{12}$ mixtures, using very short reaction times to stop the decomposition short of completion; the solid remaining was then analyzed by HPLC. Retention times and response factors are given in Table 4, and the analyses from typical runs, together with residue weights and the weights and compositions of the RDX or RDX–$K_2B_{12}H_{12}$ mixture initially present, are given in Table 1. No attempt was made to characterize the residue.

The following trends emerge from Table 1. 1) $K_2B_{12}H_{12}$ appears to accelerate the decomposition of RDX because a typical run with it present (line 6) shows much more depletion of RDX and formation of MRDX and DRDX than do typical runs on pure RDX under similar conditions (lines 1, 4, and 5). 2) Almost all of the weight of the $K_2B_{12}H_{12}$ remains behind in the solid residue. This follows from the fact that approximately 100 ± 35% recovery is obtained when residue weight is estimated by adding the following: 1) the measured weight of any $K_2B_{12}H_{12}$ initially present to 2) the weight found for MRDX, DRDX, and remaining RDX, and 3) 5% of the weight of the starting RDX (estimated weight of the organic residue from RDX decomposition),[20] regardless of whether $K_2B_{12}H_{12}$ was present in the run in question.

Note that the experiments summarized in Table 1 involved several weighings to get the tare weight of the quartz tube, weight of initial sample, and weight of material remaining after the experiment; these weighings were followed by HPLC-UV analysis of the material remaining. During these operations, uncertainties added up; presumably, this accounts for the scatter in the last column of Table 1 (100 ± 30% recovery) and for some small inconsistencies in the results. However, we feel that the important thing is the internal consistency of the data in Table 1, for example, longer reaction times or higher reaction temperatures led to greater extent of reaction (less RDX remaining and/or more MRDX and DRDX formed).

Pyroprobe–GCMS Studies

Pure RDX as well as mixtures of RDX with 19% of added $K_2B_{12}H_{12}$ were decomposed in a pyroprobe at set temperatures of

Table 2 HPLC data: response factors × 10^3 (mg/ml) for RDX and nitrosoamines

Compound	Retention time, min	Area	Height	Relative response Area	Relative response Height
RDX	7.2	82.7	3.84	1.00	1.00
MRDX	6.1	90.9	5.43	1.10	1.41
DRDX	4.9	99.9	7.21	1.21	1.88
TRDX	3.9	128.0	12.7	1.55	3.31

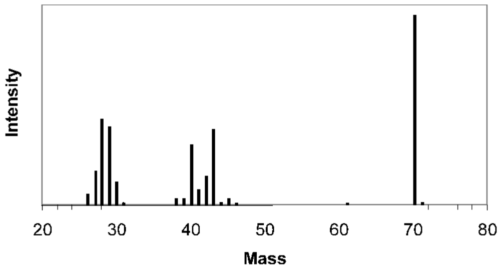


Fig. 1 Mass spectrum of unknown A.

Table 3 Peaks in total ion chromatograms from RDX and RDX-$K_2B_{12}H_{12}$ decompositions

Time, min	Occurrence	Remarks[a]
Approximately 0–1	All conditions	Includes permanent gases (N_2O, CO_2), 1,3,5-triazine and a peak (unknown A) with highest mass at m/e 70 (1,2,4-oxadiazole?) (Fig. 1)
Approximately 1–2.5	All conditions	Especially at low temperatures, this region difficult to characterize; sometimes includes broad, variable peaks whose spectra resemble that of formamide.
1.7 ± 0.2	All conditions	Appears under all conditions. Looks like a mixture. A: Most intense = 99. B: Most intense = 73. Is B HC(=0)NHC(=)H?
2.1	High-T catalyzed	m/e 53, 40, 45, 79, 44, 52, 43, 51, 80, and 39. Sometimes present at high temperature, from decomposition with added $K_2B_{12}H_{12}$.
3.3	Low-T uncatalyzed	Is this mostly 1,3,5-triazine N-oxide (m/e 97, 98, 81, 70, 54)? Sometimes appeared at low (250°C) temperature for RDX alone; not seen at higher temperatures or with added $K_2B_{12}H_{12}$.
4.6	Low-T uncatalyzed	m/e 44, 85, 43, 42, 45, 55, 41, 40, 113, 54, and 58. From decomposition at low (250, 400°C) temperature, without added $K_2B_{12}H_{12}$.
3.0 ± 0.4	All conditions	Present under all conditions, especially at high temperature with added $K_2B_{12}H_{12}$. Looks like a mixture. A: Most intense = 108/109. B: Most intense = 96.
4.9	Low-T uncatalyzed	m/e 96, 42, 43, 44, 45, 69, 68, 40, 41, 53, and 97. From some decomposition runs at low (250, 400°C) temperature, without added $K_2B_{12}H_{12}$.
Approximately 5–7	All	This region included a number of weak peaks, especially from decomposition at low (250, 400°C) temperature, with added $K_2B_{12}H_{12}$.
7.6 ± 0.1	Catalyzed; low-T uncatalyzed	m/e 42, 44, 41, 43, 45, 40, 46, 100, 58, 67, 100, 110, 114, 149, and 177 also sometimes present. Not reproducible. Usually highest mass = 100, sometimes 110, 114, 149, or 177. Not seen for RDX alone at high temperature.
8.2	Catalyzed	m/e 71, 44, 43, 42, 41, 45, 40, 149, 55, and 81. Largest mass is 143. Sometimes occurred, especially in presence of $K_2B_{12}H_{12}$.
8.6 ± 0.1	Catalyzed; low-T uncatalyzed	m/e 42, 44, 41, 43, 46, 40, 45, 58, 56,and 54. Largest mass is 116. Not seen for RDX alone at high temperature.
9.20 ± 0.2	All conditions	Occurred under most conditions, even weakly at high (800°C) temperature. Has m/e 132; is this MRDX or DRDX?
9.40 ± 0.1	All conditions	Occurred under most conditions, even weakly at high (800°C) temperature. Has m/e 132; is this MRDX or DRDX?
9.90 ± 0.2	All conditions	Unreacted RDX; always present regardless of temperature or presence of $K_2B_{12}H_{12}$.
10.5	All conditions	m/e 44, 42, 43, 73, 55, 45, 57, 60, 46, 69, 71, 139, and 256. Often present regardless of temperature or presence of borohydride.

[a] Peaks of m/e listed in order of decreasing intensity.

Table 4 Some area ratios of mass-spectral peaks in the weakly retained products, pyroprobe at stated temperature for 20 s

			Area ratios ($\times 10^2$)						
Run	Catalyzed?	Temperature °C	44/Total intensity	54/Total intensity	70/Total intensity	81/Total intensity	54/44	70/44	81/44
46[a]	No	250	53.4	——[c]	7.96	——[c]	——[c]	15.3	——[c]
50[a]	No	250	58.4	7.21	4.80	8.16	12.4	8.39	14.0
58[a]	No	250	52.2	6.96	4.82	7.94	13.3	9.22	15.2
72[b]	No	250	11.9	——[c]	1.23	——[c]	——[c]	10.3	——[c]
60[a]	Yes	250	62.0	7.63	——	8.76	12.3	——	14.1
61[a]	Yes	250	67.7	5.39	2.36	6.28	7.96	3.52	9.28
67[a]	Yes	250	61.6	——[c]	3.71	——[c]	——[c]	6.02	——[c]
74[b]	Yes	250	14.5	1.25	0.789	1.40	8.62	5.43	9.65
78[b]	Yes	250	15.2	0.830[d]	0.579	0.891[d]	5.48[d]	3.82	5.88[d]
49[a]	No	400	52.2	——[c]	10.4	——[c]	——[c]	20.0	——[c]
51[a]	No	400	50.6	——[c]	9.7	——[c]	——[c]	19.5	——[c]
55[a]	No	400	46.7	——[c]	—	——[c]	——[c]	—	——[c]
56[a]	No	400	50.5	8.84	6.6	10.1	17.5	14.3	20.0
71[b]	No	400	9.36	2.02[d]	1.72	2.31[d]	21.6[d]	18.3	24.6[d]
63[a]	Yes	400	63.7	——[c]	2.65	——[c]	——[c]	4.48	——[c]
66[a]	Yes	400	61.0	——[c]	3.82	——[c]	——[c]	6.27	——[c]
75[b]	Yes	400	10.4	——[c]	1.25	——[c]	——[c]	12.1	——[c]
52[a]	No	600	42.8	10.6	8.05	11.6	24.8	19.3	27.1
57[a]	No	600	39.8	11.7	5.47	12.6	29.8	13.9	31.6
70[b]	No	600	7.03	2.19	0.26	2.45	31.2	3.69	39.8
64[a]	Yes	600	53.6	9.90	4.03	11.3	18.5	7.56	21.1
68[a]	Yes	600	49.2	9.24	4.02	10.5	18.8	8.16	21.3
76[b]	Yes	600	9.13	0.872[d]	1.23	0.927[d]	9.54[d]	13.4	10.2[d]
53[a]	No	800	47.0	9.67	1.06	10.7	20.5	2.30	22.6
54[a]	No	800	46.2	8.46	1.08	9.53	18.3	2.35	20.6
59[a]	No	800	56.6	4.06	0.835	4.80	7.18	1.48	8.47
69[b]	No	800	9.69	1.45	0.34	1.62	15.0	3.50	16.8
73[b]	No	800	9.80	1.41	0.34	1.57	14.4	3.47	16.0
62[a]	Yes	800	58.2	7.17	2.38	7.81	12.3	4.13	13.4
65[a]	Yes	800	55.9	7.77	2.30	8.68	13.9	4.00	15.5
77[b]	Yes	800	8.01	0.770	0.580	0.832	9.61	7.23	10.4

[a]Masses 35–400 scanned. [b]Masses 3–400 scanned. [c]Complex (two or more clear peaks). [d]Slight complexity (shoulder or small second peak).

Table 5 Effect of alternating catalyzed and uncatalyzed runs on areas and area ratios of some mass-spectral peaks in the weakly retained products

			Area ratios ($\times 10^2$)						
Run	Catalyzed?	Temperature, °C	44/Total intensity	54/Total intensity	70/Total intensity	81/Total intensity	54/44	70/44	81/44
31[a]	Yes	600	81.6	——	——	——	——	——	——
32[a]	No	600	56.8	8.4	6.51	10.0	15.0	11.5	18.0
33[a]	Yes	600	74.5	3.3	1.36	4.3	4.4	1.82	5.8
34[a]	No	600	55.1	7.51	3.92	8.9	13.6	7.12	16.0
35[a]	Yes	600	60.3	5.5	3.11	6.4	9.1	5.16	11.0
43[a]	Yes	600	42.8	8.66	4.40	9.19	20.2	10.29	21.0
44[a]	No	600	37.8	10.1	4.77	11.2	26.7	12.61	30.0
45[a]	Yes	600	45.8	9.0[e]	4.86	9.6[e]	19.7[e]	10.6	20.9[e]
23[a,b]	Yes	250	58.9	——[f]	5.53	——[f]	——[f]	9.39	——[f]
25[a,c]	No	250	59.4	——[f]	5.89	——[f]	——[f]	9.91	——[f]
27[a,d]	Yes	250	64.1	——[f]	4.26	——[f]	——[f]	6.64	——[f]
29[a,b]	No	250	53.4	——[f]	6.94	——[f]	——[f]	12.99	——[f]

[a]Masses 35–400 scanned. [b]Fresh tube. [c]Tube used for run 23, probably contained $K_2B_{12}H_{12}$ residue. [d]Tube used for runs 23–25. [e]Slight complexity (shoulder or small second peak). [f]Complex (two or more clear peaks).

250, 400, 600, and 800°C, and the effluent gases and other products were analyzed by GCMS as described in the experimental section. Because the permanent gases, which all emerged in one peak at the beginning of the chromatogram, have been studied by a number or authors,[12–15,20] the emphasis in the present work was on the less volatile products.

Typical total ion chromatograms from decomposition of pure RDX, and those from decomposition of RDX-$K_2B_{12}H_{12}$ mixtures, are given by Schroeder.[25] The peaks in these chromatograms are summarized in Table 3, along with some comments as to mass spectra and as to possible identities of the compounds responsible for the peaks. Actual spectra for most of these peaks are reproduced in an earlier report.[25]

In the chromatograms from all runs, the initial and by far the largest peak, retention time approximately 0.5 min, was due to the gaseous products (N_2O, H_2CO, NO, N_2, CO_2, CO, etc.) of RDX decomposition. Also, in all runs, one of the most strongly retained peaks, retention time approximately 10 min, was identified by library searches as unreacted RDX. The peaks immediately before this, at 9.1 and 9.4 min, are believed, on the basis of their mass spectra, to be the nitrosoamines MRDX and possibly DRDX. These nitrosoamines have been detected among the products of RDX decomposition.[16,20,24,26–29]

One intermediate peak, with a retention time of approximately 0.6 min, was identified as 1,3,5-triazine, by its mass spectrum and retention time. Its mass spectrum was in agreement with literature mass spectra[30–32] of 1,3,5-triazine but disagreed with spectra for 1,2,3-triazine[33] or 1,2,4-triazine.[19] As far as we are aware, this represents the first chromatographic detection and identification of 1,3,5-triazine among RDX decomposition products. Previously, 1,3,5-triazine has been detected[34] as a major product in gas-phase RDX decomposition by IR multiphoton dissociation; this is a sort of simulated thermal decomposition in which the vibrational modes are excited by IR radiation rather than by heat. In addition, 1,3,5-triazine has recently been detected[35] by mass spectrometry among the vaporized products from laser pyrolysis of RDX. Note that 1,3,5-triazine appears to be formed in amounts of approximately 1–5%. This is estimated from the ratios 54/total intensity and 81/total intensity in Table 4, from the runs in which all masses (3–400) were scanned; this seems reasonable because the total intensity includes all of the 80–90%-recovery gaseous products.

Another interesting peak (unknown A) had its highest mass at m/e 70, and the intensity ratios of its M and M + 1 peaks were consistent[36] with a molecular formula of $C_2H_2N_2O$. The spectrum corresponding to this peak is shown in Fig. 1; possibly, this is the same as the m/e 70 product detected earlier[37] from pyrolysis–mass spectrometric and from flow-reactor–mass spectrometric studies on HMX decomposition, whose mass spectrum was stated to have been similar to that of a known spectrum of 1,2,4-oxadiazole. Other possible structures for this compound include N-cyanoformamide and C-cyanoformamide.

It can be seen from Table 3 and from the ion chromatograms given in a preliminary report on this work[25] that there is a noticeable effect of added $K_2B_{12}H_{12}$ on pyrolysis–GCMS product distributions from RDX decomposition; addition of $K_2B_{12}H_{12}$ causes an increase in the number of products detected, whereas an increase in temperature causes a decrease in the number of products detected.

To evaluate the effect of temperature and of $K_2B_{12}H_{12}$ on formation of 1,3,5-triazine and of unknown A, the intensities of the m/e 54 and 81 (triazine) and of the m/e 70 peak (unknown A) were normalized against the total intensity of the permanent-gas peak and of its m/e 44 component (Tables 4 and 5). Added $K_2B_{12}H_{12}$ appears to decrease formation of triazine, whereas increasing temperature increases its formation except at the highest temperature setting used (800°C). Added $K_2B_{12}H_{12}$ causes a decrease in formation of unknown A at the lower temperatures; however, at the higher temperatures, this decrease actually turns into an increase. This seems significant because it may suggest a change in acceleration mechanism with temperature.

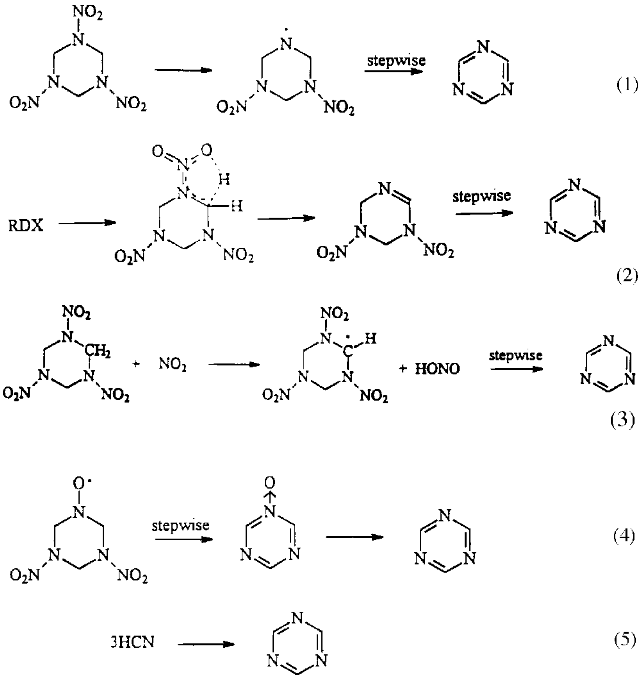
Discussion of Chemical Mechanisms

Possible chemical mechanisms that may be involved in acceleration of HMX and RDX decomposition and combustion by $K_2B_{12}H_{12}$ have been discussed in a previous paper.[11] The discussion that follows is concerned primarily with the possible chemical mechanisms for formation of 1,3,5-triazine in thermal decomposition of RDX.

The goal of the present work is to understand the chemical mechanisms involved in borohydride catalysis of nitramine decomposition. To accomplish this, it will, of course, be necessary to understand the thermal decomposition of uncatalyzed nitramines as a baseline for our understanding of the borohydride-catalyzed decomposition and combustion of these materials. There is a large amount of work in this area, especially for HMX and RDX. This work has been reviewed,[12–21] and the subsequent work[22,24,34,35,37–39] referred to in the present paper is only a fraction of the work done since these reviews. The accelerated decomposition of these nitramines is as yet not well understood, and still more work is needed.

The identification in the present work of 1,3,5-triazine seems of considerable interest because of its potential mechanistic significance with regard to RDX decomposition. This significance arises because its presence indicates the occurrence of pathways not involving initial C–N cleavage; however, these pathways could involve initial N–NO_2 cleavage, HONO elimination, or hydrogen abstraction by NO_2 or other radical species formed in the decomposition of RDX. Followup steps leading to triazine formation involve various combinations of HONO elimination, C–H cleavage, and N–NO_2 cleavage; these steps are expected to be accelerated by adjacent double bonds or radical centers formed in preceding steps.

Possible mechanisms for formation of 1,3,5-triazine include 1) formation via primary N–NO_2 cleavage with loss of NO_2 [reaction (1)], 2) formation via primary HONO elimination [reaction (2)], 3) formation via initial abstraction of a hydrogen atom by NO_2 or some other radical species formed in the decomposition [reaction (3)], 4) formation via the nitroxide reported[38,39] on the basis of electron spin resonance studies [reaction (4)], and 5) trimerization of HCN formed in the decomposition of RDX [reaction (5)].



Formation of 1,3,5-triazine by trimerization of HCN [(reaction (5)] seems relatively unlikely because trimerization of nitriles closely related to HCN, such as CH_3CN, appears[40] to require not only elevated temperatures but pressures in the range of 8–10 kbars and reaction times of hours (as opposed to 20 s at atmospheric pressure in the present work).[40] HCN itself trimerizes under milder conditions, but acid catalysis is apparently required.[40] Note, however, that some acid products such as HONO and HNO_3 can be formed in HMX and RDX decomposition.[20] Thus, although HCN trimerization seems unlikely, it is difficult to rule it out conclusively except by scrambling studies on thermal decomposition of mixtures of fully ring-labeled and unlabeled RDX.

The following observations suggest, by analogy, that the 1,3,5-triazine detected in this work was formed directly from the starting RDX, without disruption of its six-membered ring system. 1) Zhao et al.[34] have detected 1,3,5-triazine among the products of the IR multiphoton dissociation of RDX in a molecular beam. This 1,3,5-triazine presumably was formed from RDX without disruption of the ring structure because it seems most unlikely that HCN could have trimerized to 1,3,5-triazine under the high-vacuum conditions of this experiment. 2) A species identified as a 1,3,5-triazine oxide has been detected[26–29,41–43] among the products of RDX decomposition by simultaneous thermogravimetry modulated beam mass spectrometry[26–29] and pyrolysis–atmospheric pressure chemical ionization mass spectrometry,[41–43] and by isotope scrambling studies, it was indicated that the triazine oxide was formed with retention of the original ring structure from the RDX.[26]

The chromatographic detection of 1,3,5-triazine among the thermal decomposition products of RDX seems relevant to our understanding of RDX decomposition and flame chemistry. First, even from the viewpoint of RDX thermal decomposition chemistry, the chromatographic detection of 1,3,5-triazine, generated in situ by thermal decomposition of RDX, is an interesting complement to its detection in the multiphoton-decomposition experiments of Zhao et al.[34]

Also, it has been reported,[44] in studies of laser-assisted combustion of RDX, that a peak at m/e 81 was detected, by mass spectrometric means, near the surface during laser-induced decomposition of RDX. Our chromatographic detection of 1,3,5-triazine among the thermal decomposition products of RDX indicates that this peak is most likely the molecular ion of 1,3,5-triazine formed by thermal decomposition of RDX in the flame zone.

In addition, it has been suggested, in a very recent paper,[45] that mechanisms involving 1,3,5-triazine and analogous aromatic compounds were involved in the thermal decomposition, at pressures up to 1.2 GPa, of RDX as well as of a number of related compounds, including TRDX, 1,3,3,5,5-pentanitropiperidine, hexahydro-5-methyl-1,3,5-trinitropyrimidine, and hexahydro-1,3,5,5-tetranitropyrimidine. This was based on negative activation volumes, detection of the expected aromatic products in some cases (but not 1,3,5-triazine from RDX), and comparison of decomposition temperatures and order of thermal stability between compounds that have and those that do not have six-membered rings that could lead to aromatic compounds analogous to 1,3,5-triazine. It does not seem unreasonable to suppose that these aromatic compounds were formed stepwise as in reaction (2), with each successive HONO elimination involving the same molecule proceeding faster than the preceding one(s) involving that molecule because of resonance of the forming C=N double bond with the double bond(s) already present as a result of previous HONO eliminations involving the same molecule.

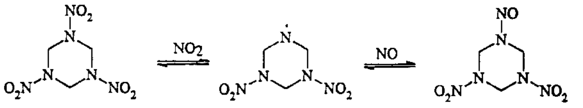
Furthermore, it would seem that even the detection of 1,3,5-triazine in slow-heating-rate experiments would warrant its inclusion in reaction mechanisms assumed for modeling purposes; activation energies and frequency factors for the reactions involved in its formation and decomposition would be estimated and used to derive its concentration profiles under combustion conditions.

Possible pathways for formation of 1,3,5-triazine have been discussed and are illustrated by reactions (1–5). As already discussed, reactions (1–4), involving formation of 1,3,5-triazine from RDX with the original ring structure intact, seem most likely. However, without scrambling studies, it is difficult to rule out with absolute certainty formation of 1,3,5-triazine by trimerization of HCN formed from decomposition of RDX.

One possible pathway for the disappearance of 1,3,5-triazine under thermal decomposition or combustion conditions might involve hydrolysis by water (also produced[20] in the decomposition of RDX), with formation of formic acid[46,47] and possibly formamide.[48] In accord with this, 1,3,5-triazine is reported to be extremely susceptible to hydrolysis, even in neutral distilled water; the products are formic acid and ammonia,[46,47] both of which have been detected among the products of RDX decomposition,[49] although their formation was attributed to hydrolysis of hydroxymethylformamide and related compounds and polymers. Under combustion conditions, a more likely pathway for disappearance of 1,3,5-triazine would probably involve pyrolysis. It is sometimes stated that 1,3,5-triazine decomposes thermally at 600°C to give three molecules of HCN, but we have been unable to identify or locate the original reference describing this experiment. However, this general picture makes a great deal of sense, in view of the following. 1) Thermal decomposition[50] of 1,3,5-triazine and several other nitrogen-containing aromatics on Pt(111) results in desorption products of H_2, HCN, and C_2N_2. 2) Following $S_1 \leftarrow S_2$ or 248-nm excitation, s-tetrazine reverts[51] to a highly vibrationally excited ground electronic state, which then decomposes to $2HCN + N_2$ via concerted triple dissociation. 3) In a molecular beam, 1,3,5-triazine can be photodissociated into three HCN molecules at 248 and 193 nm.[52] 4) Calculations using both ab initio and nonlocal density functional theory[53,54] are in agreement with the idea that 1,3,5-triazine can decompose by a concerted triple dissociation reaction in which the triazine ring dissociates in one step to form three molecules of HCN.

Our chromatographic detection, from partially thermally decomposed samples of RDX, of the nitrosoamines MRDX and DRDX is important to our understanding of combustion because these compounds are actually involved in combustion of RDX and of RDX-containing solid propellants; we have detected them by HPLC analysis of the scrapings from the burned surfaces of burned/quenched samples of RDX and of XM39 propellant.[55] Our detection of these compounds from decomposition of pure RDX is complementary to the work of Hoffsommer and Glover,[24] who followed their appearance and disappearance on decomposition of RDX in solution.

Possible mechanisms for formation of nitrosoamines in RDX decomposition have been discussed previously.[16,20,26–29] These include the following: 1) formation of nitrosoamine by recombination of NO with the nitrogen-centered radical formed by N–NO_2 cleavage [reaction (6)] and 2) abstraction of oxygen from a nitro grouping of RDX by radical species (such as H or NO_2) formed in RDX decomposition.[16,20] Isotope scrambling studies[26] indicate that mechanism 1 is dominant for low-temperature, low-pressure decomposition of RDX, but the bimolecular reaction mechanism 2 should probably also be considered for higher pressure combustion of RDX and HMX:



(6)

After being formed during either combustion or simple thermal decomposition, these nitrosoamines presumably go on to decompose by mechanisms similar to those followed by RDX and HMX themselves.

Finally, it seems worthwhile to mention a very recent report[56] that multivariate regression was employed to remove the IR spectra of the major, gaseous products (NO_2, N_2O, NO, H_2CO, CO, CO_2, etc.) from the IR spectrum of the vapor-phase products resulting from pyrolysis (thin film, 800°C, 4 atm Ar) of RDX. This enabled small amounts of certain minor products to be uncovered; these included MRDX, a triazine derivative modeled as 1,3,5-triazine, C-hydroxy-N-methylformamide, and unreacted RDX. This seems qualitatively in agreement with the present work and with our previous work[55] on chemical analysis of surface layers of burned/quenched propellant samples.

Summary

The thermal decomposition of the nitramine oxidizer RDX, in the presence and in the absence of the burning-rate accelerant $K_2B_{12}H_{12}$, has been studied by two methods. In the first method, the samples were decomposed in an adapter attached to the inlet of a gas chromatograph, and the less-volatile products were examined by GCMS. These pyrolysis-GCMS studies resulted in the chromatographic detection of the mechanistically-significant 1,3,5-triazine as a product of RDX thermal decomposition; they also indicated that added $K_2B_{12}H_{12}$ changes the product distribution obtained from RDX decomposition. In the second series of experiments, the decomposition was quenched short of completion, and the non-volatile residue was analyzed by HPLC. These residue-analysis studies confirmed the formation of MRDX and related nitrosoamines during the thermal decomposition of RDX, and also produced evidence for chemical acceleration, by added $K_2B_{12}H_{12}$, of the thermal decomposition of RDX. Some possible mechanisms for the formation and breakdown of these nirtosoamines and of 1,3,5-triazine during RDX thermal decomposition are discussed.

Acknowledgments

The authors are grateful to J. C. Hoffsommer and to T. B. Brill for furnishing generous TRDX samples. We also thank T. B. Brill for providing an MRDX sample. This paper is Part 2 of a series

entitled "Acceleration of Nitramine Decomposition and Combustion by Boron Hydrides."

References

[1] Juhasz, A. A., "Workshop Report: Boron Hydrides in Very High Burning Rate (VHBR) Applications," *Journal of Energetic Materials*, Vol. 6, Nos. 1–2, 1988, pp. 81–106.

[2] Fifer, R. A., "Workshop Report: Combustion of Very High Burning Rate (VHBR) Propellants," U.S. Army Ballistic Research Lab., AD-A121 668, Aberdeen Proving Ground, MD, Rept. BRL-TR-02441, Nov. 1982.

[3] Fifer, R. A., and McBratney, W. F., "Catalysis of Nitramine Propellants by Metal Borohydrides," U.S. Army Ballistic Research Lab., Rept. BRL-MR-03300, AD-A133 215, Aberdeen Proving Ground, MD, July 1983.

[4] Fisher, E. B., and Hollar, W., "Very High Burning Rate (VHBR) Combustion and Formulation Research," Final Summary Rept. for Period July 1987–Jan. 1988, Contract DAAA15-87-C-0046, Veritay Technology, Inc., East Amherst, NY, Jan. 1988.

[5] Barnes, J. T., Fisher, E. B., Hollar, W., White, K. J., and Juhasz, A. A., "Characterization of the Combustion Behavior of HYCAR-Based VHBR Propellants," *Proceedings of the 25th JANNAF Combustion Meeting*, CPIA Publ. 498, Vol. 2, Chemical Propulsion Information Agency, Laurel, MD, Oct. 1988, pp. 289–302.

[6] Barnes, J. T., and Fisher, E. B., "Combustion Characteristics of VHBR Propellant Formulations," *Proceedings of the 26th JANNAF Combustion Meeting*, CPIA Publ. 529, Vol. 1, Chemical Propulsion Information Agency, Laurel, MD, Oct. 1989, pp. 245–253.

[7] Barnes, J. T., and Fisher, E. B., "Combustion Characteristics of VHBR Propellant Formulations," *Proceedings of the 27th JANNAF Combustion Meeting*, CPIA Publ. 557, Vol. 3, Chemical Propulsion Information Agency, Laurel, MD, Nov. 1990, pp. 1–17.

[8] Salizzoni, R. M., Hsieh, W. H., Peretz, A., and Kuo, K. K., "Some High Pressure Characteristics of VHBR Propellants," *Proceedings of the 26th JANNAF Combustion Meeting*, CPIA Publ. 529, Vol. 1, Chemical Propulsion Information Agency, Laurel, MD, Oct. 1989, pp. 255–265.

[9] Barnes, J. T., and Fisher, E. B., "Combustion Rate of Very High Burn Rate (VHBR) Propellant," Veritay Technology, Inc., U.S. Army Research Lab., CR-242 (AD-A299 478), Sept. 1995, pp. 52–56.

[10] Bauer, S. H., "Oxidation of B, BH, BH$_2$, and B$_m$H$_n$ Species: Thermochemistry and Kinetics," *Chemical Reviews*, Vol. 96, No. 6, pp. 1907–1916.

[11] Schroeder, M. A., "Possible Chemical Mechanisms for Boron Hydride Acceleration of Nitromine Decomposition: Literature Review," *Journal of Propulsion and Power* Vol. 14, No. 6, 1998, pp. 981–990.

[12] Fifer, R. A., "Chemistry of Nitrate Ester and Nitramine Propellants," *Fundamentals of Solid Propellant Combustion*, edited by K. K. Kuo and M. Summerfield, Vol. 90, Progress in Astronautics and Aeronautics, AIAA, New York, 1984, Chap. 4, pp. 177–237.

[13] Boggs, T. L., "The Thermal Behavior of Cyclotrimethylenetrinitramine (RDX) and Cyclotetramethylenetetranitramine (HMX)," *Fundamentals of Solid Propellant Combustion*, edited by K. K. Kuo and M. Summerfield, Vol. 90, Progress in Astronautics and Aeronautics, AIAA, New York, 1984, Chap. 3, pp. 121–176.

[14] Alexander, M. H., Dagdigian, P. J., Jacox, M. E., Kolb, C. E., Melius, C. F., Rabitz, H., Smooke, M. D., and Tsang, W., "Nitramine Propellant Ignition and Combustion Research," *Progress in Energy and Combustion Science*, Vol. 17, No. 4, 1991, pp. 263–296.

[15] Adams, G. F., and Shaw, R. W., Jr., "Chemical Reactions in Energetic Materials," *Annual Reviews of Physical Chemistry*, edited by H. L. Strauss, G. T. Babcock, and S. R. Leone, Vol. 43, Annual Reviews, Inc., Palo Alto, CA, 1992, pp. 311–340.

[16] Schroeder, M. A., "Critical Analysis of Nitramine Decomposition Results: Some Comments on Chemical Mechanisms," *Proceedings of the 16th JANNAF Combustion Meeting*, CPIA Publ. 308, Vol. 2, Chemical Propulsion Information Agency, Laurel, MD, Sept. 1979, pp. 17–34.

[17] Schroeder, M. A., "Critical Analysis of Nitramine Decomposition Data: Some Suggestions for Needed Research Work," U.S. Army Ballistic Research Lab., Rept. BRL-MR-3181, AD-A116 194, Aberdeen Proving Ground, MD, June 1982.

[18] Schroeder, M. A., "Critical Analysis of Nitramine Decomposition Data: Preliminary Comments on Autoacceleration and Autoinhibition in HMX and RDX Decomposition," U.S. Army Ballistic Research Lab., Rept. BRL-MR-03370, AD-A146 570, Aberdeen Proving Ground, MD, Aug. 1984.

[19] Schroeder, M. A., "Critical Analysis of Nitramine Decomposition Data: Activation Energies and Frequency Factors for HMX and RDX Decomposition," U.S. Army Ballistic Research Lab., Rept. BRL-TR-2673, AD-A160 543, Aberdeen Proving Ground, MD, Sept. 1985.

[20] Schroeder, M. A., "Critical Analysis of Nitramine Decomposition Data: Product Distributions From HMX and RDX Decomposition," U.S. Army Ballistic Research Lab., Rept. BRL-TR-2659, AD-A159 325, Aberdeen Proving Ground, MD, June 1985, available from National Technical Information Service, Springfield, VA.

[21] Schroeder, M. A., "Critical Analysis of Nitramine Decomposition Data: Update, Some Comments on Pressure and Temperature Effects, and Wrap-Up Discussion of Chemical Mechanisms," *Proceedings of the 21st JANNAF Combustion Meeting*, CPIA Publ. 412, Vol. 2, Chemical Propulsion Information Agency, Laurel, MD, Oct. 1984, pp. 595–614.

[22] Oyumi, Y., and Brill, T. B., "Thermal Decomposition of Energetic Materials. 5. High-Rate, In Situ, Thermolysis of Two Nitrosoamine Derivatives of RDX by FTIR Spectroscopy," *Combustion and Flame*, Vol. 62, No. 2, 1985, pp. 233–241.

[23] Gordon, A. J., and Ford, R. A., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, Wiley, New York, 1972, p. 194.

[24] Hoffsommer, J. C., and Glover, D. J., "Thermal Decomposition of 1,3,5-Trinitro-1,3,5-Triazacyclohexane (RDX): Kinetics of Nitroso Intermediate Formation," *Combustion and Flame*, Vol. 59, No. 3, 1985, pp. 303–310.

[25] Schroeder, M. A., "Thermal Decomposition of RDX and RDX-Borohydride Mixture," U.S. Army Ballistic Research Lab., Rept. BRL-MR-3699, AD-A199 371, Aberdeen Proving Ground, MD, Sept. 1988.

[26] Behrens, R., Jr., and Bulusu, S., "Thermal Decomposition of Energetic Materials. 4. Deuterium Isotope Effects and Isotopic Scrambling (H/D, ^{13}C/^{18}O,^{14} N/^{15}N) in Condensed-Phase Decomposition of 1,3,5-Trinitrohexahydro-s-triazine," *Journal of Physical Chemistry*, Vol. 96, No. 22, 1992, pp. 8891–8897.

[27] Behrens, R., Jr., and Bulusu, S., "Thermal Decomposition of Energetic Materials. 3. Temporal Behaviors of the Rates of Formation of the Gaseous Pyrolysis Products from Condensed-Phase Decomposition of 1,3,5-Trinitrohexahydro-s-triazine," *Journal of Physical Chemistry*, Vol. 96, No. 22, 1992, pp. 8877–8891.

[28] Behrens, R., Jr., "Thermal Decomposition of Energetic Materials. 2. Deuterium Isotope Effects and Isotopic Scrambling in Condensed-Phase Decomposition of Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine," *Journal of Physical Chemistry*, Vol. 5, No. 15, 1991, pp. 5838–5845.

[29] Behrens, R., Jr., "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," *Journal of Physical Chemistry*, Vol. 94, No. 17, 1990, pp. 6706–6718.

[30] Judson, C. M., Francel, R. J., and Weicksel, J. A., "s-Triazine. IV. The Mass Spectrum," *Journal of Chemical Physics*, Vol. 22, No. 7, 1954, pp. 1258, 1259.

[31] Preston, P. N., Steedman, W., Palmer, M. H., Mackenzie, S. M., and Stevens, M. F. G., "The Mass Spectra of s-Triazines," *Organic Mass Spectrometry*, Vol. 3, No. 7, 1970, pp. 863–874.

[32] Heller, S. R., and Milne, G. W. A., "EPA/NIH Mass Spectral Data Base, Supplement 1, 1980," U.S. Dept. of Commerce, National Bureau of Standards, Washington, DC, Dec. 1980, p. 80.

[33] Itoh, T., Okada, M., Nagata, K., Yamaguchi, K., and Ohsawa, A., "The Ring Transformations of 1,2,3-Triazines," *Chemical and Pharmaceutical Bulletin*, Vol. 38, No. 8, 1990, pp. 2108–2111.

[34] Zhao, X., Hintsa, E. J., and Lee, Y. T., "Infrared Multiphoton Dissociation of RDX in a Molecular Beam," *Journal of Chemical Physics*, Vol. 88, No. 2, 1988, pp. 801–810.

[35] Ostmark, H., Bergman, H., and Ekvall, K., "Laser Pyrolysis of Explosives Combined with Mass Spectral Studies of the Ignition Zone," *Journal of Analytical and Applied Pyrolysis*, Vol. 24, No. 2, 1992, pp. 163–178.

[36] Silverstein, R. M., Bassler, G. C., and Morrill, T. C., "Spectrometric Identification of Organic Compounds," 4th ed., Wiley, New York, 1981, p. 9.

[37] Shackelford, S. A., Coolidge, M. B., Goshgarian, B. B., Loving, B. A., Rogers, R. N., Janney, J. L., and Ebinger, M. H., "Deuterium Isotope Effects in Condensed-Phase Thermochemical Decomposition Reactions of Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine," *Journal of Physical Chemistry*, Vol. 89, No. 14, 1985, pp. 3118–3136.

[38] Pace, M. D., "Thermal Decomposition of RDX: Evidence for a Nitronylnitroxyl Free Radical Intermediate," *Journal of Energetic Materials*, Vol. 3, No. 4, 1985, pp. 279–291.

[39] Pace, M. D., Britt, A. D., Moniz, W. B., and Stec, D., III, "Paramagnetic Decomposition Products from Energetic Materials," *Proceedings of the 8th Symposium (International) on Detonation*, Naval Surface Weapons Center, White Oak Lab., NSWP-MP-86-194 (AD-A247 997), Silver Spring, MD, July 1985, pp. 734–741, available from the National Technical Information Service, Springfield, VA.

[40] Martin, D., Bauer, M., and Pankratov, V. A., "Cyclization of Cyano Compounds Into 1,3,5-Triazines," *Russian Chemical Reviews*, Vol. 47, No. 10, 1978, pp. 975–990.

[41] Snyder, A. P., Kremer, J. H., Liebman, S. A., Schroeder, M. A., and Fifer,

R. A., "Characterization of Cyclotrimethylenetrinitramine (RDX) by N,H Isotope Analyses with Pyrolysis-Atmospheric Pressure Ionization Tandem Mass Spectrometry," *Organic Mass Spectrometry*, Vol. 24, No. 1, 1989, pp. 15–21.

[42] Snyder, A. P., Liebman, S. A., Schroeder, M. A., and Fifer, R. A., "Characterization of Cyclotrimethylenetrinitramine (RDX) by Pyrolysis H_2O/D_2O Atmospheric-Pressure Chemical Ionization Tandem Mass Spectrometry," *Organic Mass Spectrometry*, Vol. 25, No. 1, 1990, pp. 61–66.

[43] Snyder, A. P., Liebman, S. A., Bulusu, S., Schroeder, M. A., and Fifer, R. A., "Characterization of Cyclotetramethylenetetranitramine (HMX) Thermal Degradation by Isotope Analysis with Analytical Pyrolysis-Atmospheric Pressure Ionization Tandem Mass Spectrometry," *Organic Mass Spectrometry*, Vol. 26, No. 12, 1991, pp. 1109–1118.

[44] Litzinger, T. A., Fetherolf, B. L., Lee, Y., and Tang, C.-J., "Study of the Gas-Phase Chemistry of RDX: Experiments and Modeling," *Journal of Propulsion and Power*, Vol. 11, No. 4, 1995, pp. 698–703.

[45] Wang, J., Brower, K. R., and Naud, D. L., "Evidence of an Elimination Mechanism in Thermal Decomposition of Hexahydro–1,3,5–Trinitro–1,3,5–Triazine and Related Compounds Under High Pressure in Solution," *Journal of Organic Chemistry*, Vol. 62, No. 26, 1997, pp. 9055–9060.

[46] Grundmann, C., and Kreutzberger, A., "1,3,5–Triazine," *Journal of the American Chemical Society*, Vol. 76, No. 2, 1954, pp. 632, 633.

[47] Grundmann, C., and Kreutzberger, A., "Triazines. IX. 1,3,5-Triazine and Its Formation from Hydrocyanic Acid," *Journal of the American Chemical Society*, Vol. 76, No. 22, 1954, pp. 5646–5650.

[48] Joule, J. A., and Smith, G. F., "Heterocyclic Chemistry," 2nd ed., Van Nostrand Reinhold, New York, 1978, p. 125.

[49] Cosgrove, J. D., and Owen, A. J., "The Thermal Decomposition of 1,3,5–Hexahydro 1,3,5–Triazine (RDX)-Part I: The Products and Physical Parameters," *Combustion and Flame*, Vol. 22, No. 1, 1974, pp. 13–18.

[50] Kingsley, J. R., and Hemminger, J. C., "Generation of Cyanogen from the Decomposition of Several Nitrogen-Containing Aromatics on Pt(111)," *Langmuir*, Vol. 2, No. 2, 1986, pp. 460–464.

[51] Zhao, X., Miller, W. B., Hintsa, E. J., and Lee, Y. T., "A Concerted Triple Dissociation—The Photochemistry of s–Tetrazine," *Journal of Chemical Physics*, Vol. 90, No. 10, 1989, pp. 5527–5535.

[52] Ondrey, G. S., and Bersohn, R., "Photodissociation Dynamics of 1,3,5–Triazine," *Journal of Chemical Physics*, Vol. 81, No. 10, 1984, pp. 4517–4520.

[53] Pai, S. V., Chabalowski, C. F., and Rice, B. M., "Ab Initio Study of Reactions of sym-Triazine," *Journal of Physical Chemistry*, Vol. 100, No. 14, 1996, pp. 5681–5689.

[54] Pai, S. V., Chabalowski, C. F., and Rice, B. M., "Comparative Study of Nonlocal Density Functional Theory and ab initio Methods: The Potential Energy Surface of sym-Triazine Reactions," *Journal of Physical Chemistry*, Vol. 100, No. 38, 1996, pp. 15368–15382.

[55] Schroeder, M. A., Fifer, R. A., Miller, M. S., Pesce-Rodriguez, R. A., and Singh, G., "Condensed-Phase Processes During Solid-Propellant Combustion. Part II: Chemical and Microscopic Examination of Conductively Quenched Samples of RDX, XM39, JA2, M30, and HMX-Binder Compositions," U.S. Army Ballistic Research Lab., Rept. TR-3337 (AD-A250 799), May 1992.

[56] Gongwer, P. E., and Brill, T. B., "Thermal Decomposition of Energetic Materials 73: The Identity and Temperature Dependence of Minor Products from Flash-Heated RDX," *Combustion and Flame*, Vol. 115, No. 3, 1998, pp. 417–423.