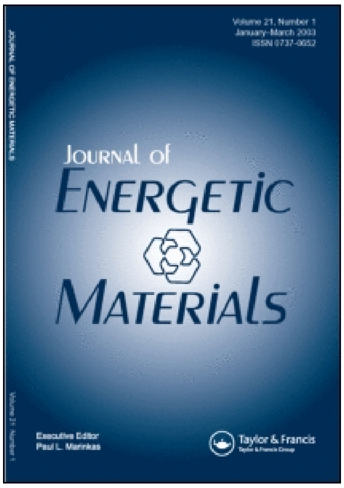

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An investigation of the thermal decomposition of 1,4-butanediammonium dinitrate

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AN INVESTIGATION OF THE THERMAL DECOMPOSITION OF 1,4-BUTANEDIAMMONIUM DINITRATE

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ABSTRACT

This paper describes the investigation of the thermal decomposition of 1,4-butanediammonium dinitrate (BDD). Analytical techniques used for this work were differential scanning and accelerating rate calorimetry, thermogravimetry, tandem gas chromatography/mass spectrometry and high performance liquid chromatography. It was shown that BDD decomposes thermally from the molten state via a multistep process that produces a variety of condensed phase and gaseous products. The nature of the products suggest that a proton transfer

reaction from cation to anion followed by C-N bond rupture occurs early in the decomposition process. The presence of early heterocyclic reaction products demonstrates that one of the reaction mechanisms involves cycloelimination. Later reactions appear to be competitive and may proceed through transient, primary nitramine and nitrosamine species.

INTRODUCTION

Organodiammonium dinitrate salts have been of interest to the explosives community as an ingredient in composite energetic materials for many years.[1] In particular, 1,2-ethanediammonium dinitrate (EDD) was of interest because it forms a low-melting eutectic mixture with ammonium nitrate (AN).[2] While the thermal chemistry of AN has been extensively studied,[3-5] only minimal information is available on organodiammonium dinitrate salts. It is generally concluded that the initial step in the thermal decomposition of AN[6] and simple aliphatic ammonium nitrates, $[RNH_3]NO_3$,[7,8] is predominantly dissociation followed by, or in conjunction with, exothermic decomposition. The initial step in the decomposition process for more complex ammonium nitrate salts, e.g., pentaerythrityltetrammonium tetranitrate (PTTN),[9a] EDD,[9b] and 1,4-butanediammonium dinitrate (BDD)[10] was also found to be similar. The results of early thermolysis experiments with EDD show the decomposition to be autocatalytic. While the reaction residue was not fully characterized, the data suggested that both nitramine- and nitrosamine-containing compounds were formed during the EDD decomposition process.[11]

This paper describes the results of an investigation of the thermal decomposition of BDD that were obtained by using differential scanning calorimetry (DSC), deuterium labeling, thermogravimetric analysis (TGA), tandem gas chromatography/mass spectrometry (GC/MS), high performance liquid chromatography (HPLC), and accelerating rate calorimetry (ARC). Particular attention was paid to the induction period of the isothermal DSC decomposition curve for molten BDD. The induction period is defined as the time elapsed from t=0 at isothermal temperature until the initial deflection of the exothermic acceleratory phase from the horizontal baseline. Gaseous and volatile products have been identified, and degradation steps are postulated to account for their formulation.

EXPERIMENTAL

DSC and TG analyses were performed with a DuPont Instruments 1090 Thermal Analyzer equipped with Models 910 DSC and 951 TGA plug-in modules, respectively, and a Perkin-Elmer DSC-4/Thermal Analysis Data Station System. The ARC technique was developed by the Dow Chemical

Company, and ARC instrumentation is manufactured commercially by Columbia Scientific Industries Corporation. Mass spectra were acquired with a Chemical Data Systems Model 310 Concentrator and a Finnigan Model 4500 GC/MS. Infrared spectra were obtained with Perkin-Elmer Model 683 and Biorad (Digilab Division) Model FTS-50 Infrared Spectrophotometers. TGA and DSC residues were transferred to the GC/MS from a concentrator oven at 155°C with helium flow at 20 cm^3/min. Volatile components were concentrated on a Tenax GC trap and then flash heated to 200°C to effect the transfer to the GC. A 15 meter, 0.53 mm I.D. J & W Scientific DB-1 (methyl silicone coating) fused quartz capillary column, programmed to 180°C at 20°C/min, was used to separate the components. The helium carrier gas was partially removed from the GC effluent prior to reaching the MS by using an in-line jet separator.

ARC samples were heated in specially mounted 0.25-inch I.D. Pyrex glass tubes. Prior to heating, each sample was purged with high purity helium, pressurized to 23 psia and leak-tested to insure that no air was present. The reaction tube was equipped with a 0.25 mm I.D. empty fused quartz capillary tube for gas sampling. Gaseous products were transferred from the ARC to the GC/MS through a 20 meter long, 0.53 mm I.D., capillary column (methyl-silicone coating) attached to a Nutech

Model 320 sample injection valve. Care was taken to insure the absence of impurities and leaks during the transfer.

Anion and cation separations, respectively, were accomplished by using: (i) a Waters Associates Model ILC-1 Chromatograph equipped with an IC-PAK A column and (ii) a Waters Associates Model ILC-2 Chromatograph equipped with IC-PAK C column. Samples were filtered through Waters Associates Sep-Pak C18 cartridges prior to injection into the chromatograph to remove nonionized organic components.

BDD-1,1,4,4-d_4 and BDD-2,2,3,3-d_4 were prepared according to the procedures described elsewhere.[12] These materials were used to help elucidate mass spectral data.

PN was prepared by reacting pyrrolidine (PYR) with concentrated nitric acid in a 1:1 mole ratio in a manner similar to that described by McKenney.[13] The tan product was a viscous oil to semisolid at room temperature; IR (neat) 3000 (vs, br), 1750 (w), 1709 (m), 1613 (m), 1375 (vs, br), 1030 (s), 912 (m), 880 (w), 826 (s), 716 (w) cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.9 (m, 4H), 3.2 (t, 4H), 8.9 (br s, 2H); mass spectrum (70 eV), m/e (relative intensity): (no molecular ion), 71 (9.3), 70 (12.8), 46 (24.9), 43 (100), 42 (17.4), 41 (15.3), 39 (9.8), 30 (19.8), 27 (11.2).

RESULTS

Dynamic TGA Experiment

BDD (20 mg) was heated in a TG analyzer at a rate of 5°C/min. A AgCl disposable IR plate was exposed to the furnace exhaust port effluent during the temperature range 200-215°C. Total weight loss during the exposure period was approximately 40 µg. The spectrum obtained from the material collected on the IR plate contained strong, broad absorption bands at 3100 and 1380 cm^{-1}. Other weak bands were observed at 2410, 1750, 1580, and 830 cm^{-1}. AN exhibits characteristic absorptions at 3125 (s,br), 3020 (sh), 2380 (vw), 1750 (vw), 1360 (vs,br), 830 (w) and 720 (vw) cm^{-1}.

Isothermal TGA Experiment I

BDD (61 mg) was heated at 230°C for 400 min, during which time the sample lost 66% of its original weight. Volatile material was deposited on the cooler portion of the furnace tube that extended beyond the heater; a white solid being collected nearest the heater. The IR spectrum of the solid exhibited absorptions at 3000 (s, br), 2000 (w, d), 1740 (m), 1615 (s), 1590 (sh), 1505 (vw), 1470 (vw), 1345 (vs, br), 1105 (w), 1030 (w), 910 (w), 880 (w), 825 (w), 755 (w) and 720 (w) cm^{-1}. Pure BDD (KBr) exhibits bands at 3010 (s, br), 2010 (w), 1980 (w, br), 1745 (w), 1620 (m), 1590 (sh), 1510 (vw), 1465 (vw), 1350 (vs, br), 1105 (m), 1025 (w), 910 (m), 875 (m), 830 (m), 755 (w) and 725 (w) cm^{-1}. The prominent absorption at 1105 cm^{-1} is characteristic of BDD. The IR spectrum of the brown viscous liquid that was collected beyond the solid showed no evidence of BDD.

Isothermal TGA Experiment II

BDD (28 mg) was heated at 229°C for 840 min, during which time the sample lost 84% of its original weight. A brown viscous effluent was deposited on the furnace tube. The viscous effluent was analyzed by chemical ionization (CI) mass spectrometry using methane (CH_4) as the reagent gas. The GC/MS (CI/CH_4) reconstructed ion chromatogram (RIC) that was obtained for the viscous effluent revealed the presence of four relatively minor products (I, II, III, IV) and one major product (V) (See Figure 1). As an aid to interpretation, spectra were also obtained using (1) CD_4 reagent gas and (2) products from deuterium labeled salts.[12] Products III, IV, and V were identified as being 1,3-dinitratobutane (1,3-DNBu), 1,4-dinitratobutane (1,4-DNBu) and N-nitrosopyrrolidine (PNSA), respectively. Products I and II were not identified. Mass spectral results are summarized in Table 1.

Isothermal Degradation Experiment

BDD (2.0 mg) was heated in a partially evacuated glass bulb at 210°C until the liquid at the bottom of the bulb began to bubble and darken. The volatile materials that emanated from the bulb were transferred to the mass spectrometer. The RIC, shown in Figure 2, is composed of four significant products (III, IV, V and X) and twelve minor products (I, VI, VII, VIII, IX, XI, XII, XIII, XIV, XV, XVI and XVII). The mass spectra (CI/CH_4) associated with compounds I, III, IV and V of Figure 2 are identical to those obtained from the similarly labeled RIC peaks shown in Figure 1.

The EI and CI mass spectral fragment patterns for product X are shown in Tables 2 and 3, respectively. Also included are the predicted fragment patterns for 4-nitrato-1-butene and its expected deuterated analogs.

Minor products for which sufficient mass spectral data to support tentative identification could be obtained are listed in Table 4. The identification of compounds VIII (tetrahydrofuran) and XV (N-nitropyrrolidine), as shown in Figures 3 and 4, respectively, is supported by EI mass spectral data that closely matches that of authentic samples. The mass spectral (CI/CH_4) pattern associated with compound XIV exhibits a base ion at m/e = 101 and ions of low to moderate abundance at m/e = 73, 76 (CH_2NO_3), 87, 118 ($M-NO_3$) and 181 ($M + H$). This suggests yet another dinitratobutane (DNBu) isomer, the most logical choice being the 2,3-isomer.

A summary of the identified condensed phase reaction products from the DSC experiment is shown in Table 5. The remaining nine minor products (I, VI, VII, IX, XI, XII, XIII, XVI and XVII) cannot be characterized sufficiently with the available mass spectral data for tentative identification.

Ion Chromatography Experiment

Several 2.0 mg samples of BDD were sealed in partially evacuated glass bulbs and heated to 190°C. Samples were viewed by using a microscope and were removed from the hot stage at various stages of decomposition as subjectively determined by discoloration. The samples were analyzed within 10 min. after removal. The results of chromatographic analysis are shown in Table 6.

ARC Experiment

BDD, 200 mg, was heated in an ARC reaction vessel at 176-184°C for 266 min. No significant self-heating occurred during this time; hence, this time is considered to be within the induction period. Aliquots of the helium atmosphere above the molten sample were removed at 30 min. intervals and then analyzed by GC/MS. The gases found (N_2, NO, N_2O, CO_2, and H_2O) were all evolved at rates between 0.98 and 2.0×10^{-3} mole/min. Nitrogen dioxide could not be detected reliably from either sample aliquot or standard gas; however, other researchers have verified its presence.[14] The total nitrogen (N) evolved, calculated from the total amounts of N_2, NO, and N_2O evolved during the course of the experiment, was 0.10 percent of the total nitrogen (N) available from BOD.

Another ARC experiment was carried out under conditions similar to those described above. Analysis of the product mixture using GC/MS revealed the presence of ethene, propene, 1,3-butadiene and carbon monoxide, in addition to the products shown above. GC retention times and mass spectral patterns associated with these compounds corresponded with those obtained from authentic samples.

Cumulative Induction Period (DSC) Study

Cumulative thermolysis experiments were carried out with BOD at 190°C in air. The sample was removed from the heat source and quenched on dry ice after a timed fraction of the induction period had occurred. The sample was then reheated to 190°C and held until the end of the induction period. This experiment was repeated two more times. The average of the combined times for each experiment was compared with the average induction time obtained from six experiments carried out at the same temperature. The results are shown in Table 7.

Thermolysis Of Pyrrolidinium Nitrate (PN)

PN (0.1 mg) was introduced into the GC/MS through a concentrator oven as described previously. The resulting RIC, shown in Figure 5, is characterized by one major product. The mass spectrum (CI/CH_4) of this product is identical to that of product V from the decomposition of BDD and is identified as being N-nitrosopyrrolidine (PNSA).

DISCUSSION

The data generated from this investigation suggest that the BDD induction period is characterized by competitive, endothermic reactions that create conditions that ultimately lead to exothermic decomposition. This conclusion is supported by the results of the cumulative induction period study where it was demonstrated that the induction period is afforded a "memory." Isothermal DSC experiments with BDD in vented sample pans are typified by subtle endotherms of long duration followed by rapid exothermic decomposition. Loss of volatiles, thought to occur during this endothermic period, was confirmed by isothermal TGA at a temperature as low as $180^{0}C$ in a flowing N_2 atmosphere.[15] BDD has been shown previously to completely dissociate into 1,4-butanediamine (BDA) and HNO_3 at elevated temperature in high vacuum with no other decomposition reactions apparent.[10] The presence of BDD in the effluent from isothermal TGA Experiment I suggests that dissociation/association also occurs to some small extent at atmospheric pressure. The shape of relatively low temperature TGA curves at atmospheric pressure, however, suggests reactions other than dissociation are occurring. While AN was not detected in the effluent from isothermal TGA experiments, the effluent from a specific time/temperature period of a dynamic TGA experiment yielded a white solid that produced an IR spectrum that indicated the presence of AN. Even though the total weight loss over this period was minimal, the presence of AN indicates that C-N bond rupture occurs early in the BDD decomposition process at atmospheric pressure. The detected AN is thought to result from the reaction of NH_3 with HNO_3 in the vapor phase.[14]

In an effort to identify more of these early products, BDD was decomposed in a sealed bulb under partial vacuum at $190^{o}C$, and the reaction residue was analyzed by cation/anion chromatography. The reactions were quenched at various stages of reactivity as judged by qualitative observation of color change in the reaction residue. Very small percentages (relative to total sample reacted) of ammonium and pyrrolidinium cations were detected with the former being detected first. The order of appearance is consistent with the findings of Brill[14] and appears to support the existence of the following early reactions:

(1) $[H_3N(CH_2)_4NH_3]2NO_3 \rightleftharpoons [H_3N(CH_2)_4NH_2]NO_3 + HNO_3$

BDD BDM

(2) $BDM \rightleftharpoons H_2N(CH_2)_4NH_2 + HNO_3$

BDA

(3) $BDM \longrightarrow [\overline{CH_2CH_2CH_2CH_2N}H_2]NO_3 + NH_3$

PN

(4) $PN \rightleftharpoons \overline{CH_2CH_2CH_2CH_2N}H + HNO_3$

PYR

(5) $NH_3 + HNO_3 \rightleftharpoons NH_4NO_3$

AN

BDM and PN have not been directly confirmed as intermediate reaction products in the condensed phase by analysis. BDM, however, is a logical choice as a precursor to the cycloelimination reaction that leads to PYR. This reaction is consistent with the theoretical findings of Politzer,[16] wherein a $C\text{-}NH_3^+$ bond was calculated to be weaker than a $C\text{-}NH_2$ bond; hence, the former is favored for C-N bond fission. PN, on the other hand, has been identified by Brill[14] in the aerosol above decomposing BDD, but its formation in the condensed phase does not seem likely. It is unstable above 100^oC at atmospheric pressure and would not be expected to be stable in the condensed phase under these experimental conditions. Based on these data, it is probably best to describe the early decomposition of BDD in terms of equations 1 through 5 plus equations 6 and 7.

(6) $BDM \longrightarrow PYR + AN$

(7) $BDA \longrightarrow PYR + NH_3$

The finding of PNSA among the reaction products, coupled with the fact that PN yields significant amounts of PNSA upon thermolysis, strongly suggests that PN is formed as a transient species at some point during the early BDD thermolysis process. Subsequent decomposition of PN to form PNSA may then occur, perhaps through a dehydration reaction to form transient N-nitropyrrolidine (PNA). Small amounts of PNA have been detected in the BDD reaction products, but PNA has not been detected among the products of PN decomposition. It is postulated that PNA decomposes in a manner similar to that of dimethylnitramine,[17] thereby forming PNSA as the primary decomposition product.

The presence of N_2O and N_2 in the BDD decomposition effluent suggests that transient, primary nitramine and nitrosamine functional groups may also appear during the thermolysis process. Nitrous oxide, however, may also result via degradation of AN, which has been shown to form early in the process. The degradation of relatively unstable primary nitramine and nitrosamine species in the presence of HNO_3 may also account for the presence of the three DNBu isomers. The degradation may, for example, proceed via the corresponding diazonium and diazonium oxide ions, thus leading to formation of the DNBu isomers through solvolysis/elimination reactions[18a] coupled with carbon to carbon migration of hydride ion.[18b]

Based on condensed phase and gaseous products identified from BDD thermolysis effluent and residue, additional reactions are postulated to occur later in the thermal decomposition process. While the decomposition chemistry occurring in molten BDD is believed to be complex, many of the proposed reactions shown below are presented as unimolecular and, in some cases, in a stepwise, simplistic manner for purposes of clarity.[19]

$$(8)\quad \mathrm{PN} \longrightarrow \overline{\mathrm{CH_2CH_2CH_2CH_2N}}\mathrm{NO_2} + \mathrm{H_2O}$$

PNA

$$(9)\quad \mathrm{PNA} \longrightarrow \overline{\mathrm{CH_2CH_2CH_2CH_2N}}\mathrm{NO} + \text{other products}$$

PNSA

$$(10)\quad \mathrm{BDD} \longrightarrow \mathrm{O_2NNH(CH_2)_4NHNO_2} + 2\mathrm{H_2O}$$

BDNA

$$(11)\quad \mathrm{BDNA} \longrightarrow -[-\mathrm{CH_2CH_2NN(O)OH}]_2$$

(a)

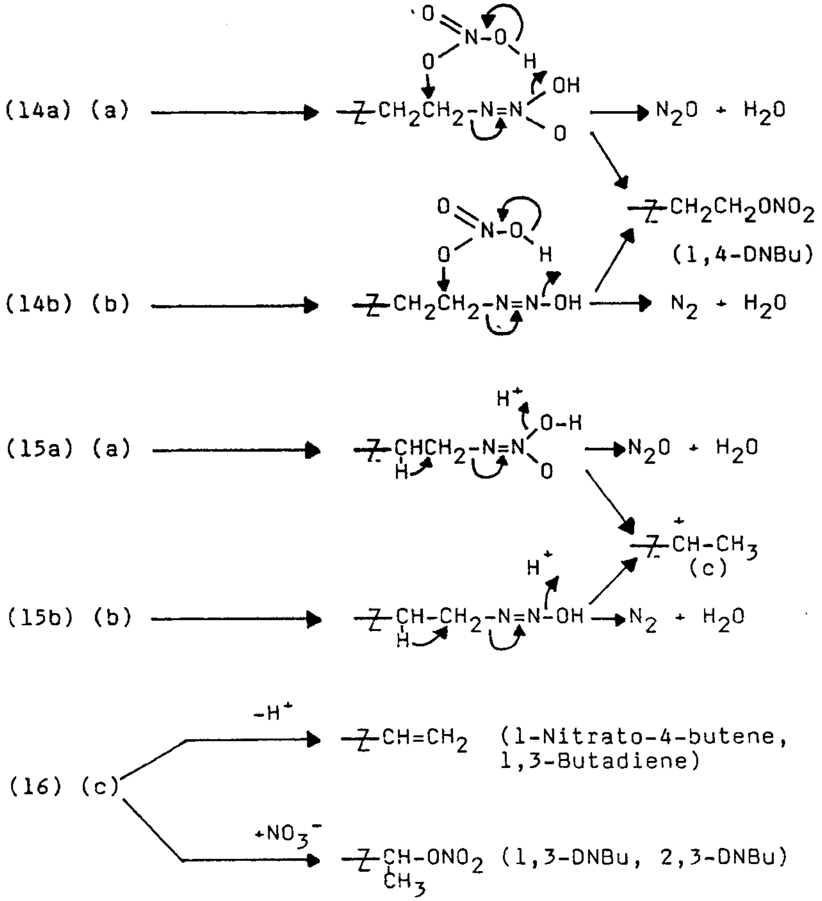
$$(12)\quad \mathrm{BDNA} \longrightarrow \mathrm{ONNH(CH_2)_4NHNO} + \text{other products}$$

BDNSA

$$(13)\quad \mathrm{BDNSA} \longrightarrow -[-\mathrm{CH_2CH_2NNOH}]_2$$

(b)

Specifically, equations (14) through (19) may be representative of the reactions taking place in the condensed phase leading to the products, 1,4-DNBu, 1,3-DNBu, 2,3-DNBu, 1-nitrato-4-butene and 1,3-butadiene. Electron paramagnetic resonance studies[20] have confirmed the presence of free radicals in the exothermic decomposition process that follows the non-radical (probably ionic) induction period. Equations 17-19 reflect a possible radical mediated route to known products.



$$(17)\ \text{BDD} \xrightarrow{-\ 2H^{\bullet}} -\!\!\![\text{-CH}_2\dot{\text{C}}\text{HNH}_3]_2$$

(f)

$$(18)\ (f) \longrightarrow 2[\text{CH}_2\text{=CHNH}_3]\text{NO}_3 \longrightarrow \text{H}_2\text{C=}\dot{\text{C}}\text{H} + \dot{\text{N}}\text{H}_3\text{NO}_3$$

(g) (h)

$$(19)\ (h) \longrightarrow \text{H}_2\text{C=CH}_2 \bullet \text{1,3-butadiene}$$

As shown earlier, other products from the decomposition process were found in minor quantities, but most were not tentatively indentified due to lack of sufficient mass spectral data. It is believed NO, CO, CO_2 and NO_2 are produced by attack of HNO_3 on the backbone of the organic cation. This oxidation process also appears to occur early, but not to such an extent to cause measurable self-heating.

CONCLUSIONS

It has been shown that BDD decomposes thermally from the molten state via a multistep process that produces a variety of condensed phase and gaseous products. The nature of the products suggest that a proton transfer reaction from cation to anion followed by C-N bond rupture occurs early in the decomposition process. The presence of early heterocyclic reaction products demonstrates that one of the reaction mechanisms involves cycloelimination. The reactions of this latter process appear to be competitive and may proceed through transient, primary nitramine and nitrosamine species. The degradation of these relatively unstable species in the presence of HNO_3 may account for the presence of the three DNBu isomers, as well as, 1-nitrato-4-butene and 1,3-butadiene. Future work with BDD includes a study to determine the kinetics associated with its thermal degradation process and an attempt to relate the kinetics to the thermal and impact sensitivities of its composites with ammonium and potassium nitrates.

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TABLE 1. Mass Spectral Data For Products I-V

Original Salt	Product	m/e (tentative assignment)	Type Expt
BDO	I M=69	70[base] (M+H) 84 98(M+(C_2H_5) 110(M+C_3H_5)	CI/CH_4
		71[base] (M+D) 103(M+C_2D_5)	CI/CD_4
BDO	II M=98	71 76 99[base](M+H) 127(M+C_2H_5) 139(M+C_3H_5)	CI/CH_4
BDO	III	71 73 76(CH_2NO_3) 88 101 118[base](M-NO_3) 181(M+H)	CI/CH_4
BDO	M=180	71 73 76(CH_2NO_3) 88 102 118[base](M-NO_3) 181(M+H)182(M+D)	CI/CD_4
BDO-1,1,4,4-d_4	M=184	73 74[base] 75 90 101 122(M-NO_3) 185(M+H)	CI/CH_4
BDO-2,2,3,3-d_4	M=184	73 74 76(CH_2NO_3) 92 104 121 122[base](M-NO_3) 185(M+H)	CI/CH_4
BDO		43 46[base](NO_2) 74 73 76(CH_2NO_3) 90($C_2H_4NO_3$)	EI[a]
BDO-1,1,4,4-d_4		46[base](NO_2) 78(CD_2NO_3) 92($C_2H_2D_2NO_3$)	EI
BDO-2,2,3,3-d_4		46[base](NO_2) 76(CH_2NO_3) 90($C_2D_2H_2NO_3$)	EI
Predicted	1,3-DNBu	46 76 90	EI

TABLE I. Mass Spectral Data For Products I-V (cont.)

Original Salt	Product	m/e (tentative assignment)	Type Expt
BDO	IV	71[base]73 $76(CH_2NO_3)$ 88 101 $118(M-NO_3)$ 181(M+H)	CI/CH_4
BDO	M-180	71[base] $76(CH_2NO_3)$ $118(M-NO_3)$ 181(M+H)182(M+D)	CI/CD_4
BDO-1,1,4,4-d_4	M-184	74[base] 89 $122(M-NO_3)$ 185(M+H)	CI/CH_4
BDO-2,2,3,3-d_4	M-184	74 75[base] 76 92 $122(M-NO_3)$ 185(M+H)	CI/CH_4
BDO		$46[base](NO_2)$ $76(CH_2NO_3)$	EI[b]
BDO-1,1,4,4-d_4		$46[base](NO_2)$ $78(CD_2NO_3)$	EI
BDO-2,2,3,3-d_4		$46[base](NO_2)$ $76(CH_2NO_3)$	EI
Authentic Sample	1,4-DNBu	46 76	
BDO	V	70 84 101[base](M+H) $129(M+C_2H_5)$ $141(M+C_3H_5)$	CI/CH_4
BDO	M=100	102[base](M+D) $134(M+C_2D_5)$ $146(M+C_3D_5)$	CI/CD_4
BDO		39 41[base]42 43 68 69 100(M)	EI[c]
Authentic Sample	PNSA	39 41[base]42 43 68 69 100	

a. Spectrum consistent with ion fragment pattern expected from 1,3-dinitratobutane (1,3-DNBu)

b. Spectrum consistent with ion fragment pattern for authentic 1,4-dinitratobutane (1,4-DNBu)

c. Spectrum consistent with ion fragment pattern for authentic N-nitrosopyrrolidine (PNSA)

TABLE 2. Mass Spectral (EI) Data For Product X (4-Nitrato-1-butene)

Source	m/e (tentative assignment)							
BDD	39	41[base](CH_2CHCH_2)				46(NO_2)	55($CH_2CHCH_2CH_2$)	76(CH_2ONO_2)
Predicted		41				46	55	76
BDD-1,1,4,4-d_4	40	41	42	43 (CD_2CHCH_2)		46[base](NO_2)	59($CD_2CHCH_2CD_2$)	78(CD_2ONO_2)
Predicted		41		43		46	59	78
BDD-2,2,3,3-d_4	40	41	42	43	44(CH_2CDCD_2)	46[base](NO_2)	58($CH_2CDCD_2CH_2$)	76(CH_2ONO_2)
Predicted					44	46	58	76

TABLE 3. Mass Spectral (CI) Data For Product X (4-Nitrato-1-butene)

Source	m/e (tentative assignment)			
BDD	71[base]($CH_2CHCH_2CH_2O$)	76(CH_2ONO_2)	87($C_4H_7O_2$)	118(Molecular ion+H)
BDD-1,1,4,4-d_4	75	78[base]	90	122
BDD-2,2,3,3-d_4	74	76[base]	90	121

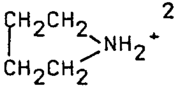
TABLE 4. Mass Spectral Data For Products VIII, XIV and XV

ID #	COMPOUND	MW	MS/(CI/CH_4)
VIII	Tetrahydrofuran	72	73(M+H) 101(M+C_2H_5)
XIV	2,3-Dinitratobutane	180	181(M+H)
XV	N-Nitropyrrolidine	116	117(M+H)

TABLE 5. Products Identified From BDD Thermolysis Residue

Product #	Product Name
III	1,3-Dinitratobutane
IV	1,4-Dinitratobutane
V	N-Nitrosopyrrolidine
VIII	Tetrahydrofuran
X	4-Nitrato-1-butene
XIV	2,3-Dinitratobutane
XV	N-Nitropyrrolidine

TABLE 6. Ion Chromatography Data From BDD Thermolysis Residue

Sample	Observation	NO_3^- [1]	NH_4^+ [2]	 [2]
1.	Not heated	1.00	0.0000	0.000
2.	Sample splattered on top of bulb turned dark yellow	1.05	<0.0001	0.000
3.	Liquid in bottom of bulb turned yellow and started to bubble	1.05	<0.0001	0.000
4.	Liquid in bottom turned red-brown and bubbled vigorously	1.00	0.0001	0.002
5.	Liquid in bottom turned dark brown, no further evidence of reaction	0.35	0.0004	0.006

(1) Normalized areas.
(2) Percent of original sample weight.

TABLE 7. Comparison of Cumulative and Non-Cumulative Induction Period Times For BDD in Air at 190°C

Exp't	Segment 1	Segment 2	Total
	Induction Period (min.)		
1	3.73	3.87	7.60
2	3.73	3.88	7.61
3	4.35	3.54	7.89
		Average	7.70
4	7.70±0.76		7.70±0.76

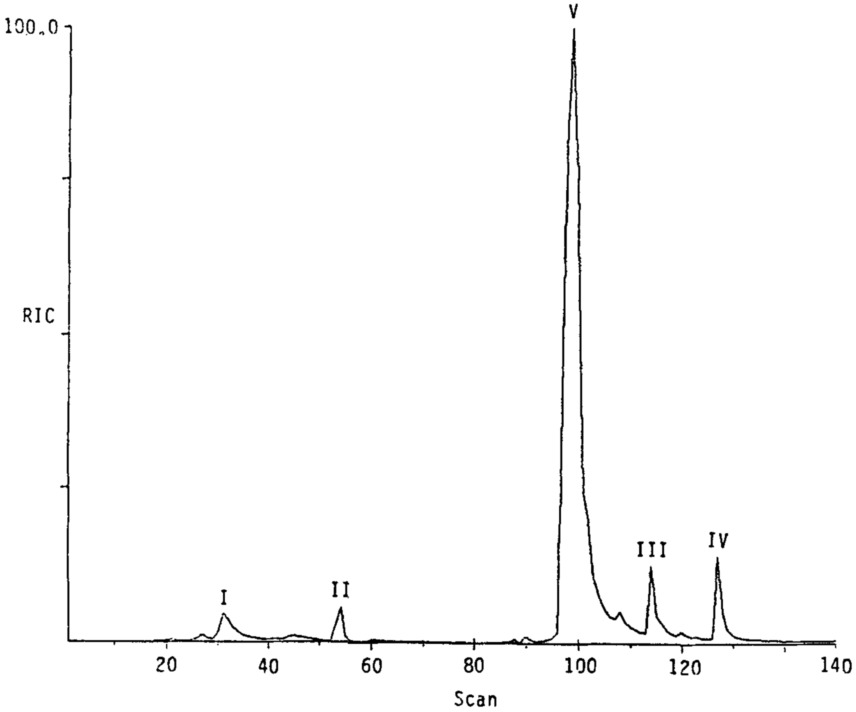


FIGURE 1. Reconstructed Ion Chromatogram of BDD Decomposition Products From Isothermal TGA Experiment II.

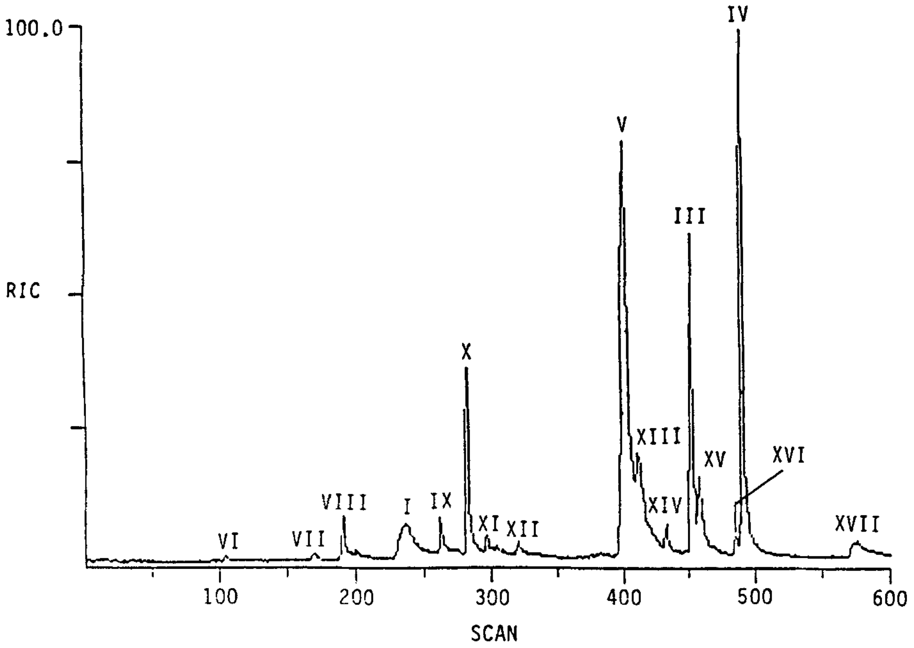


FIGURE 2. Reconstructed Ion Chromatogram of BDD Decomposition Products From Isothermal DSC Experiment.

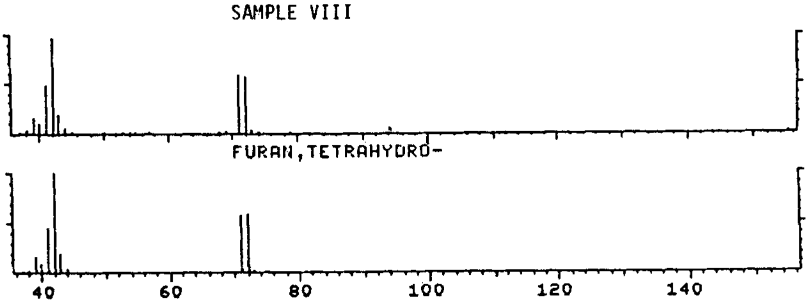


FIGURE 3. EI Mass Spectrum of Compound VIII Compared to That of Tetrahydrofuran.

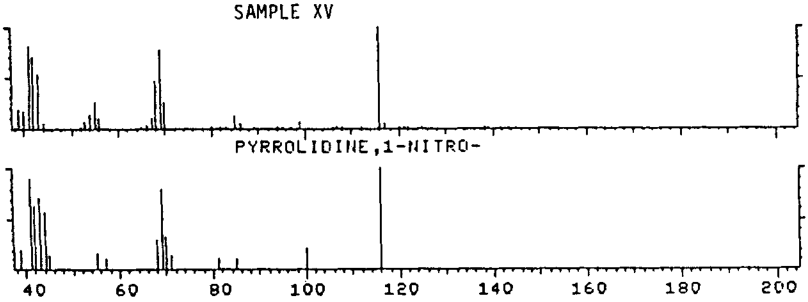


FIGURE 4. EI Mass Spectrum of Compound XV Compared to That of N-Nitropyrrolidine.

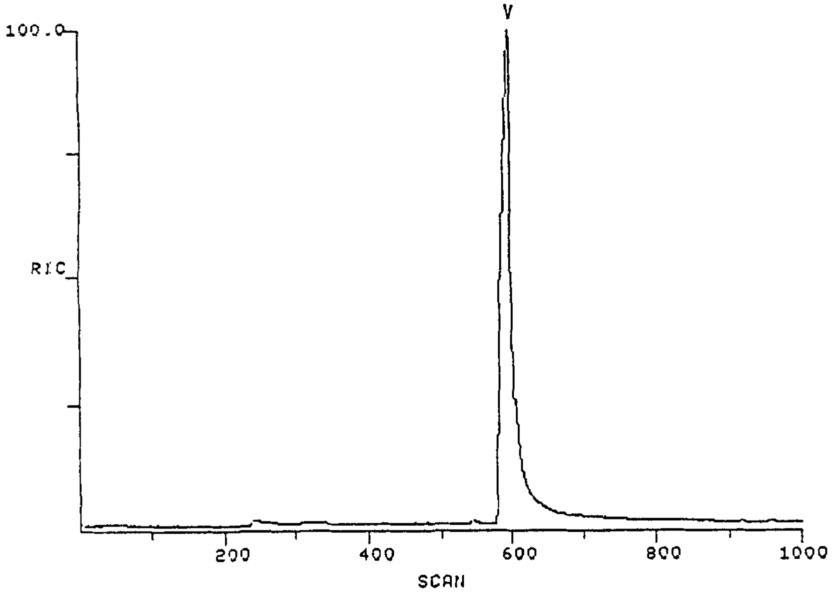


FIGURE 5. Reconstructed Ion Chromatogram of PN Decomposition Products.

LIST OF ABBREVIATIONS

AN	Ammonium Nitrate
ARC	Accelerating Rate Calorimeter
BDA	1,4-Butanediamine
BDD	1,4-Butanediammonium Dinitrate
BDM	1,4-Butanediamine $\cdot HNO_3$
BDNA	1,4-Butanedinitramine
BDNSA	1,4-Butanedinitrosamine
CI	Chemical Ionization
DNBu	Dinitratobutane
DSC	Differential Scanning Calorimeter
EDD	1,2-Ethanediammonium Dinitrate
EI	Electron Impact
GC/MS	Gas Chromatography/Mass Spectrometry
HPLC	High Performance Liquid Chromatography
IR	Infrared
PN	Pyrrolidinium Nitrate
PNA	N-Nitropyrrolidine
PNSA	N-Nitrosopyrrolidine
PTTN	Pentaerythrityltetrammonium Tetranitrate
PYR	Pyrrolidine
RIC	Reconstructed Ion Chromatogram
TGA	Thermogravimetric Analysis

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19. The role played by water in the BDD decomposition process has not been studied in detail. Results from isothermal DSC experiments, to be included in another publication, clearly show that DIE values are influenced by the presence of free oxygen in the heated sample pans. Care was taken to dry all samples by the same

procedure to universally minimize the influence of water, if any.

20. Unpublished experiments carried out at The Frank J. Seiler Research Laboratory, U.S. Air Force Academy, for this project.