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**SOLID-PHASE THERMAL DECOMPOSITION OF 2,4-DINITROIMIDAZOLE
(2,4-DNI)**

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ABSTRACT

The solid-phase thermal decomposition of the insensitive energetic nitroaromatic heterocycle 2,4-dinitroimidazole (2,4-DNI: mp 265-274°C) is studied utilizing simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) between 200° and 247°C. The pyrolysis products have been identified using perdeuterated and ¹⁵N-labeled isotopomers. The products consist of low molecular-weight gases and a thermally stable solid residue. The major gaseous products are NO, CO₂, CO, N₂, HNCO and H₂O. Minor gaseous products are HCN, C₂N₂, NO₂, C₃H₄N₂, C₃H₃N₃O and NH₃. The elemental formula of the residue is C₂HN₂O and FTIR analysis suggests that it is polyurea- and polycarbamate-like in nature. The rates of formation of the gaseous products and their respective quantities have been determined for a typical isothermal decomposition experiment at 235°C. The temporal behaviors of the gas formation rates indicate that the overall decomposition is characterized by a sequence of four events; 1) an early decomposition period induced by impurities and water, 2) an induction period where CO₂ and NO are the primary products formed at relatively constant rates, 3) an autoacceleratory period that peaks when the sample is depleted and 4) a final period in which the residue decomposes. Arrhenius parameters for the induction period are $E_a = 46.9 \pm 0.7$ kcal/mol and $\text{Log}(A) = 16.3 \pm 0.3$. Decomposition pathways that are consistent with the data are presented.

INTRODUCTION

The relatively new energetic aromatic heterocycle, 2,4-dinitroimidazole (2,4-DNI), has performance characteristics between that of HMX and TNT and has better thermal stability and shock and impact insensitivity than these two commonly used materials [1]. The crystal structure of 2,4-DNI (Figure 1) is thought to contribute to the enhanced stability observed for 2,4-DNI [2]. Since there is potential use for 2,4-DNI as an insensitive high explosive, characterizing the solid-phase thermal reaction chemistry is important to gain insight into the reactions controlling the release of energy from this material. Such insight can provide information required to probe correlations between molecular structure and performance, to evaluate the reactions that may affect the long-term aging of systems using 2,4-DNI, and to build predictive models for assessing the long-term stability of 2,4-DNI. To our knowledge there is little information pertaining to 2,4-DNI thermal decomposition chemistry. We have utilized simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) to characterize the mass spectrum of 2,4-DNI [3] and are now applying this method to characterize the reaction mechanisms and chemical kinetics associated with the thermal decomposition of 2,4-DNI in the solid phase. The identities and rates of formation of the gaseous reaction products are reported as well as characteristics of the solid residue formed during pyrolysis.

EXPERIMENTAL

Instrument description and data analysis.

The STMBMS apparatus used to conduct the thermal decomposition experiments and the basic data analysis procedures have been described previously [5-7]. The sample sizes used for this study are approximately 10 mg. The alumina reaction cell used to contain the samples during the experiments is typically fitted with a 25μ-diameter orifice. A nominal electron

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energy of 20 eV is used to minimize fragmentation of the reaction products in the mass spectrometer.

Sample preparation and analysis.

Unlabeled 2,4-DNI samples were obtained from P. Pagoria at LLNL (~98% pure) and used as received. 2,4-DNI isotopomers were synthesized as published.[8] Pyrolytic residues are analyzed using FTIR spectroscopy and elemental analysis. The FTIR spectra are recorded from pressed KBr pellets with 8 cm^{-1} resolution using a Bio-Rad FT-40 FTIR spectrometer. Elemental analyses are performed by Huffman Laboratories, Inc., Boulder, CO.

RESULTS AND DISCUSSION

Solid-Phase Thermal Decomposition Characteristics

The identities of the reaction products and the temporal behaviors of their rate of formation from the isothermal decomposition of 2,4-DNI in the solid phase between 200° and 247°C can be characterized by four different periods as illustrated in Figure 2. The major gaseous products formed are NO, CO₂, H₂O, HNCO, N₂, CO and HCN (Table I). Minor amounts of other gaseous products with similar temporal behaviors include C₂N₂, NO₂, NH₃, imidazole and C₃H₃N₃O₃. The four characteristic events of the thermal decomposition of 2,4-DNI at 235°C, illustrated in Figure 2, are: 1) an early decomposition [I]; 2) an induction period [II]; 3) an autoacceleratory period that peaks when the unreacted 2,4-DNI [III] is depleted; and 4) a slow decomposition of the polymeric residue that continues until the temperature is decreased [IV]. Absorption bands at 3296, 3156, 1748, 1628, 1572 and 1304 cm^{-1} in the infrared spectra of the nonvolatile polymeric residue suggests that it contains urea and carbamate functionalities.

Figure 2. Gas formation rates of products from the isothermal decomposition of 10.3 mg of 2,4-DNI at 235°C. Four periods characterize the decomposition: I) early thermal decomposition, II) an induction period, III) an autoacceleration period and IV) decomposition of the residue.

Figure 1. The hydrogen bonding in a ribbon layer of 2,4-DNI molecules. The crystal structure consists of stacked layers that are not linked by hydrogen bonds.[4]

Table I. Solid-phase 2,4-DNI decomposition products and product distribution at 235°C.

mass (m/z)	Product Formula (and Source)	Product (mg)	Molar Ratio ^a
17	NH ₃	< 0.01	< 0.01
18	H ₂ O	0.17	0.45
27	HCN (N from ring)	0.06	0.10
28	CO	0.06	0.11
	N ₂ (N from ring)	0.13	0.22
30	NO (N from C-2 and C-4 nitro group in ~50:50 ratio)	0.74	1.18
43	HNCO (N from ring)	0.18	0.21
44	CO ₂	0.55	0.60
46	NO ₂ (NO ₂ mostly from C-2)	0.01	0.01
52	C ₂ N ₂ (N from ring)	0.02	0.02
68	imidazole	< 0.01	< 0.01
129	C ₃ H ₃ N ₃ O ₃ (N from ring)	< 0.01	< 0.01

2,4-DNI evaporated (mg) 7.04

2,4-DNI decomposed (mg) 3.28

residue (mg) 1.33

total mol gas/mol 2,4-DNI decomp 2.9

^aRatio of moles of product formed to moles of decomposed 2,4-DNI for an unlabeled sample at 235°C. Orifice diameter is 25μ.

The early decomposition period (I) involves the effect of impurities on the decomposition of 2,4-DNI whereas the induction and autoacceleratory periods (II and III) result from only the decomposition of 2,4-DNI. These three periods are illustrated in the data shown in Figure 3 for decomposition at 235°C. The temporal behaviors of the ion signals representing the gaseous decomposition products HNCO ($m/z=43$), H₂O ($m/z=18$), CO₂ ($m/z=44$), and a residual impurity from synthesis, 4-nitroimidazole (4-NI; $m/z=113$), are typical of all the solid-phase decomposition experiments. The decomposition is characterized by the five following events: 1) An immediate evolution of contaminants and impurities occurs as the sample approaches the isothermal temperature. In this case, 235°C was obtained at approximately 2200 seconds. 2) Simultaneous with 4-NI evolution is the desorption of H₂O from the 2,4-DNI. 3) An early decomposition occurs from near the onset of the isothermal temperature to approximately 4000 seconds. 4) An induction period ensues that is determined from the onset of isothermal temperature to the time that an increase in the HNCO is observed after the early decomposition is complete (~9000

seconds). 5) Following the induction period, the HNCO signal shows an accelerating rate of evolution. The initial portion of the accelerating rate can be approximated by a linear rate of increase up to approximately 15000 seconds. Then other product ion signals, such as H₂O and CO₂, start to show autoaccelerating rate as well.

Figure 3. Ion signals representing the early evolution of the products HNCO, H₂O, CO₂ and the impurity 4-NI from the thermal decomposition of 2,4-DNI at 235°C.

Early decomposition period. The early decomposition period (I) observed near the onset of the isothermal temperature is due to many factors such as the presence of impurities and the condition of the crystal lattice. Imperfections within the lattice caused by the presence of contaminants, including adsorbed and occluded H₂O molecules, can initiate the decomposition

of 2,4-DNI molecules not stabilized by the lattice. Separate studies of 4-NI thermal decomposition show that under similar experimental conditions, 4-NI undergoes substantial evaporation with little decomposition. However, the dinitroimidazole isomers of 1,4-DNI and 4,5-DNI decompose and melt at temperatures below 200°C, and the temporal behaviors of ion signals associated with the decomposition products from these dinitroimidazole isomers indicate their presence during the early decomposition period. However, these contaminants are typically less than ~1% (w/w) of the 2,4-DNI sample and cannot account for the entire early decomposition. The major contributor to the early decomposition is H₂O. The end of the early decomposition stage, shown in Figure 3, coincides with the decrease in the H₂O signal at about 4000 seconds. The H₂O signal observed during the initial stages of 2,4-DNI degradation is suspected to originate from adsorbed and occluded H₂O, not from H₂O as a thermal reaction product.

Effect of H₂O on 2,4-DNI thermal decomposition. The effect of H₂O on 2,4-DNI decomposition is important to understand since it has a measurable affect on the early decomposition process and may affect the thermal stability and long-term aging of a system that contains 2,4-DNI. To determine if H₂O is a factor in the early decomposition, the 235°C isothermal experiment was repeated with a 1.5 hour hold at 120°C to reduce the amount of any adsorbed H₂O. The resulting strong H₂O signal and absence of signals from other products during the 120°C hold, shown in Figure 4, supports the origin of water from adsorbed H₂O and not from the decomposition of 2,4-DNI at this temperature. As 235°C is reached (~6000 seconds), the H₂O signal again increases as remaining H₂O desorbs from the sample, indicating that water is still present with the material. The peak widths of the decomposition products HNCO and CO₂ are narrow, relative to the corresponding peak widths in the experiment without the 120°C hold (Figure 3), suggesting a lesser amount of these products has evolved. Similar to the evolution of products shown in Figure 3, the early HNCO and CO₂ signals decrease with the decrease in the H₂O signal. This again suggests that the early decomposition is correlated to the presence of H₂O.

Figure 4. Ion signals representing the early evolution of H₂O, CO₂ and HNCO during the thermal decomposition of 2,4-DNI with an isothermal hold at 120°C until ~5000 seconds and a ramp to a second isothermal hold at 235°C (reached at about 6000 seconds).

We have deduced a general thermal decomposition mechanism for 2,4-DNI (Figure 5) that involves the formation of an isocyanate intermediate. The development of this mechanism is based on our decomposition studies conducted using 2,4-DNI isotopomers. Initially a nitro-nitrite rearrangement occurs yielding NO and an oxy radical. This mechanism is first order with respect to 2,4-DNI and probably occurs with the nitro group in the 2,4-DNI molecule that is not hydrogen bonded. As can be seen from Figure 1, half of the nitro groups from the C-2 position and half of the nitro groups from the C-4 position do not participate in hydrogen bonding. The equal contribution of the NO product from both positions is observed experimentally from thermal decomposition of 2,4-DNI-(2-¹⁵NO₂) where the product ion signals for NO ($m/z=30$)

and ^{15}NO ($m/z=31$) are observed to have similar temporal behaviors and intensities. Furthermore, quantification of the early decomposition period at 235°C results in a molar ratio for NO to 2,4-DNI consumed of 1.05, indicating that one mole of NO is formed (two are available) per one mole of 2,4-DNI consumed. The oxy radical remaining after the formation of NO can then rearrange to form an intermediate with an isocyanate functionality ($\text{R}-\text{N}=\text{C}=\text{O}$). The isocyanate functionality is stable, but reactive, and readily reacts with H_2O to yield CO_2 . As the integrity of the crystal structure is disturbed from the early events, the H_2O trapped in the crystal lattice has an increased opportunity to interact with available isocyanates. After the impurities are depleted, including the desorbed and occluded H_2O , the early decomposition event ceases and decomposition of pure 2,4-DNI in the induction period continues. Based on initial evaluations, the duration of the induction period does not appear to be changed significantly by the amount of the early decomposition that occurs, being approximately 7500 seconds for the 235°C isothermal experiments represented in Figures 3 and 4. Further experiments to evaluate the effect of H_2O on the early decomposition of 2,4-DNI are presently being conducted.

Figure 5. Initial mechanisms for 2,4-DNI condensed-phase thermal decomposition.

Induction and autoacceleration period characteristics. Decomposition intermediates accumulate during the induction period. These intermediates appear to be prepolymeric "subunits" that readily combine with one another at an accelerating rate as the crystal lattice weakens. The low-molecular weight gaseous products are produced as the prepolymeric subunits form and combine with each other. A number of different reactions are likely to occur during this period and two examples are presented in Figure 6. Formation of the isocyanate intermediate (Figure 5) is a likely principal intermediate. However, other intermediates that have amino and hydroxy functionalities, as well as radical intermediates, are likely to form simultaneously and consecutively with the isocyanate intermediate. The intermediates either decompose further or combine with another intermediate. The isocyanate functionality readily reacts with hydroxy and amine groups to form predominately carbamates ($\text{R}-\text{NH}-\text{C}(\text{O})-\text{OR}'$) and ureas ($\text{R}-\text{NH}-\text{C}(\text{O})-\text{NH}-\text{R}'$), respectively. During the early stages of the decomposition the intermediates can not readily interact with each other due to constraints of the lattice. As dissolution of the lattice increases, more nitro groups are free from hydrogen bonding and can undergo nitro-nitrite rearrangement and form the intermediates that become prepolymer subunits. Consequently, higher concentrations of intermediates lead to increased rates of interaction, which result in the observed autoacceleratory behavior and the formation of the polymeric residue. From the FTIR analysis, the polymeric residue is found to contain functional groups that show absorption bands at frequencies that are characteristic of compounds containing urea and carbamate functionalities. The autoacceleration period continues until one of the primary building blocks, 2,4-DNI, is depleted. As the polymerization occurs, gaseous products with low molecular weights (see Table I) are released. If the experiment is allowed to continue after the

2,4-DNI is depleted, the polymeric residue continues to rearrange in some fashion while continuously releasing low-molecular weight products.

Figure 6. Example of likely reactions occurring during the induction and autoacceleratory periods of 2,4-DNI solid-phase decomposition.

Induction Period Kinetics

Assuming that the early decomposition does not affect the normal thermal degradation of pure 2,4-DNI, the induction period, obtained from the temporal behavior of HNCO as a function of temperature (Table II), may be used to obtain kinetic parameters. The temperature dependence is shown in Figure 7. The Arrhenius parameters are $E_a = 46.9 \pm 0.7$ kcal/mole and $\text{Log}(A) = 16.3 \pm 0.3$. These parameters can be used to evaluate the duration of the induction period at specific temperatures. For example, at the upper limit of the storage temperature of the stockpiled munitions, 70°C , the duration of the induction period for 2,4-DNI is 1×10^6 years, as extrapolated from the data. This value reflects the high thermal stability of 2,4-DNI. However, the duration of the induction period may be influenced by other factors, such as material compatibility or containment issues, not considered in this study.

Table II. 2,4-DNI decomposition data.

Number	Temp ($^\circ\text{C}$)	Orifice Diameter (μm)	Induction time (sec)
1	200.4	10	212000
2	209.8	25	70000
3	210.5	25	68000
4	225.4	25	17100
5	225.0	25	16000
6	235.2	25	6850
7	235.2	25	6600
8	246.9	25	2250

Figure 7. Temperature dependence of the 2,4-DNI induction period.

CONCLUSIONS

The thermal decomposition of 2,4-DNI in the solid-phase between 200° and 247°C is characterized by the following four events. 1) An early decomposition period occurs near the onset of the isothermal temperature that is attributed to the presence of impurities remaining from the synthesis and from adsorbed and occluded H_2O in the 2,4-DNI crystal lattice. 2) When the impurities are depleted, an apparent induction period is observed that is defined to be from the onset of the isothermal temperature to time of the increase of the HNCO signal. 3) The induction period is followed by an autoaccelerating rate period. The initial accelerating rate of this period

can be approximated with a linear rate of increase. The maximum autoaccelerating rate occurs just prior to final depletion of the 2,4-DNI sample. 4) The solid residue that forms during the decomposition continues to release low-molecular weight gases until the experiment is stopped.

The presence of adsorbed and occluded H₂O in the crystal structure of 2,4-DNI increases the rate of thermal decomposition of 2,4-DNI. The increase of the ion signals from the early decomposition products, CO₂ and HNCO, occurs shortly after the increase of the ion signal from adsorbed H₂O. These ion signals then decrease with the decreasing H₂O ion signal. Partial dehydration of the adsorbed water on the 2,4-DNI crystal before pyrolysis results in reduction in the amount of the early decomposition products. However, the presence of H₂O impurity does not significantly affect the induction time at 235°C. Further studies are being conducted to evaluate the effect of H₂O in detail.

A set of reaction pathways have been developed that are consistent with the data. Initially a nitro-nitrite rearrangement leads to the formation of NO and an oxy radical intermediate. This reaction is first order relative to 2,4-DNI and the rearrangement occurs at the nitro group that is not hydrogen bonded in the 2,4-DNI lattice. The oxy radical intermediate rearranges to form an isocyanate functionality. The isocyanate functionality is stable but reactive and, in the presence of H₂O, readily reacts to produce CO₂. This pathway dominates the early decomposition observed for 2,4-DNI and ceases when adsorbed and occluded H₂O is depleted. During the induction period the isocyanate intermediates and other intermediates with amine and hydroxy functionalities accumulate, producing low-molecular weight gases as they form and react. The intermediates readily combine with isocyanate functionalities and result in the formation of a polymeric residue that is polyurea- and polycarbamate-like in character. The buildup of the polymeric residue occurs at an increasing rate due to dissolution of the crystal lattice, thus increasing the interaction frequency between the intermediates, and accounting for the observed increase in reaction rate.

The Arrhenius parameters for the induction period are $E_a = 46.9 \pm 0.7$ kcal/mole and $\text{Log}(A) = 16.3 \pm 0.3$. These parameters are based on the assumption that the early decomposition does not affect the kinetics of pure 2,4-DNI thermal decomposition. Using the parameters to extrapolate to 70°C, an induction time of 1×10^6 years is obtained. The long induction time is a reflection of the high thermal stability of 2,4-DNI. However, the induction time may be affected by other factors relating to compatibility and containment issues and by factors influencing the early decomposition period.

Further studies are being conducted to evaluate the early decomposition in detail. A more detailed analysis of 2,4-DNI solid-phase decomposition will be presented in a future paper.

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