

Analysis of evolved gases during the thermal decomposition of ammonium diniramide under pressure

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Abstract

Ammonium dinitramide (ADN) is one of the most promising new solid oxidizers for rocket propellants, since its oxygen balance and energy content are relatively high, and it does not contain halogens. To gain a better understanding of the thermal decomposition mechanism of ADN, the thermal behavior and gaseous products from decomposition of ADN under pressurized condition (0.1–2.1 MPa) were investigated. The main reaction under all pressures was the decomposition of ADN to ammonium nitrate and nitrous oxide, although a new significant exothermic reaction was observed to occur beforehand. The relative amount of nitrogen dioxide decreased with increasing pressure. These results of this work indicate that condensed phase reactions involving nitrogen dioxide take place during the initial stage of the thermal decomposition of ADN. It was thought that the generation and decomposition of highly reactive materials to ammonium nitrate (AN) were promoted by nitrogen dioxide, and the reaction mechanism changed when the amount of AN in condensed phase increases.

Keywords: ammonium dinitramide, solid propellant, thermal decomposition, evolved gas analysis

1. Introduction

Energetic materials are now evaluated not only with regard to their performance but also their current or potential environmental and health impacts. Ammonium perchlorate (AP, NH_4ClO_4) has been used as a solid rocket propellant oxidizer for decades due to its superior oxygen balance, energy density and stability, as well as its relative ease of handling. However, AP contains Cl, so its combustion generates considerable quantities of HCl as a reaction product. Because HCl is a toxic, corrosive gas, such emissions are an environmental concern including ozone depletion and acid rain. Hydrazine is widely used as

a liquid monopropellant for the attitude control of rockets and space satellites, since it has good performance characteristics. However, it is also highly toxic and carcinogenic, so the handling of this compound is difficult. To eliminate these problems, it would be beneficial to replace AP and hydrazine with a new halogen-free oxidizer and a less toxic monopropellant, respectively. As a result, many studies have pursued the development of new, environmentally safe (or “green”) propellants containing less toxic or halogen-free ingredients that provide suitable performance in terms of burning rate, specific impulse, stability and other important

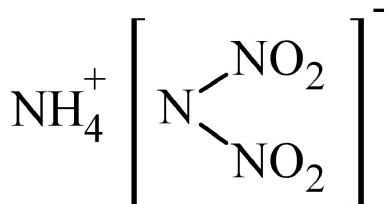
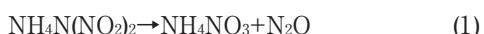


Figure 1 Molecular structure of ADN.

performance parameters^{1)–11)}.

A promising new energetic material considered as a replacement for AP and hydrazine is ammonium dinitramide [ADN, $\text{NH}_4\text{N}(\text{NO}_2)_2$]^{12)–14)}, shown in Figure 1. ADN possesses a high oxygen balance and can provide suitable energy levels. It is also halogen-free and is less toxic than hydrazine, which makes it a candidate for use as an environmentally-friendly, low-toxicity oxidizer in propellants and other energetic systems. The present study focused on the thermal decomposition of ADN, since knowledge of decomposition behavior is vital to understanding combustion, predicting safe storage lifetimes and choosing appropriate stabilizers. This type of investigation requires analyses under various conditions of heating rate, sample mass, atmosphere and additives. Many studies concerning the thermal decomposition mechanism of ADN have previously been conducted,^{9),15)–28)} and it is generally agreed that the main decomposition mechanism involves the generation of ammonium nitrate (AN) and N_2O in Equation (1).



In addition, it has been reported that ADN can decompose into numerous other products, including N_2O , NO_2 , NO, NH_4NO_3 , HNO_3 , N_2 , HONO , H_2O and NH_3 . The work reported herein focuses on the thermal decomposition behavior of ADN under pressure, since measurements under pressure enable a greater understanding of the influence of volatile and reactive species such as NO_2 and HNO_3 . Muravyev *et al.*²⁹⁾ demonstrated changes in the melting point and activation energy of ADN depending on ambient pressure using high pressure differential scanning calorimetry (PDSC). In our own previous study³⁰⁾, ADN was heated at a constant rate under pressure and the thermal behavior and change in the composition of the condensed phase were assessed simultaneously using PDSC and Raman spectrometry. Only under pressure was a significant exothermic reaction not involving the generation of AN observed in the early stage of ADN decomposition. The goal of the present study was to improve our understanding of this unique oxidizer by studying its thermal decomposition under pressure. For this purpose, the gases evolved during ADN decomposition under pressure during constant rate heating were examined, and the associated thermal decomposition mechanism of ADN was investigated.

2. Experimental

ADN was obtained from the Hosoya Pyro-Engineering Co., Ltd. and used as received without further purification.

A combined system consisting of PDSC in conjunction

with infrared spectroscopy (PDSC-IR) and mass spectrometry (PDSC-MS)³¹⁾ was constructed to allow the concurrent analysis of thermal behavior and evolved gases. During the PDSC trials, samples approximately 10 mg were loaded into open aluminum pans, and subsequently heated from 30 to 350 °C at 5 K min^{−1} using a DSC27HP (Mettler Toledo). The samples were heated under a 200 mL min^{−1} flow of argon (during PDSC-IR) or helium (during PDSC-MS), at pressures of 0.1, 0.6, 1.1, or 2.1 MPa. The evolved gases were sent to the IR spectrometer (Shimadzu Co. Ltd., IRPrestige-21) or mass spectrometer (Shimadzu Co. Ltd., GCMS-QP2010) through stainless steel transfer tubing maintained at 200 °C. The gas cell of the IR spectrometer was heated to 200 °C, while the mass spectrometer was operated at an oven temperature of 200 °C in the electron impact ionization mode.

3. Results and discussion

3.1 Thermal behavior of ADN under pressure

The PDSC curves obtained from the ADN at each pressure are shown in Figure 2. The endotherm associated with the melting of the ADN was observed at approximately 92 °C in each case. After melting, two exothermic events occurred between 130 and 220°C at each pressure, and the heat values and onset temperatures in this range, Q_{DSC} and T_{DSC} , are summarized in Table 1. T_{DSC} was defined as the point at which the exothermic power reached a value of 0.2 W g^{−1} above the baseline. Although it can be seen that the values of Q_{DSC} and T_{DSC} values were quite similar at all pressures, the early exothermic peak became more evident as the pressure was increased. These results indicate a condensed phase exothermic reaction involves compounds that are readily volatilized at normal atmospheric pressure and that is promoted by pressurization. In contrast, the shape of the second exothermic peak at 180 °C was almost constant with pressure, suggesting that the associated reaction at second exothermic peak was not affected by pressurization. A prior study found similar results during PDSC with pressurization by nitrogen gas, similar results were gained over the pressure range of 0.1–2.1 MPa³⁰⁾. These results demonstrate that the ambient

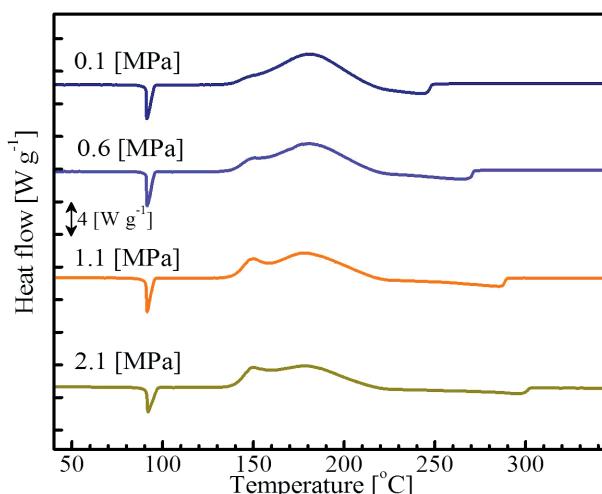
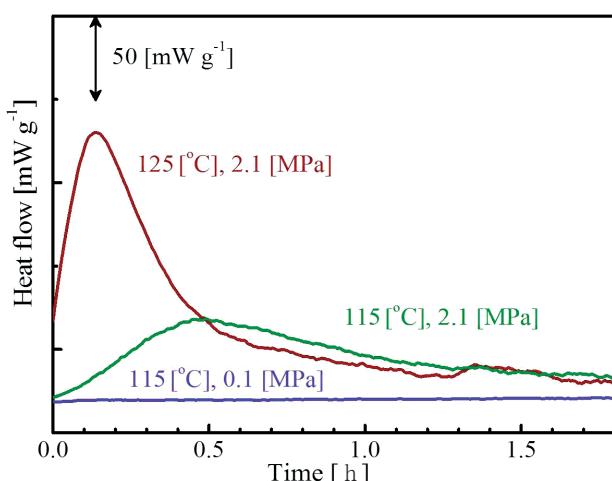


Figure 2 The results of PDSC trials with ADN (5 K min^{−1}).

Table 1 Summary of PDSC results.

P [MPa]	Q_{DSC} [kJ g ⁻¹]	T_{DSC} [°C]
0.1	1.9	136
0.6	1.9	136
1.1	1.9	136
2.1	1.7	135

**Figure 3** The results of PDSC isothermal test with ADN.

gas (nitrogen and argon in this case) does not have an effect on the thermal decomposition of ADN.

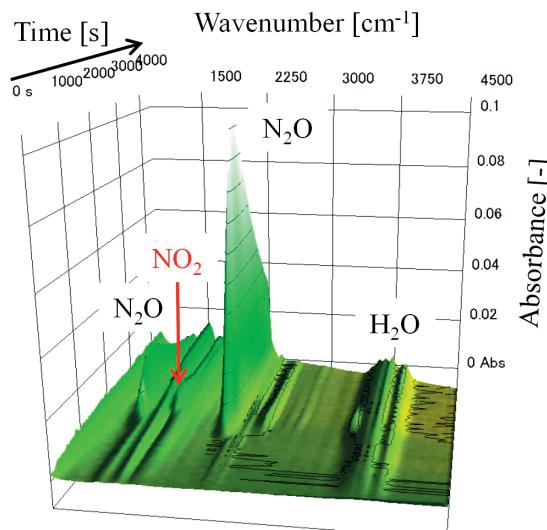
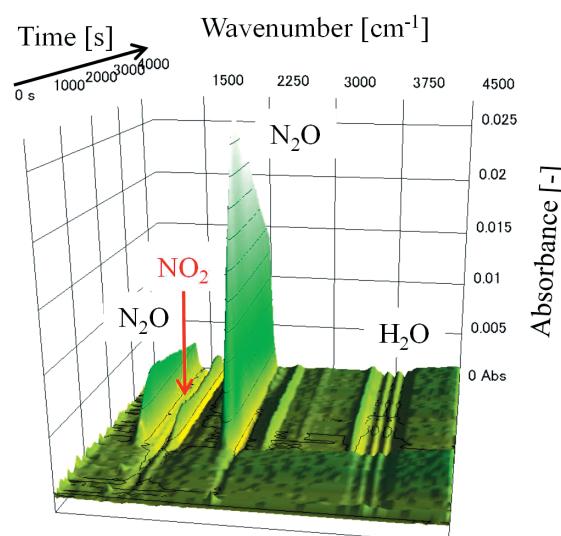
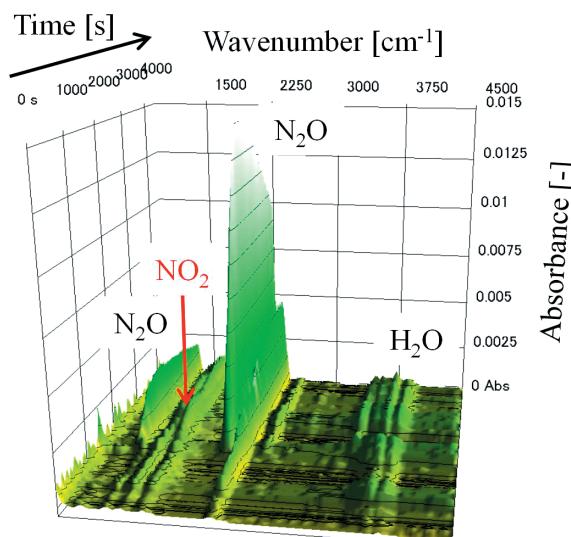
Endotherm events were observed from 220 °C, and their shapes became broad as surrounding pressure increased. Analyzes in condensed phase during heating by Raman spectrometry in our previous study showed that the endothermic events come from vaporization of AN. The vaporization is inhibited and AN decomposes exothermically in the condensed phase when the surrounding pressure was high³⁰.

Figure 3 summarizes the exothermal behavior observed during isothermal tests under 0.1 and 2.1 MPa as a means of examining the low temperature reactions in detail. An exotherm was generated only under the pressurized conditions and, from the shape of the peak, this reaction seems to be autocatalytic reaction. No other peaks were observed, even upon prolonged heating of the ADN, showing that the initial reaction did not trigger other subsequent reactions.

3.2 Effect of pressure on the evolved gases during ADN decomposition

Figures 4–7 show 3D IR spectra of the evolved gas obtained from ADN decomposition over time under 0.1, 1.1, and 2.1 MPa. At 0.1 and 1.1 MPa, peaks attributed to N₂O (3500–3400, 2250–2100 and 1350–1200 cm⁻¹), NO₂ (1650–1550 cm⁻¹) and H₂O (4000–3400 and 2000–1300 cm⁻¹) are observed. However, at 2.1 MPa, NO₂ is evidently no longer generated.

Figure 8 summarizes the generation of N₂O and NO₂ during heating under each pressure, based on the absorbances at 1338 and 1624 cm⁻¹. At atmospheric pressure (0.1 MPa), N₂O was produced beginning at 138 °C

**Figure 4** 3D IR spectrum of evolved gases from ADN decomposition (0.1 MPa).**Figure 5** 3D IR spectrum of evolved gases from ADN decomposition (0.6 MPa).**Figure 6** 3D IR spectrum of evolved gases from ADN decomposition (1.1 MPa).

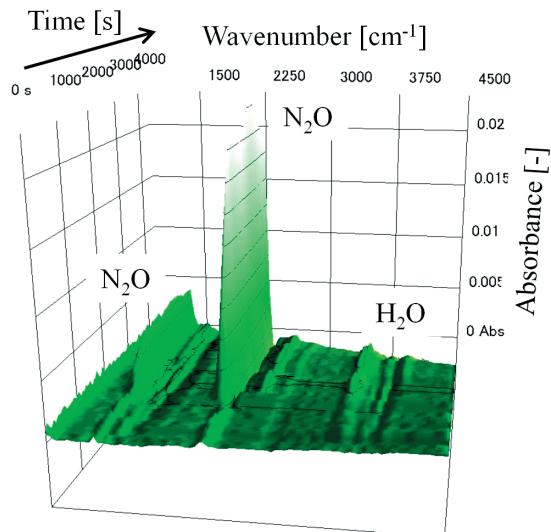


Figure 7 3D IR spectrum of evolved gases from ADN decomposition (2.1 MPa).

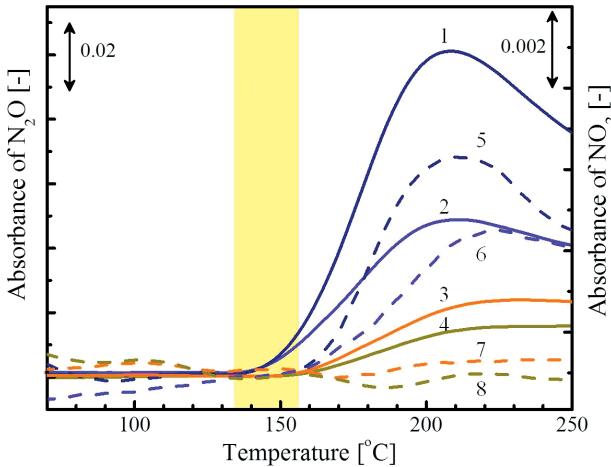


Figure 8 Generation gases from ADN during heating (PDSC-IR). (1) N₂O at 0.1 MPa. (2) N₂O at 0.6 MPa. (3) N₂O at 1.1 MPa. (4) N₂O at 2.1 MPa. (5) NO₂ at 0.1 MPa. (6) NO₂ at 0.6 MPa. (7) NO₂ at 1.1 MPa. (8) NO₂ at 2.1 MPa.

which is almost equal to the value of T_{DSC} . NO₂ was evolved from approximately 150 °C, thus, the onset of N₂O generation was about 15 K higher than T_{DSC} under pressure as shown in Table 2 although the exothermic peak in PDSC curve was remarkable. These results indicate that the exothermic reaction observed during the early stage of decomposition under pressure was not the N₂O-generation reaction shown in Equation (1), which is typically considered to be the main reaction associated with the thermal decomposition of ADN. The ratio of the intensities of the N₂O and NO₂ peaks at 40 min under 0.1 and 1.1 MPa were 16:1 and 25:1, respectively, demonstrating that the relative amount of NO₂ decreased with increasing pressure. Therefore it is thought that reactions involving the release of NO₂ occurred preferentially throughout the initial stage of decomposition.

The PDSC-MS results acquired under 0.1 and 1.1 MPa are shown in Figure 9. The total ion chromatogram (TIC) data provide evidence that the start temperature of onset

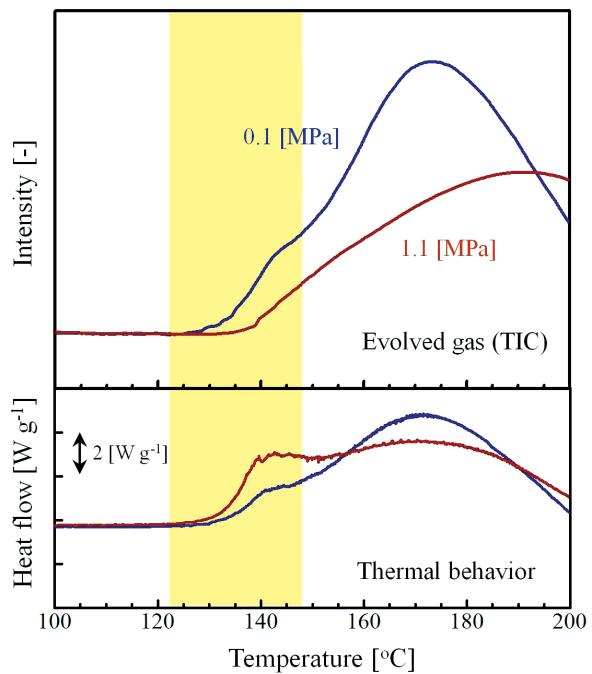


Figure 9 PDSC-MS total ion count data acquired during heating of ADN at 0.1 MPa and 1.1 MPa.

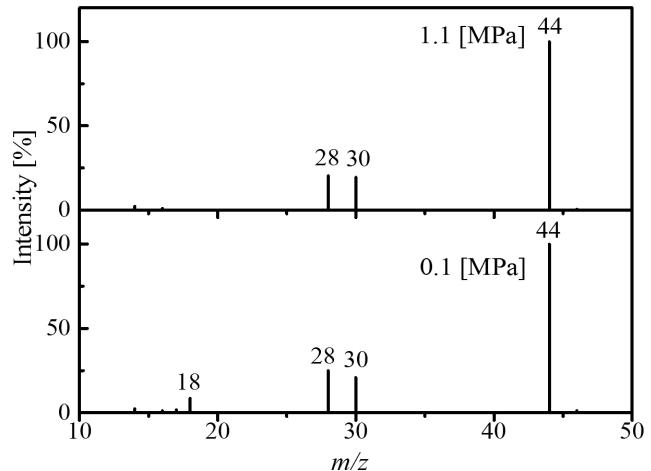


Figure 10 Mass spectra of evolved gases from ADN between 125 and 145 °C.

temperature for gas generation at 1.1 MPa was 15 K higher than at 0.1 MPa. Therefore, only a minimal amount of gaseous product was released during the first exotherm. The mass spectra of the evolved gases obtained between 125 and 145 °C were shown in Figure 10. A peak at $m/z = 18$ (corresponding to H₂O) is not observed in the case of the 1.1 MPa trial, while the remaining gaseous products which are thought to be N₂O ($m/z = 44$, 30 and 28) and N₂ ($m/z = 28$) are essentially the same at both pressure. These data indicate that H₂O was consumed by condensed phase reactions.

3.3 ADN condensed phase thermal decomposition mechanism of ADN during the initial stage

Important information concerning the initial stage of the thermal decomposition of ADN was generated by the experimental work in this study. Specifically, it can be said that

- (i) An exothermic reaction proceeds,
- (ii) the presence of

Table 2 Onset temperatures for N₂O generation during PDSC-IR trials.

P [MPa]	T _{N₂O} [°C]
0.1	132
1.1	140
2.1	146

NO₂ affects the condensed phase decomposition in condensed, and (iii) no gaseous products are observed during this early stage.

In addition, our previous studies^{27,30)} showed that (iv) AN, which is one of the main products of decomposition, is not observed, and (v) the presence of AN in the condensed phase means that the initial exotherm does not appear. Finally, this prior work also suggested that (vi) dinitramic acid [HN(NO₂)₂] is generated by the dissociation of molten ADN and subsequently reacts with CuO to form copper dinitramide during the initial stage of decomposition as in Equations 3 and 4.



The above points can be used to propose a thermal decomposition mechanism for condensed phase ADN. We suggest that, initially, the ADN melts and dissociates in Equations (3) or (5).



Once in the liquid phase, it is thought that almost all of ADN dissociates as in Equation (5), since the stability of HN(NO₂)₂ is much lower than that of N(NO₂)₂⁻^{32,33)}. Subsequently, NO₂ is generated as in Equation (6).



There are several possible reactions involving this NO₂. These include the oxidation of NH₃, as in Equations (7) and (8).



In addition, nitric acid, N(NO₂)₃ and N₂O₄ could be generated, as in Equations (9), (10), and (11).

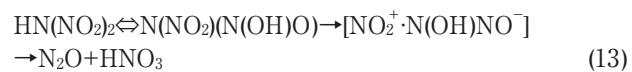


From points (i) and (iii) above, it is highly probable that Equations 9 and 11 occur in the initial exothermic reaction. The H₂O in Equation (9) is thought to come from the decomposition of ADN or from water occluded in the ADN crystals. HN(NO₂)₂, N(NO₂)₂⁻ and HNO₃ have an equilibrium relation, as Equation (12).



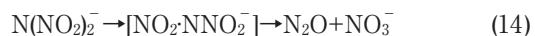
Although almost all the molten ADN exist as NH₄⁺ and N(NO₂)₂⁻, HN(NO₂)₂ tends to form with as the concentration of HNO₃ is increased by the reaction in Equation (9). Since HN(NO₂)₂ is much less stable than N(NO₂)₂⁻, it decomposes

immediately after generation, as in the Equation (13).



The formation of additional HNO₃ by this process reinforces the reaction in Equation (12), thus generating more HN(NO₂)₂ and promoting the overall decomposition. It should be noted that AN is also produced in Equation (12). HNO₃ is lost not only by the reaction in Equation (12) but also via the oxidation of NH₃ and by vaporization. In contrast, the AN accumulates because it is more stable than HNO₃. Point (v) above suggests that the initial reaction is inhibited by the generation of AN. It is thought that in the initial stage of ADN decomposition, HN(NO₂)₂ is generated and subsequently decomposed by the formation of NO₂, while the concentration of AN in the condensed phase gradually increases as the reaction proceeds. This forces the reaction in Equation (12) to the left such that the amount of HN(NO₂)₂ decreases. The observation that the thermal decomposition of ADN is promoted under a NO₂ atmosphere agrees with the reports of Oxley¹⁶⁾ and Vyazovkin¹⁷⁾.

The results of the present study show that the exothermic reaction that takes place at higher temperatures, in the vicinity of 175 °C under the conditions in this work, generates N₂O and is unaffected by pressure. Furthermore, the analysis of the condensed phase composition in our previous study demonstrated that AN was the main product at this temperature. This reaction is believed to consist of the decomposition of N(NO₂)₂⁻ to N₂O and NO₃⁻ via the transition state compound [NO₂:NNO₂⁻] as in Equation (14).



The other N₂O-generating reaction is thought to be the decomposition of AN evolved from the prior degradation of the ADN. In the PDSC trials, an endotherm was observed after two exotherms and the intensity of this endotherm was reduced at higher pressures. These data suggest that the AN that would otherwise have vaporized at normal pressure instead remained in the condensed phase and decomposed exothermically.

4. Conclusion

The mechanisms associated with the initial stage of the thermal decomposition of ADN were investigated based on assessing the thermal behavior and evolved gases exhibited by ADN heated to high temperatures under pressure. Exothermic reactions at this initial stage became more significant with increases in pressure. The results of evolved gas analysis showed that the initial reaction involves NO₂ generated exothermically from the condensed phase. During the thermal decomposition of ADN, NO₂ promotes the generation and decomposition of highly reactive material, HN(NO₂)₂ to AN and N₂O. As the amount of AN in the condensed phase increases, it is thought that the decomposition of N(NO₂)₂⁻ to NO₃⁻ and N₂O becomes the primary process.

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