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Thermal behavior of ammonium dinitramide and amine nitrate mixtures

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Abstract

This paper focuses on the thermal behavior of mixtures of ammonium dinitramide (ADN) and amine nitrates. Because some mixtures of ADN and amine nitrate exhibit low melting points and high-energy content, they represent potential liquid propellants for spacecraft. This study focused on the melting behavior and thermal-decomposition mechanisms in the condensed phase of ADN/amine nitrate mixtures during heating. We measured the melting point and exothermal behavior during constant-rate heating using differential scanning calorimetry and performed thermogravimetry–differential thermal analysis–mass spectrometry (TG–DTA–MS) to analyze the thermal behavior and evolved gases of ADN/amine nitrate mixtures during simultaneous heating to investigate their reaction mechanisms. Results showed that the melting point of ADN was significantly lowered upon the addition of amine nitrate with relatively low molecular volume and low melting point. TG–DTA–MS results showed that the onset temperature of the thermal decomposition of ADN/amine nitrates was similar to that of pure ADN. Furthermore, during thermal decomposition in the condensed phase, ADN produced highly acidic products that promoted exothermic reactions, and we observed the nitration and nitrosation of amines from the dissociation of amine nitrates.

Keywords Ammonium dinitramide · Amine nitrate · Energetic ionic liquid propellant · Thermal analysis · Evolved-gas analysis

Introduction

Energetic materials are currently evaluated with regard to their performance and their current or potential impact on health and the environment [1, 2]. Hydrazine is widely used as a liquid monopropellant for the attitude control of rockets and space satellites because it readily decomposes to form hot gases in the presence of catalysts and can be stored at room temperature. However, this compound is also highly toxic and generates combustible vapors, making it difficult to handle and reducing its operability for spacecraft. To address these issues, replacing hydrazine with a less toxic monopropellant would be beneficial. Herein, we focused on ammonium dinitramide (ADN), which has attracted attention as a novel environmentally friendly (or "green") oxidizer for solid rocket propellants; ADN has replaced ammonium perchlorate because it possesses high oxygen balance, can provide suitable energy levels, and is a halogen-free compound [2, 3]. ADN-based liquid propellants are deemed potential replacements for hydrazine [4–9]. ADN can generate more energy than hydrazine while being less toxic, and because the melting point of ADN is 92 °C [4–7], it exists as a solid at room temperature and must be transitioned from solid to liquid before use. Previous studies reported that ADN could be dissolved in water and/or methanol to allow its use as a liquid propellant [8, 9]. These propellants are close to being suitable for use in real-world applications, but continue to

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face challenges related to ignition and combustion owing to the presence of the solvent. A previous study described the successful preparation of ADN-based liquids at room temperature by forming a eutectic mixture with solid fuels, monomethylamine nitrate (MMAN), and urea, with kinetics analysis revealing that the liquid exhibited higher stability than pure ADN in the liquid phase [10]. Several studies have investigated the eutectic behavior of energetic materials [11–13] because many devices use a mixture of energetic oxidizers and fuels. Eutectic mixtures such as these are called deep eutectic solvents and share properties with ionic liquids [14], which exhibit desirable characteristics for liquid propellants, including low volatilities and low liquidus temperatures [15]. Low volatility decreases the risk of exposure during handling, as well as the threat of explosion, and low liquidus temperatures enable the preparation of high-energy liquid propellants based on the absence of solvents. Previous studies of energetic ionic liquid propellants (EILPs) indicate that their use in spacecraft requires proper design. In our previous study, we observed that amine nitrates significantly decrease the melting point of ADN [10, 16, 17]. In the present study, we confirmed the thermal characteristics of ADN/amine nitrates and investigated the influences of amine nitrates on the mechanisms associated with ADN melting point and thermal decomposition using differential scanning calorimetry (DSC) and thermogravimetry–differential thermal analysis–mass spectrometry (TG–DTA–MS) for thermal and evolved-gas analyses. In the investigation of energetic materials, DSC is generally used to understand not only phase change behavior [11–13, 18] but also long term stability [19] along with energy generation behavior from condensed-phase reactions [20, 21]. TG–DTA–MS is also used to analyze the thermal-decomposition mechanism [16, 21–23].

Materials

ADN and amine nitrates, MMAN, dimethylamine nitrate (DMAN), diethylamine nitrate (DEAN), trimethylamine nitrate (TMAN), cyclohexylamine nitrate (CyAN), monoethanolamine nitrate (MEAN), and ammonium nitrate (AN) were used as samples. ADN was obtained from Hosoya Pyro-engineering Co., Ltd. (Tokyo, Japan). MMAN, TMAN, and MEAN were synthesized in our laboratory. Methylamine (40%) aqueous solution, trimethylamine (30%) aqueous solution, and ethanolamine (Wako Pure Chemical Industries, Ltd., Osaka, Japan) were reacted with nitric acid (1.38 g cm^{-3}; Wako Pure Chemical Industries, Ltd.) and dried under vacuum. DMAN, DEAN, and CyAN were obtained from Showa Chemical Co., Ltd. (Tokyo, Japan), and AN was obtained from Wako

Pure Chemical Industries, Ltd. The purity of DMAN, DEAN, and CyAN was over 98.5% and that of AN was over 99.0%. The reagents were used without further purification. The reagents were used without further purification. ADN was mixed with each amine nitrate in a 1:1 mass ratio.

Experimental

The eutectic behaviors of ADN/amine nitrates under heating were visually observed. Samples were prepared by physically mixing 1 g of ADN and the amine nitrates in glass bottles. The sample bottles were stored in a thermostatic oven at 10 °C, 35 °C, and 60 °C for several hours under atmospheric pressure to evaluate whether the samples melted. Since Sécordel [13] reported binary ADN-AN phase diagrams, and as the calculated melting point showed good agreement with experimental data under the assumption of an ideal solution, the melting points of the samples were compared using calculations from Le Chatelier–Schröder's equation [24]:

$$\text{ADN: } T = \left(\frac{1}{T_{f_{ADN}}} - \frac{R}{\Delta H_{f_{ADN}}} \ln X_{ADN} \right)^{-1} \tag{1}$$

$$\text{Additives: } T = \left\{ \frac{1}{T_{f_{additive}}} - \frac{R}{\Delta H_{f_{additive}}} \ln(1 - X_{ADN}) \right\}^{-1}, \tag{2}$$

where T is the melting point of the mixture, T_f is the melting point of each element, ΔH_f is the fusion heat for each element, X is the molar ratio, and R is the gas constant. T_f was defined as the onset temperature of the endothermic peak of DSC measurements. The experimental melting point range obtained from the oven temperature when a part or the entirety of the samples melted were compared with the calculated eutectic point, i.e., the intersection of Eqs. (1) and (2). The thermal behavior of the samples was characterized using sealed-cell DSC (SC-DSC; Shimadzu DSC-60 Plus; Shimadzu, Kyoto, Japan). DSC was calibrated using the melting temperature and enthalpy change for 99.99% indium. Samples containing 1 mg of either pure ADN or an ADN/amine nitrate mixture were loaded into a high-pressure stainless steel cell. ADN and amine nitrates were prepared by physically mixing them in the cells. They were sealed under atmospheric air and then heated from 30 to 350 °C at 5 K min^{-1}. During sample heating, the attendant mass loss and decomposition gases were simultaneously analyzed using TG–DTA–MS. The TG–DTA–MS apparatus comprised two units: a TG–DTA instrument (NETZSCH TG–DTA 2000SE; Netzsch, Selb, Germany) and a mass spectrometer (JEOL JMS-Q1500GC; JEOL, Tokyo, Japan). Samples were loaded

into open aluminum pans and heated to 350 °C at 5 K min^{-1} under helium flow (100 mL min^{-1}). The evolved gases were transferred to the mass spectrometer operating at an oven temperature of 250 °C in electron-impact ionization mode.

Results and discussion

Eutectic behavior

Table 1 shows a comparison of the eutectic behaviors of ADN/amine nitrates between predictions from Eqs. (1) and (2) and the experimental results. In this study, we deemed that ADN and amine nitrates did not react during this experiment because gas generation and a change in the color of the liquid was not observed by sight. At 10 °C, the states of ADN/TMAN, ADN/DEAN, ADN/CyAN, and ADN/AN were solid, as shown in the predictions; however, ADN/MMAN, ADN/DMAN, and ADN/MEAN were partly liquid. This indicates that the eutectic point was lower than that predicted from Le Chatelier–Schröder's equation, which includes thermodynamic parameters. This result suggests that the depressed melting points of ADN/MMAN, ADN/DMAN, and ADN/MEAN were controlled by both thermodynamic factors and other parameters. One possible explanation involves chemical interactions between molecules. MMAN, DMAN, and MEAN have comparatively small cations, and when these are mixed with ADN, chemical interactions between methylamine, dimethylamine, or ethanolamine cations and dinitramide anions in ADN increase, with this interaction decreasing the molecular balance of ADN to a higher degree than that observed in other additives, thereby resulting in a significant depression of the melting point. At 60 °C, the state of all samples was partly or completely liquid. Amine nitrates can lower the melting point of ADN to near its predicted

eutectic point according to Le Chatelier–Schröder's equation by not being dependent upon the type of amine cation.

Thermal behavior

SC-DSC results for ADN, amine nitrates, and their mixtures are shown in Fig. 1. In the pure materials, one or two exothermic peaks caused by thermal decomposition were observed during heating. In the case of pure ADN, the endotherm from the melting point was observed at 92 °C, and two major exotherms from thermal decomposition appeared between 135–210 °C (first peak) and 210–260 °C (second peak). The first peak described the thermal decomposition of ADN in the condensed phase to AN and N$_2$O [25–38] and appeared to be a collection of two peaks at around 165 °C and 185 °C. At low temperature in the first peak, the reaction likely involved dinitramic acid (HDN) and NO, which are highly reactive materials derived from ADN decomposition (Eqs. 3, 4) [38].

$$NH_4^+N(NO_2)_2^- \rightarrow NH_3 + HN(NO_2)_2 \tag{3}$$

$$HN(NO_2)_2 \rightarrow HNO_3 + N_2O \tag{4}$$
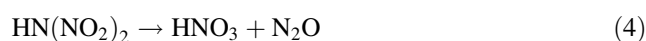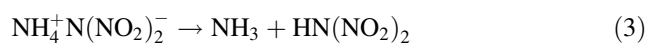
At high temperature in the first peak, the main reaction of ADN decomposition occurred according to Eq. (5) [30].

$$NH_4^+N(NO_2)_2^- \rightarrow NH_4^+NO_3^- + N_2O \tag{5}$$
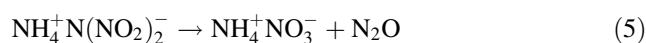
At the second peak, AN further decomposed to produce the following gaseous products (Eq. 6) [25, 31].

$$NH_4^+NO_3^- \rightarrow N_2O + 2H_2O \tag{6}$$

In the case of pure amine nitrates, they decompose to amine and nitric acid, followed by further decomposition of these products [31, 32]. In the case of ADN/amine nitrate mixtures, the endothermic peak from melting was not observed; however, exothermic events began at 135 °C, which was a temperature similar to that observed for pure ADN. However, the initial exothermic reaction at the first

Table 1 Melting behaviors of ADN/amine nitrates

|	ADN	MMAN	DMAN	TMAN	DEAN	MEAN	CyAN	AN
Melting point of pure materials (DSC)/°C	92	110	76	136	105	51	115	168
Melting point of the mixture at eutectic point with ADN (Calc.)/°C	92	28	31	53	52	45	69	47
State at 10 °C	Solid	Liquid + Solid	Liquid + Solid	Solid	Solid	Liquid + Solid	Solid	Solid
State at 35 °C	Solid	Liquid	Liquid + Solid	Liquid + Solid	Solid	Liquid	Solid	Solid
State at 60 °C	Solid	Liquid	Liquid + Solid	Liquid + Solid	Liquid + Solid	Liquid	Liquid + Solid	Liquid
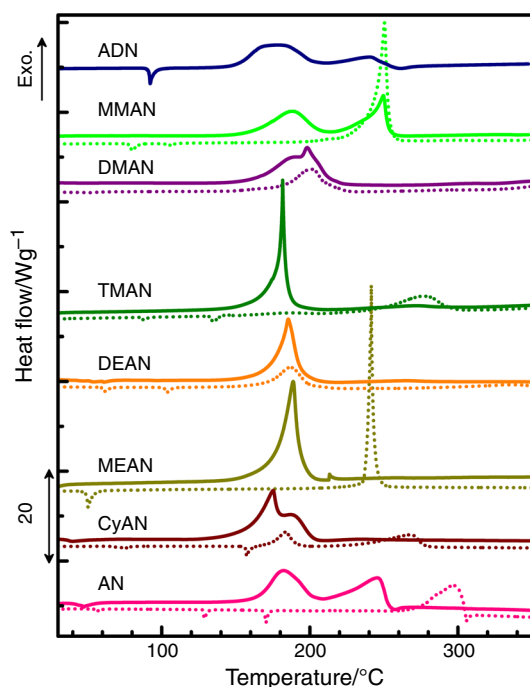
Fig. 1 SC-DSC results for ADN/amine nitrates. Dotted lines show the results for pure amine nitrates, and solid lines show the results for the ADN and ADN/amine nitrate mixtures

peak ($\sim$ 165 °C) was not observed. Because this inhibition was observed upon the addition of all amine nitrates used in this study, we observed that NO_3^- inhibited the generation of highly reactive materials, such as HDN. Kazakov [28] showed the equilibrium reaction of the dinitramide anion in the presence of HNO_3 (Eq. 7), which showed that the generation of HDN is decreased by the addition of amine nitrates. The reaction in Eq. (7) might describe one of the explanations for ADN-based EILP having higher stability relative to pure ADN liquid.

$$N(NO_2)_2^- + HNO_3 \rightleftarrows HN(NO_2)_2 + NO_3^- \qquad (7)$$

The exotherms obtained from the decomposition of amine nitrates varied by sample. In MMAN and DMAN, exotherms were observed at higher temperatures than that for the first peak and at the same temperature as that for the decomposition of pure amines. On the other hand, no peaks were observed for MEAN, TMAN, and CyAN following the first peak. The second exothermic peak due to the decomposition of AN was not observed for ADN/amine nitrate mixtures even though AN is the main product of ADN decomposition (Eq. 6). It is considered that ADN or an intermediate product of its decomposition is consumed during the reaction with amine nitrate, and hence, AN was not generated during decomposition. The heat value per ADN mass of the first peak was 1.8 kJ g^{-1} for pure ADN, 4.4 kJ g^{-1} for ADN/MMAN, 5.8 kJ g^{-1} for ADN/TMAN, and 7.2 kJ g^{-1} for ADN/MEAN. The increase in the heat

value at the first peak for ADN/MMAN, ADN/TMAN, and ADN/MEAN indicated that these types of amine nitrates reacted with ADN in the condensed phase in the same temperature range as that of the decomposition of ADN. The presence or absence of an exotherm after the first peak identifies a possible difference in the reactivity of amines generated by dissociation or products from the reaction between ADN and amines. Although the oxygen balances of the mixtures were negative (ADN/TMAN: − 39.5%, ADN/MEAN: − 12.9%), exothermic peaks were not observed at the same temperatures as those of pure amine nitrates in ADN/TMAN and ADN/MEAN. These results show that TMAN and MEAN have especially high reactivity with ADN. The degree of reaction between ADN and DEAN could not be evaluated under these experimental conditions because the exothermic peaks of DEAN appeared in the same temperature range as that of ADN. The ADN/AN mixture did not show an increase in the heat value of the first peak. A previous study reported that AN hardly dissociates to NH_3 in the condensed phase [41]; therefore, AN did not react with ADN in the condensed phase under this experimental condition.

Decomposition mechanism of ADN/amine nitrate mixtures

The TG–DTA curves for ADN, MMAN, DMAN, TMAN, ADN/MMAN, ADN/DMAN, and ADN/TMAN are shown in Fig. 2. ADN exothermically decomposed with mass loss at 135 °C and an endotherm was observed after the exotherm. MMAN showed endotherms with a mass loss resulting from vaporization from 155 °C. DMAN showed a
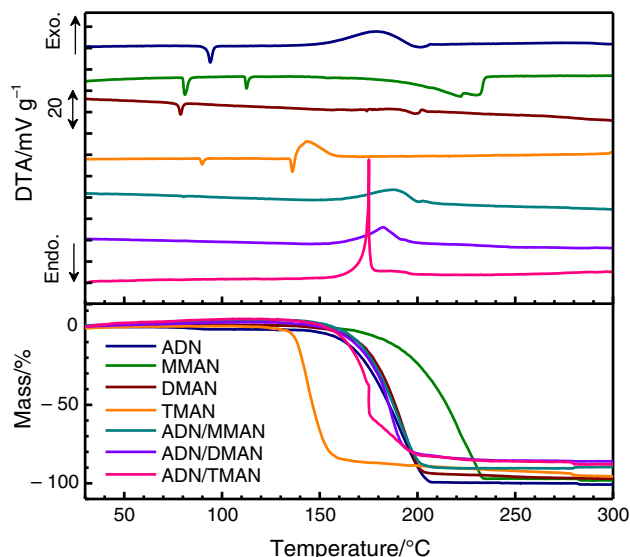

**Fig. 2** TG–DTA results for ADN, MMAN, DMAN, TMAN, and their mixtures

small endotherm with mass loss from 140 °C and two exotherms from 150 °C. TMAN showed exotherms and mass loss from 125 °C and endotherms derived from the melting point in the middle of the exotherm. In the case of ADN/amine nitrate mixtures, exotherms were observed beginning at $\sim$ 135 °C, which was the same temperature as the onset temperature for ADN decomposition. In ADN/MMAN and ADN/TMAN results, no endotherm or exotherm derived from pure MMAN and TMAN was observed. The peak shapes for ADN/DMAN and ADN/TMAN were sharper than those for pure ADN. Specifically, the peak shape for ADN/TMAN was the sharpest in the ADN/amine nitrate samples. These results showed that ADN and amine nitrates reacted exothermically in the condensed phase, even in an open pan; furthermore, the highest reactivities with ADN were observed in TMAN, DMAN, and MMAN in descending order and in agreement with the SC-DSC results. However, ADN and ADN/amine nitrates showed one major exotherm, unlike the SC-DSC results. One explanation is that the reaction products from the exothermic reaction at 135 °C transferred to the gas phase.

The MS spectra of evolved gas during the decomposition of each sample in each temperature range are shown in Fig. 3. In the case of pure ADN, gaseous products with mass/charge (m/z) ratios of 17, 18, 28, 30, 44, 46, and 63 were generated, which we attribute to an exothermic reaction generating N_2O (m/z = 44, 30, and 28), N_2 (m/z = 28), NO_2 (m/z = 46 and 30), HNO_3 (m/z = 63, 46, and 30), and H_2O (m/z = 18 and 17). The main gas product throughout the reaction was NO, which was derived from ADN decomposition (Eq. 5). A gas with m/z = 63 (HNO_3) was generated later in the reaction, with AN being possibly generated (Eq. 5) and dissociated in the gas phase. In the case of MMAN, gaseous products with m/z = 18, 28, 30, and 31 were observed in low temperature ranges and immediately following the initiation of mass loss. This suggested that MMAN dissociation to methylamine (m/z = 30, 31, and 28) and nitric acid (m/z = 46, 30, and 63) had occurred, as mentioned in previous studies [39, 40]. Although a peak at m/z = 63 was not observed, HNO_3 was consumed in the condensed phase reaction. The main gaseous products in the high temperature range were m/z = 17, 18, 27, 28, 29, 42, 43, 44, and 46. According to previous studies [39, 40], these gaseous products were likely derived from H_2O (m/z = 18 and 17), N_2 (m/z = 28), CO_2 (m/z = 44 and 28), N_2O (m/z = 44, 30, and 28), $HCONH_2$ (m/z = 45, 29, 17, and 44), CH_3ONO (m/z = 30, 29, 28, and 31), NO_2 (m/z = 30 and 46), and HCN (m/z = 27 and 26) and were generated by further decomposition of methylamine and nitric acid. Although the main products in this study (generation of m/z = 42 and 43) were not mentioned in previous studies, it is possible that these

peaks were derived from methyl diazohydroxide via nitrosation of methylamine as follows:

$$H_3CNH_2 \xrightarrow[-H_2O]{+HNO_2} H_3NHNO \rightarrow H_3CN{=}NOH \qquad (8)$$
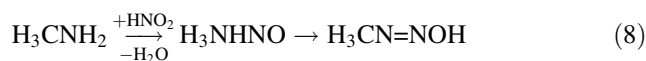
However, methyl diazohydroxide is unstable under acidic conditions and decomposes to CH_3^+ and N immediately after generation [42]:

$$H_3CN = NOH \xrightarrow[-H_2O]{+H^+} H_3CN{\equiv}N \rightarrow CH_3^+ + N_2 \qquad (9)$$
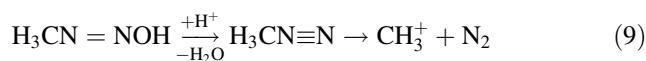
Therefore, it is also possible that m/z = 42 and 43 identifies other species, such as isocyanic acid, fulminic acid, or ethyleneimine. The main evolved gas from the decomposition of ADN/MMAN rarely differed from that of pure ADN and pure MMAN. This indicated that their thermal decomposition also occurred in mixture form. During the early stage of decomposition, monomethylamine (m/z = 31) was not observed, as methylamine was consumed by the reaction with ADN. The peak at m/z = 76, which was thought to identify nitromethylamine or methyl nitrate, appeared at a lower level in the main reaction range. Nitromethylamine is generated via nitration of methylamine:

$$H_3CNH_2 + NO_2^+ \rightarrow H_3CNHNO_2 \qquad (10)$$

NO_2^+ is an intermediate of HNO_3 decomposition [42, 43], and its generation is promoted under acidic conditions. Nitromethylamine decomposes under acidic conditions as follows [34]:

$$H_3CNHNO_2 + H^+ \rightarrow CH_3^+ + N_2O + H_2O \qquad (11)$$
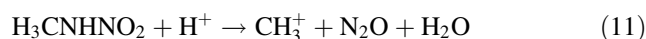
Methyl nitrate is generated by the reaction of CH_3^+ (Eqs. 9, 11) with NO_3^- from ADN decomposition. The peak at m/z = 42 became significantly lower as compared with results observed for pure MMAN. Because ADN decomposition produces acidic products such as $HN(NO_2)_2$ and HNO_3, it is possible that the reactions described in Eqs. (8) and (9) were promoted. The generation of gaseous products at m/z = 59 and 81 was more substantial and attributable to methyl formamide (m/z = 59, 30, and 28) and 1,3,5-triazine (m/z = 81, 54, 28, and 27), respectively. Methyl formamide is generated from the reaction between CH_3^+ (Eqs. 9, 11) and formamide, and 1,3,5-triazine is generated by the polymerization of three HCN molecules, the formation of which is promoted by ADN. Additionally, formamide and HCN are products of MMAN decomposition [40].

Evolved gas from DMAN contained *N*-nitrosodimethylamine (m/z = 74, 42, 43, and 15) as a major decomposition product, and dimethylamine (m/z = 45) was rarely observed at the early stage of decomposition. These results showed that DMAN initially dissociated to dimethylamine
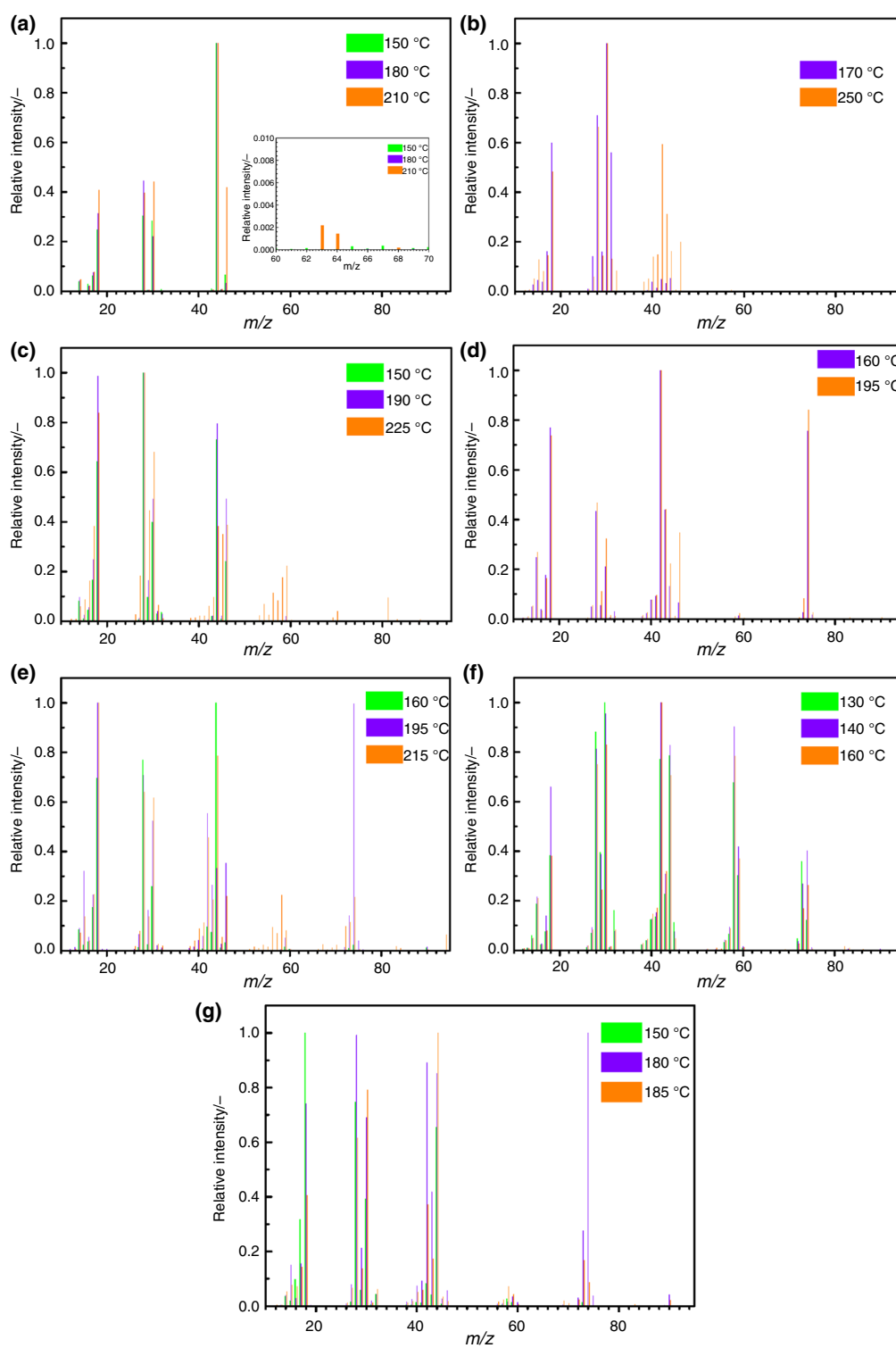
Fig. 3 MS spectra of evolved gas from sample decomposition at each temperature. **a** ADN, **b** MMAN, **c** ADN/MMAN, **d** DMAN, **e** ADN/DMAN, **f** TMAN, and **g** ADN/TMAN
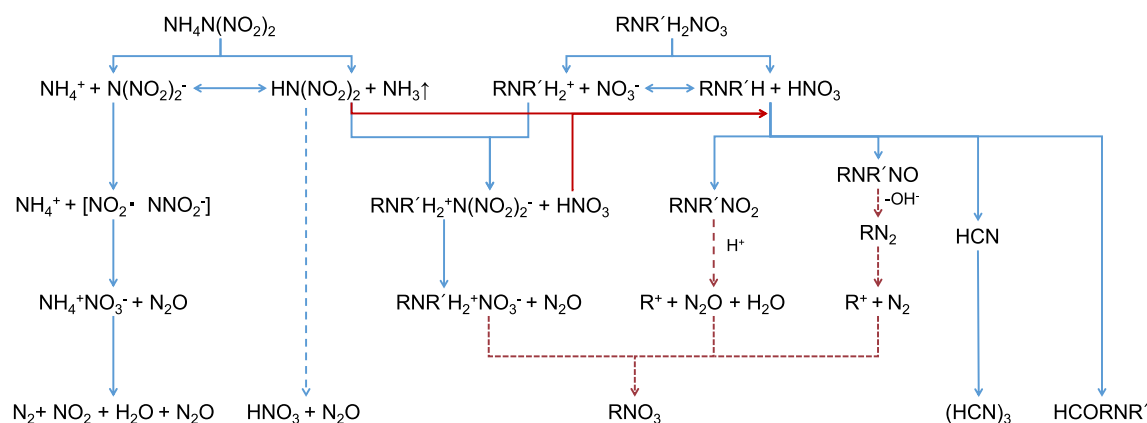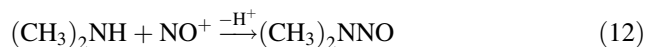
Fig. 4 Reaction scheme of ADN/amine nitrate mixtures in the condensed phase and that based on our results

and nitric acid and that dimethylamine underwent nitrosation by NO^+ from nitric acid.

$$(CH_3)_2NH + NO^+ \xrightarrow{-H^+} (CH_3)_2NNO \tag{12}$$

Secondary N-nitrosoamine is relatively stable [44]; therefore, N-nitrosodimethylamine generated during decomposition likely vaporized without further decomposition. Because peaks derived from N,N-dimethylformamide (m/z = 73, 44, and 42) were also observed, the DMAN-decomposition route is likely similar to that of MMAN. The ADN/DMAN mixture generated N-dimethylnitrosoamine and N_2O, similar to results observed from pure samples. This indicated that their subsequent thermal decomposition also occurred, even in mixture form, similar to ADN/MMAN. The difference from crude ADN and DMAN was the generation of gas with m/z = 90, which was attributed to N-nitrodimethylamine. The results suggested that ADN promoted nitration of amines derived from dissociation from amine nitrates. TMAN decomposition generated trimethylamine (m/z = 58 and 59) mainly from dissociation and, given the presence of trimethylamine, underwent nitrosation to generate nitrosodimethylamine (m/z = 74, 42, 43, and 15). In the ADN/TMAN mixture, although nitrosodimethylamine was generated, trimethylamine was rarely observed during decomposition. These results showed that ADN promoted nitrosation of amines from amine nitrates during the condensed phase. Because the ratio of amines in evolved gas was higher than MMAN and DMAN, a large amount of amines reacted with ADN. This might explain why ADN/TMAN exhibited significantly severe exothermic reactions according to SC-DSC and TG–DTA results as compared with those observed for pure ADN and TMAN.

The main scheme describing ADN/amine nitrate decomposition when amines are represented by primary or secondary aliphatic amines is shown in Fig. 4. The main reaction in the condensed phase involves separate decomposition of ADN and amine nitrate, even in the case of their mixture. ADN generates highly acidic products, such as $HN(NO_2)_2$ and HNO_3, through decomposition, with these products promoting nitration and nitrosation of amines dissociated from amine nitrates. Nitroamine and nitrosamine derived from primary amines are unstable and further decompose to carbocations and gaseous products. In the case of tertiary amine nitrates, secondary nitrosamine was produced by reaction with NO^+, with ADN promoting this reaction.

Conclusions

In this study, we analyzed the thermal behavior and evolved gas from ADN/amine nitrate mixtures to elucidate their properties and decomposition characteristics. Adding MMAN, DMAN, and MEAN, which have relatively low molecular volumes and melting points, depressed the ADN melting point, with the degree of melting-point depression lower than that predicted from thermodynamic calculation. Our results suggested that other factors also work between ADN and the amine nitrates. The onset temperature of thermal decomposition of ADN/amine nitrates was similar to that of pure ADN. Nitrate anion inhibited increases in $HN(NO_2)_2$ during the condensed phase, inhibiting the generation of an exotherm during the early stage reaction. Evolved-gas analysis revealed that thermal decomposition of crude ADN and crude amine nitrate in the condensed phase also occurred, even in mixture form. In the cases of ADN/MMAN and ADN/DMAN, the decomposition of crude materials represented the primary reaction, and ADN/TMAN showed different reaction characteristics from those for ADN and TMAN. Additionally, reactivity between ADN and amine nitrates was dependent upon amine levels derived from dissociation. The role of ADN during condensed phase reactions involved the production

of highly acidic products, such as $HN(NO_2)_2$ and HNO_3 and the promotion of nitration and nitrosation of amines derived from the dissociation of amine nitrates, which is thought to occur in mixtures of ADN and any aliphatic amine nitrate.

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