Influence of copper compounds on the exothermic reactions of an ammonium dinitramide-based energetic ionic liquids

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Abstract
We have been developing an ignition system for small satellites that uses energetic ionic liquid propellant (AMU) containing ammonium dinitramide (ADN), monomethylamine nitrate (MMAN), and urea. In this study, we investigated the effect of adding copper compounds to AMU in promoting the exothermic reaction of AMU in the condensed phase and increasing its ignitability by heating. We found that 2 wt% of basic copper nitrate (BCN) can dissolve in AMU. We used differential scanning calorimetry, thermogravimetry-differential thermal analysis, and a digital microscope to observe the condensed-phase reactions of ADN/BCN, MMAN/BCN, urea/BCN, and AMU/BCN mixtures, and we analyzed the thermal behavior to investigate the influence of BCN on their exothermic reactions. Although BCN dissolved by forming a complex with MMAN, it did not affect the initial exothermic reaction of AMU. BCN promoted the exothermic reaction at high temperatures, and the gross calorific value of the condensed-phase reaction was increased. Hence, adding BCN can potentially improve the ignitability of AMU. The promotion of exothermic reactions was attributed to the decomposition of the copper complex to copper oxide, which promotes the exothermic reaction of MMAN and ammonium nitrate, resulting from the decomposition of ADN.

Keywords: ammonium dinitramide, energetic ionic liquid, rocket propellant, thermal analysis, basic copper nitrate

1. Introduction
Small rockets and nanosatellites are becoming increasingly important for aerospace applications. The costs of handling liquid propellants need to be reduced to realize miniaturized and lightweight systems for upper-stage rockets and nanosatellites[1]. Hydrazine is widely used as a liquid propellant because it readily decomposes to form hot gases in the presence of catalysts and can be stored at room temperature. However, handling of hydrazine is difficult and costly because of its high toxicity and inflammability. Ammonium dinitramide (ADN)[2-5] and hydroxylamine nitrate (HAN)[6-8] are expected to emerge as the primary agents for liquid propellants because they can generate more energy and they are much less toxic than hydrazine. One of the problems with realizing ADN- and HAN-based liquid propellants is how to liquefy them because of their relatively high melting points (92 °C and 48 °C, respectively). They are typically dissolved in water and/or methanol when prepared as a liquid propellant; for example, LMP-103[3], FLP-106[3], and SHP-163[6] have ADN/water/methanol/ammonia, ADN/water/N-methylformamide, and HAN/ammonium nitrate (AN)/water/methanol compositions of 63/13.95/18.4/4.65, 64.6/23.9/11.5, and 73.6/3.9/16.3/6.2 (wt %), respectively. Meanwhile, we have focused on forming liquids without liquid solvents[9]
by depressing the freezing point with energetic solid fuels. Eutectic mixtures such as these are called deep eutectic solvents and share properties with ionic liquids; they exhibit desirable characteristics for liquid propellants, including low volatility and low liquidus temperature. Low volatility reduces the risk of exposure during handling and the risk of explosion, and low liquidus temperature enables the preparation of high-energy liquid propellants without solvents. This means that costs can be reduced for the handling, miniaturization, and weight reduction of propellant tanks. In addition, their ease of preparation indicates the suitability of energetic liquid propellants (EILPs) for spacecraft applications, but a proper design is needed.

In previous studies, we successfully prepared ADN-based energetic ionic liquids at room temperature with solid fuels; for example, AMU is a composition of ADN, monomethylamine nitrate (MMAN), and urea that forms a stable liquid at room temperature and was calculated to have a greater propulsion performance (specific impulse) than hydrazine. The current issue for ADN-based EILPs is the development of an ignition system. A simple ignition method is heating. When ADN-based EILPs are heated by a heater or continuous-wave laser, exothermic decomposition of the condensed phase is initiated with generation of gas. The reaction becomes violent over time, and the evolved gas eventually ignites. Because the electric power consumption of spacecraft is limited, propellants should be ignitable at low energy levels. Thus, we have focused on promoting exothermic reactions in the condensed phase to make it easier to initiate ignition by heating. In previous studies, we showed that copper oxide (CuO) promotes the thermal decomposition of ADN and nitrate salts. In the present study, we performed thermal and evolved-gas analyses to evaluate the influence of copper compounds on the thermal characteristics of AMU and the mechanisms associated with thermal decomposition.

2. Experimental

2.1 Materials

Urea, methylamine, and nitric acid were obtained from Wako Pure Chemical Industries, Ltd (Osaka, Japan). ADN was obtained from Hosoya Pyro-engineering Co., Ltd. (Tokyo, Japan). ADN, MMAN, and urea were used to prepare AMU. MMAN was synthesized in our laboratory by the reaction of aqueous solution of methylamine (40%) and nitric acid (1.38 g·cm⁻³) with the resulting product dried under vacuum. A mixture of ADN, MMAN, and urea with a mass ratio of 4/4/2 (AMU442) was prepared. AMU442 exhibited a low freezing point (<0 °C), and its specific impulse, which is an engine performance parameter calculated by using the Chemical Equilibrium Applications software developed by NASA, was greater than that of hydrazine.

The copper compounds used in this study were CuO and basic copper nitrate (BCN) because they are known accelerators for the decomposition and combustion of energetic materials. CuO and BCN were obtained from Kojundo Chemical Laboratory Co., Ltd (Saitama, Japan) and Nihon Kagaku Sangyo Co., Ltd. (Japan), respectively. They were added after the AMU liquefied completely.

2.2 Experimental Procedure

Generally, additives should be dissolved in liquid propellants to prevent the propellant piping from clogging. To evaluate the solubilities of CuO and BCN in AMU, 1 wt% and 2 wt% of the above copper compounds were added to AMU442. The mixtures were stored in a thermostatic oven at 60 °C to facilitate dissolution. Visual observation was used to determine whether the additives had dissolved.

The thermal behavior of the samples was characterized by using sealed cell differential scanning calorimetry (SC-DSC) (DSC-60 Plus; Shimadzu, Japan) and thermogravimetry-differential thermal analysis (TG-DTA) (TG-DTA 2000SE; Netzsch, Germany). For SC-DSC, 1 mg of each sample was loaded into a sealed stainless steel cell. The samples were heated to 400 °C from room temperature at 5 °C min⁻¹. For TG-DTA, 2 mg of each sample was loaded into open aluminum pans and heated to 350 °C at 5 °C min⁻¹ under a helium flow (150 mL·min⁻¹).

The decomposition behavior was observed by using a hot stage and a microscope (Thanko Inc., Dino-Lite Premier M LWD). Approximately 3 mg of each sample was placed in an open aluminum pan and set on the hot stage in an acrylic desiccator with an argon flow (150 mL·min⁻¹). The samples were heated to 400 °C from room temperature at 5 °C min⁻¹ while the decomposition behavior was observed with the microscope.

3. Results and discussion

3.1 Solubility of CuO and BCN in AMU442

Figure 1 shows pictures of the AMU442/CuO and AMU442/BCN mixtures after several hours of storage at 60 °C. We judged that CuO was insoluble in AMU442 because CuO remained at the bottom and color of liquid did not change even under 60 °C storage. On the other hand, 2 wt% of BCN dissolved in AMU442, which resulted in a deep-blue or greenish-blue color. Thus, BCN may have dissolved into AMU442 by forming some compound with ADN, MMAN, or urea. Based on the results, we chose BCN as the additive in this study.

![Figure 1 Visual observation of mixtures after several hours of storage at 60 °C: (a) 1 wt% and (b) 2 wt% of basic copper nitrate (BCN) with AMU442; (c) 2 wt% of copper oxide (CuO) with AMU442.](image)
3.2 Thermal behavior under sealed conditions (SC-DSC)

Figure 2 shows the SC-DSC curves when mixtures of ADN, MMAN, urea, and AMU with 2 wt% of BCN were heated at 5 K·min⁻¹. The onset temperature (T_DSC) and calorific value (Q_DSC) of the exotherms are summarized in Table 1. ADN melted at 92 °C and decomposed exothermically in two steps from about 130 °C. The exotherms were observed mainly due to decomposition of ADN to ammonium nitrate (AN) and nitrous oxide (N₂O) and decomposition of AN to gases, such as N₂, NO₂, N₂O, and H₂O²⁴⁻²⁵. The T_DSC was much lower in the presence of BCN than with pure ADN and was observed immediately after the melting of ADN. On the other hand, the Q_DSC remained almost the same regardless of the presence of BCN. Although BCN made ADN easy to decompose, it did not affect the total amount of energy generated. In the case of MMAN, solid-solid phase transition and melting were observed at approximately 81 °C and 107 °C, respectively. MMAN then decomposed exothermically from 200 °C. The T_DSC was lower in the presence of BCN than with pure MMAN, and Q_DSC was the same regardless of the presence of BCN. Similar to ADN, although BCN made it easy for MMAN to decompose, BCN did not affect the total amount of energy generated. With urea, BCN was not observed to cause any remarkable changes in the thermal behavior. Meanwhile, AMU decomposed exothermically in two steps at about 130 °C and 260 °C. The exothermic behavior of the first peak was very similar to that of ADN/MMAN in our previous study²⁶. In contrast, the temperature of the second exotherm was higher than that of the previous study. Because urea is known to have a stabilizing effect on AN²⁷, urea may have increased the decomposition temperature of nitrates, such as MMAN and AN (i.e., the decomposition product of ADN). In the case of AMU/BCN, the results were unlike those of ADN/BCN. Although the presence of BCN did not affect the T_DSC, it slightly increased the Q_DSC. The temperature of the second exotherm was lower than that of AMU. These results indicate that BCN promoted the exothermic reaction due to the products of the primary reaction.

3.3 Thermal behavior under open conditions (TG-DTA)

Figure 3 shows the TG-DTA curves of the samples at a heating rate of 5 K·min⁻¹. For pure ADN, a major exothermic event with mass loss was observed at 130 °C, and it was completely gasified by 220 °C. MMAN gasified endothermically from 150 °C. Urea decomposed endothermically through multiple steps immediately after melting. For AMU, mass loss began at 130 °C, and one major exotherm was observed at 150 °C. The delayed onset...
of the exotherm was attributed to the counteracting effect of the endothermic reaction of urea. Unlike the SC-DSC curves, ADN, MMAN, and AMU had fewer exothermic peaks and endotherms were observed. These results indicated that endotherms resulted from the vaporization of either AN or MMAN and counteracted the exotherms.

In the case of ADN/BCN, an exotherm was observed from 110 °C. Although the T_DSC was decreased by BCN, similar to the results obtained with SC-DSC, a significant exothermic peak was observed at 120 °C. One factor may have been the difference in atmosphere. In the high-pressure pan used for SC-DSC, the gas resulting from the decomposition remained around the sample as the pressure increased. The thermal behavior of MMAN/BCN was almost the same as that of pure MMAN up to 250 °C, and an exothermic reaction occurred at the end of endotherm. The DTA curve of urea/BCN was almost the same as that of pure urea, but the mass loss between 140 °C and 200 °C occurred at a higher rate than for pure urea. For AMU, the T_DSC was not changed by the presence of BCN, but the exothermic peak at 150 °C became sharper, and a new exothermic peak was observed at 200°C. Thus, BCN promoted the exothermic reaction due to the products from the primary thermal decomposition of ADN and reaction between ADN and MMAN in the condensed phase. In addition, BCN increased the total exothermic value from 0.8 V·s·g⁻¹ to 2.2 V·s·g⁻¹. Considering the ignition of AMU, the conditions of TG-DTA in this study were closer to the initial conditions of a rocket motor than that of the SC-DSC. Increasing the exothermic value of the condensed-phase reactions should help improve the ignitability of AMU.

### 3.4 Condensed-phase reactions of AMU/BCN

Figure 4 presents the condensed-phase reactions of ADN/BCN, MMAN/BCN, urea/BCN, and AMU/BCN at different temperatures. For ADN/BCN, immediately after ADN melted, the color of the condensed phase changed to green. Many bubbles were generated at 100 °C, and the bubbling became more violent at 120 °C. The color of the condensed phase gradually changed to greenish blue until the temperature reached 180 °C, and the generation of bubbles stopped at 180 °C. A violet solid was obtained at 200 °C, and it gradually changed to a black solid with further heating. For MMAN/BCN, MMAN melted at 110 °C and formed a blue liquid in the presence of BCN. The color of the condensed phase changed to green as the temperature increased from 150 °C to 250 °C. The gas generation became remarkable at 230 °C, and a black solid was suddenly obtained with a severe exotherm and gas generation at 250 °C. For urea/BCN, a pale blue liquid formed immediately after the urea melted, and it gradually changed to a dark brown solid. AMU/BCN was blue in color at room temperature. It gradually changed to greenish blue, and bubbles were observed at 120 °C. The bubble generation was most violent at 180 °C, and the color of the condensed phase changed to green. Although the bubbling stopped temporarily at 200 °C, it resumed at 220 °C, and a black solid was finally produced.

### 3.5 Reaction path of AMU/BCN and factors for the change in thermal behavior with BCN

The above results indicate that ADN, MMAN, and urea formed copper compounds with BCN during the condensed-phase reactions. ADN/BCN formed a green molten salt and decomposed exothermically at 120 °C, which is a significantly lower temperature than for pure ADN. The copper ammine complex of dinitramide is tetraamminecopper(II) dinitramide ([Cu(NH₃)₄][N(NO₂)₂]₂); it is reported to be violet in color, and its decomposition occurs at 178 °C – 183 °C. Hence, there is a high probability that this compound was copper(II) dinitramide [Cu[N(NO₂)₂]₂]. Dinitramic salts generally decompose exothermically into nitrate salts in the same way as pure ADN. Hence, we concluded that copper(II) dinitramide decomposes to copper(II) nitrate [Cu(NO₃)₂] as follows:

![Figure 4](Image)


\[
\text{Cu[N(NO_2)_2]_2} \rightarrow \text{Cu(NO_3)_2} + 2\text{N}_2\text{O} \tag{1}
\]

This reaction explains why BCN promotes the exothermic decomposition of ADN. Izato et al.\(^\text{18}\) reported that Cu(NO_3)_2 is greenish blue in color, which supports the argument that Cu(NO_3)_2 was obtained here. Subsequently, a violet solid was observed that finally changed to black with a slight loss of mass. These solids are thought to be diammine copper(II) nitrate \([\text{Cu(NH}_3)_2(NO_3)_2]\) and CuO, respectively. Cu(NH)_3(NO_3)_2 is generated by the reaction between Cu(NO_3)_2 and ammonia. Because significant heat generation was not observed, the ammonia was thought to come from the dissociation of AN, which is a major product obtained during decomposition of ADN. The expected reaction pathway is given below:

\[
\text{NH}_4\text{N(NO}_2)_2 \rightarrow \text{NH}_4\text{NO}_3 + \text{N}_2\text{O} \tag{2}
\]
\[
\text{NH}_2\text{NO}_3 \rightarrow \text{NH}_3 + \text{HNO}_3 \tag{3}
\]
\[
\text{Cu(NO}_3)_2 + 2\text{NH}_3 \rightarrow \text{Cu(NH}_3)_2(\text{NO}_3)_2 \tag{4}
\]

CuO, H_2O, N_2, and nitrogen oxides have been reported to be generated by the decomposition of Cu(NH)_3(NO_3)_2.\(^{32}\)

For MMAN/BCN, a blue molten salt was observed after MMAN melted. Copper and ammonia or amines form complexes easily,\(^{32}\) and Shiota et al.\(^{33}\) reported that a blue salt \(\text{[Cu(CH}_3\text{NH}_2)_2(NO}_3)_2\) is formed by the reaction between AN and BCN near the melting point of AN. For AN, we assumed that di(methylamine) copper nitrate \([\text{Cu(CH}_3\text{NH}_2)_2(NO}_3)_2\] was generated by the reaction between MMAN and BCN. Although tetrakis(methylamine) copper(II) nitrate \([\text{Cu(CH}_3\text{NH}_2)_4(NO}_3)_2\) is a well-known complex of copper nitrate and methylamine, it starts to lose its methylamine from 100 °C.\(^{32}\)

The color of the condensed phase changed to green with mass loss from 150 °C to 250 °C. The TG-DTA curve for MMAN/BCN was almost the same as that for pure MMAN up to 230 °C. These results indicate the vaporization of MMAN and loss of methylamine from di(methylamine) copper nitrate \([\text{Cu(CH}_3\text{NH}_2)_2(NO}_3)_2\) as the heating gradually progressed. Previous studies have reported that \([\text{CH}_3\text{NH}_2][\text{Cu(NO}_3)_3]\) and Cu(NO_3)_2 are greenish-blue compounds. The gas generation became remarkable from 230 °C, and a black solid suddenly formed with a severe exotherm and gas generation at 250 °C. The ammine and methylamine complexes of copper nitrates are known to lose ammonia or amines gradually and finally decompose explosively to CuO during constant-rate heating, and CuO promotes the decomposition of AN.\(^{32}\) In this study, the copper nitrate—methylamine complex appears to have decomposed exothermically to CuO and the reaction progressed autocatalytically because the methylamine complex was generated again by the reaction between unreacted MMAN and CuO.

Although the SC-DSC and TG-DTA curves exhibited that urea/BCN had almost the same thermal behavior as pure urea, it generated a pale blue compound during heating, and a high rate of mass loss was observed. Urea has been reported to form a complex with Cu(II) compounds,\(^{36}\) but this does not lead to a significant exothermic reaction. In this study, we assumed that a complex such as \(\text{Cu}[\text{urea}_2(\text{NO}_3)_2]\) formed between urea and BCN and decomposed to CuO.

AMU/BCN was a blue liquid at room temperature. The color gradually changed to greenish blue, and an exothermic reaction started around 150 °C. This indicates that CuDN was not generated during decomposition because its thermal behavior clearly differed from that of ADN/BCN. The reactivity of ADN has been reported to be inhibited when a certain amount of nitrates is present.\(^{26,37}\) The color of the liquid was similar to that observed after MMAN/BCN melted, which indicates that BCN dissolved in AMU by forming a complex with MMAN. The generation of CuDN was inhibited in AMU because of the stabilization of ADN and formation of a complex with BCN. The \(T_{\text{DSC}}\) of the exothermic reaction was almost the same as that of ADN/MMAN, which indicates that the reactions in the early stages involved thermal decomposition of ADN and a reaction between ADN and MMAN. The decomposition of the copper complex to Cu(NO_3)_2 progressed simultaneously with the exothermic reaction as evident from change in the color of the liquid to green. After that, it became mild once, and a black solid was finally obtained with a significant exotherm. The black solid, which was the final product, is thought to be CuO, as the other mixture with BCN. We assumed that the exothermic reaction became significant because the copper nitrate—methylamine complex decomposed exothermically to CuO, which promotes the decomposition of AN from ADN and MMAN.

4. Conclusion

In this study, we analyzed the thermal behavior and visual changes of AMU and copper compounds heated at a constant rate to elucidate their influence on the condensed-phase reactions. Dissolving 2 wt% of BCN in AMU/442 formed a complex between BCN and MMAN and promoted an exothermic reaction in the condensed phase. Because ignition by heating is initiated by condensed-phase reactions, the ignitability of AMU can be increased by adding BCN. In the case of ADN, adding BCN lowered the \(T_{\text{DSC}}\) for the exothermic decomposition of ADN by forming CuDN. However, in the case of AMU, adding BCN did not affect the \(T_{\text{DSC}}\) because of the presence of MMAN. The exothermic reaction of the AMU/BCN mixture initiated with the thermal decomposition of ADN and reaction between ADN and MMAN. As the temperature increased, the complex gradually lost methylamine and finally decomposed exothermically to CuO. Simultaneously, CuO promoted the exothermic reaction of MMAN and AN from the decomposition of ADN.

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