Preparation and Thermal Decomposition Behavior of High-energy Ionic Liquids Based on Ammonium Dinitramide and Amine Nitrates

By Hiroki Matsunaga,1) Katsumi Katoh,1) Hiroto Habu,2,3) Masaru Noda,1) and Atsumi Miyake3)

1) Department of Chemical Engineering, Fukuoka University, Fukuoka, Japan
2) Institute of Space and Astronautical Science, JAXA, Sagamihara, Japan
3) Institute of Advanced Sciences, Yokohama National University, Yokohama, Japan

(Received June 25th, 2017)

Certain combinations of ammonium dinitramide (ADN, melting point = 93 °C) and additives such as methylamine nitrate (MMAN) (melting point = 110 °C) and urea (melting point = 133 °C), form stable ionic liquids, even below room temperature. These mixtures, referred to as energetic ionic liquid propellants (EILPs), can be highly energetic, and yet are easy to handle. Improving the performance of EILPs will require an understanding of the effects of the additives on the melting point and reaction mechanism for ADN. Therefore, the present work examined the melting point and thermal decomposition and ignition processes for EILPs based on ADN and various amine nitrates. Some EILPs made with low molecular weight amines were found to exhibit a reduced melting point, and high speed photography demonstrated that ignition of these mixtures took place following thermal decomposition of the condensed phase. The thermal behavior and gas evolution for EILPs during heating were assessed by thermal analysis combined with spectrometry and the results showed that the decomposition products were not affected by the specific amine nitrate used in the mixture. The data also suggested that variations in the heat release and reactivity for these mixtures during thermal decomposition can influence the ignitability of the EILPs.

Key Words: Ionic Liquid Propellant, Ammonium Dinitramide, Thermal Decomposition

Nomenclature

\[ I_{\text{vac}} \]: vacuum specific impulse
\[ m/z \]: mass-to-charge ratio

1. Introduction

Hydrazine is widely used as a liquid monopropellant for attitude control of rockets and space satellites, since it readily decomposes to form hot gases in the presence of catalysts and can be stored at room temperature. However, hydrazine is also highly toxic and generates combustible vapors, and so is difficult to handle and reduces the operability of spacecraft. Propellants based on the energetic oxidizer ammonium dinitramide [ADN, NH\(_4\)N(NO\(_2\))\(_2\)]. have been considered as replacements for hydrazine because ADN can generate more energy than hydrazine and is also less toxic.\(^5\) Since the melting point (m.p.) of ADN is a relatively high 92 °C, it is typically dissolved in water and/or methanol to obtain a liquid propellant.\(^6\) These propellants are almost suitable for real world applications, but continue to face challenges related to ignition and combustion due to the presence of the solvent. To mitigate this problem, we previously prepared ADN-based liquids based on eutectic mixtures with solid fuels. As examples, ADN forms eutectic mixtures with monomethylamine nitrate (MMAN, CH\(_3\)NH\(_3\)NO\(_3\), m.p. = 110 °C) and urea (m.p. = 135 °C).\(^5\) The m.p. for such mixtures is below room temperature and they are also more stable than pure ADN in the liquid phase while potentially offering energy and specific impulse values higher than those for existing propellants.\(^5\) These mixtures can be considered as ionic liquids,\(^8\) and as such exhibit unique properties, low volatility and a low liquidus temperature, all of which are desirable for liquid propellants.\(^9\) Low volatility decreases the risk of exposure during handling as well as the threat of explosion. In addition, their low liquidus temperature eliminates the need for solvents, thus increasing the energy density for the liquid propellants. For these reasons, we have researched these mixtures as energetic ionic liquid propellants (EILPs).\(^5,10-13\)

In order to use EILPs for spacecraft, it is necessary to develop methods for designing these substances. An EILP should have a high energy density, a low melting point, and should undergo ignition readily, and our previous studies have shown that amine nitrates can significantly decrease the melting point of ADN.\(^5\) The purpose of the present study was therefore to obtain a better understanding of the eutectic behavior, ignitibility and thermal decomposition of ADN/amine nitrate mixtures. The effects of specific amine nitrates on the melting point and thermal decomposition of EILPs were investigated using thermal analysis and evolved gas analysis. The ignition of propellant droplets upon heating was also assessed by high speed photography.

2. Materials

Various amine nitrates were used in this work: MMAN, dimethylamine nitrate (DMAN, (CH\(_3\))\(_2\)NH\(_3\)NO\(_3\), m.p. =
76 °C), cyclohexylamine nitrate (CyAN, C₆H₁₁NH₃NO₃, m.p. = 158 °C) and monoethanol amine nitrate (MEAN, HO(CH₂)₂NH₃NO₃, m.p. = 51 °C). ADN was acquired from the Hosoya Pyro-engineering Co., Ltd., while MMAN and MEAN were synthesized by reacting 40% aqueous solutions of ethylamine or ethanolamine (Wako Pure Chemical Industries, Ltd.) with nitric acid (1.38 g/cm³, Wako Pure Chemical Industries, Ltd.), followed by drying under vacuum. DMAN and CyAN were obtained from the Showa Chemical Co., Ltd. In each EILP, the ADN and the amine nitrate were combined in a 1:1 mass ratio.

3. Experimental Methods

The eutectic behavior of ADN/amine nitrate mixtures during heating was assessed by visual observations. Samples were stored in an oven at 35 °C for several hours and then examined to determine if they had melted. The vacuum specific impulse values \(I_{\text{vac}}\) for those mixtures that completely liquified at 35 °C were calculated using the NASA-CEA\(^{14}\) and compared to the value for a standard hydrazine monopropellant. These calculations were based on the frozen flow assumption, with a combustion chamber pressure of 0.7 MPa and a nozzle open area ratio of 50.

The ignition behavior of liquid ADN/amine nitrate mixtures was observed using the apparatus shown in Fig. 1. An approximately 10 mg aliquot of each mixture was transferred to an aluminum cup preheated to 400 °C and the subsequent behavior was observed by a high-speed camera (Nobby Tech Co., Ltd., Phantom Miro C 110) operating at 1000 fps.

The thermal behavior of each mixture was characterized using differential scanning calorimetry (DSC, Shimadzu DSC-60 Plus). In these trials, a 1 mg sample of each ADN/amine nitrate mixture was loaded into a stainless steel cell which was then sealed under air so as to assess the thermal characteristics of both condensed phase and gas phase reactions. Each specimen was heated from 30 to 350 °C at 5 °C/min. The thermal behavior and decomposition gases generated by these same ADN/amine nitrate mixtures were also examined during heating in open pans using thermogravimetry-differential thermal analysis-mass spectrometry (TG-DTA-MS). This apparatus was composed of two units: a TG-DTA instrument (NETZSCH TG-DTA2000SE) and a mass spectrometer (JEOL JMS-Q1500GC). In each trial, a 3 mg sample was loaded into an open aluminum pan and then heated to 350 °C at 5 °C/min under a helium flow (100 mL/min). The evolved gases were transferred to the mass spectrometer, operating at an oven temperature of 250 °C in the electron impact ionization mode.

4. Results and Discussion

4.1. Investigations of various compositions

Figure 2 compares the eutectic behavior of ADN/amine nitrate mixtures at 35 °C. ADN/CyAN and ADN/DMAN were solid and partially liquid, respectively, while ADN/MMAN and ADN/MEAN were completely liquid. The m.p. values for the pure amine nitrates increased in the order of MEAN < DMAN < MMAN < CyAN, which roughly corresponds to the m.p. values for the mixtures, although ADN/MMAN evidently had a lower m.p. than ADN/DMAN. Thus, the melting properties of EILPs based on ADN and amine nitrates are not solely determined by the m.p. of the amine nitrates, but possibly also by intermolecular interactions. MMAN has a comparatively small cation, and so the mixture of MMAN and ADN would potentially lead to a stronger interaction between the methylamine cation and the dinitramide anion compared to that between the dimethylamine cation and dinitramide. Calculations using the NASA-CEA showed that the \(I_{\text{vac}}\) values for ADN/MMAN and ADN/MEAN were 294 and 271 s, respectively. Therefore, both mixtures potentially offer superior performance to that of a hydrazine monopropellant \(I_{\text{vac}} = 235\) s.

4.2. Ignition behavior

The behavior of the samples when dropped into a heated aluminum cup is shown in Fig. 3. In the case of ADN/MMAN, numerous bubbles and white smoke were generated immediately after contact of the droplet with the base of the aluminum cup. The gas generation became more violent with time and the evolved gases around the droplet eventually ignited. Thermal decomposition of pure ADN begins at approximately 130 °C and MMAN vaporizes and decomposes at approximately 200 °C, with some variations depending on the heating conditions.\(^{6,15-17}\) In addition, the decomposition of ADN proceeds both exothermically and autocatalytically.\(^{30}\) It
is thought that exothermic reactions involving the generation of combustible mixtures occur initially, increasing the temperature of the liquid phases and the evolved gases around the liquid, after which the combustible gas mixture ignites. Both ADN/MEAN and ADN/MMAN exhibited ignition of evolved gases from decomposition but the MEAN mixture showed flames quite near the droplet at almost the same time as the start of a reaction in the condensed phase. This result indicates that ADN/MEAN has greater ignitability and a shorter ignition delay than ADN/MMAN. It was suggested that ignition of both mixtures were due to heating of evolved gas by exothermal reaction in condensed phase. Therefore the difference of ignitability is estimated to be attributed to the varying amounts of heat and specific evolved gas compositions generated by these two mixtures during thermal decomposition.

4.3. Thermal decomposition

4.3.1. Exothermal behavior

The thermal characteristics of ADN, MMAN, MEAN, ADN/MMAN and ADN/MEAN during constant rate heating (5 °C/min) under sealed conditions, as determined by DSC, and under open conditions, as determined using TG-DTA, are presented in Figs. 4 and 5.

The pure ADN generated two exothermic peaks in the ranges of 130-220 °C and 220-260 °C when sealed. Previous studies have determined that the main reactions of ADN are decomposition to ammonium nitrate (AN) and nitrous oxide (equivalent to the first peak) and decomposition of the AN (responsible for the second peak), according to Eqs. (1) and (2).

\[
\begin{align*}
\text{NH}_3\text{N(NO}_3\text{)}_2 & \rightarrow \text{NH}_3\text{NO}_3 + \text{N}_2\text{O} \quad (1) \\
\text{NH}_3\text{NO}_3 & \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} \quad (2)
\end{align*}
\]

In contrast, one exothermic and one endothermic peak were generated in the region from 130 to 220 °C under open conditions. These results indicate that the reaction given by Eq. (1) proceeds exothermically in the condensed phase under both conditions and that the gasification of AN occurs prior to the reaction in Eq. (2). The second exothermic peak was observed in the case of the sealed sample because gasification was prevented.

Pure MMAN and MEAN both produced a single exothermic peak derived from their decomposition at 200 °C under sealed conditions. Since this exothermic peak was not observed in the case of open conditions, the MMAN and MEAN also must have gasified before decomposition.

ADN/MMAN exhibited two exothermic peaks when sealed but a single exothermic and endothermic peak when open, just as pure ADN did. The onset temperature for these peaks was also the same as that for pure ADN. Comparing the first exothermic peaks produced by the pure ADN and the ADN/MMAN, the peak shapes were different and the heat per unit ADN mass of ADN/MMAN (4.4 kJ) was higher than that for pure ADN (1.8 kJ), indicating that ADN reacted with
MMAN during the first exothermic peak. However, some portion of both ADN and MMAN is believed to have decomposed without a reaction between the two because the second peak was observed in the same general temperature range as the individual decomposition peaks for AN and MMAN.

ADN/MEAN produced only one peak at 130-200 °C under both conditions. This demonstrates that ADN and MEAN reacted completely in the condensed phase with little vaporization. The heat release associated with the exothermic peak was 7.2 kJ, which is higher than that generated by pure ADN and ADN/MMAN. Hence, MEAN exhibits greater reactivity with ADN than MMAN. It is possible that this affects the ignitability of the respective EILPs.

4.3.2. Evolved gases

Previous studies have shown that the primary gaseous products generated during ADN decomposition are nitrous oxide (producing ions with a mass-to-charge ratio (m/z) of 44, 30 and 28), nitrogen dioxide (m/z = 46 and 30), nitrogen (m/z = 28), and water (m/z = 18 and 17).\(^{15,21}\) The decomposition of amine nitrates starts with dissociation to amines and nitric acid.\(^{22-24}\)

The unique m/z values for monomethylamine and monoethanolamine are 31 and 61, respectively.\(^{25}\)

Mass spectra of the gases evolved from ADN/MMAN and ADN/MEAN during the exothermic peak at 130-220 °C are provided in Fig. 6. Nitrous oxide, carbon dioxide (m/z = 44 and 28), carbon monoxide (m/z = 28), nitrogen dioxide, nitrogen and water were all detected, while essentially no monomethylamine or monoethanolamine was produced.

These amines are thought to have been consumed by reaction with ADN in the condensed phase. The gaseous products were almost identical for the ADN/MMAN and ADN/MEAN samples. These results suggest that the thermal decomposition mechanism for ADN/amine nitrate mixtures in the condensed phase does not depend on the amine. It also appears that the ignition of an ADN/amine nitrate mixture involves a gas phase reaction between NOx from the decomposition of ADN and gases evolved from both ADN and the amine.

![Fig. 6. Mass spectra of gases evolved from ADN/MMAN and ADN/MEAN.](image)

5. Conclusion

Thermal data were employed to obtain a better understanding of the properties and ignition/reaction characteristics of ADN-based energetic ionic liquids.

The melting points of ADN/MMAN and ADN/MEAN were lower than that of pure ADN and of other amine nitrate mixtures. It is apparent that the combination of ADN with additives having relatively low melting points, or that undergo strong interactions tends to form ionic liquids with low melting points.

Ignition of these ionic liquids evidently occurs after thermal decomposition, and the decomposition products of ADN/amine nitrate mixtures do not vary with changes in the amine nitrate. It is possible that differences in the condensed phase reactivity of these mixture determine their ignitability.

Acknowledgments

This work was supported by JSPS KAKENHI Grant Numbers 16H06134.

References


332-337.


