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Scalable synthesis of high purities ammonium dinitramide and its decomposition characteristics

Hoi-Gu Jang[a], Min Jung Sul[b], Jung Seob Shim[b], Young Chul Park[c], Sung June Cho[a,*]

[a] Department of Chemical Engineering, Chonnam National University, 77 Yongbong-Ro, Buk-gu, Gwangju 61186, Republic of Korea
[b] Defense R & D Center Energetic Materials & Pyrotechnics, Hanwha Corporation, Yuseong, Daejeon 34060, Republic of Korea
[c] Agency for Defense Development, Yuseong, Daejeon 34186, Republic of Korea

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ABSTRACT

Scalable synthesis of high purities ammonium dinitramide (ADN), 98.2% or more has been performed through conversion of potassium dinitramide (KDN) into ammonium dinitramide using guanylurea dinitramide (GUDN) as a precursor, which can be scalable up to a few hundred grams. The obtained ADN and corresponding liquid ADN blended with fuel was subject to the decomposition reaction with and without iridium catalyst. The result of the decomposition reaction suggested that the blending of methanol with ADN gave a high performance. It has been shown that the presence of ammonium hydroxide in the blend maintained pH around 10 and also stabilized the ADN solution for more than 20 day at 60 °C.

Introduction

Recent advance in development of a highly energetic solid based on dinitramide ion, $N(NO_2)_2^-$ as oxidizer has been accomplished because the corresponding liquid blend is less susceptible to be volatile, compared to that of an highly toxic hydrazine which is standard chemical propellant [1–5]. Ammonium dinitramide (ADN) can be prepared following the scheme in Fig. 1 where the scheme 2 is preferred to scheme 1 because the byproduct formation can be minimized and it can be scalable easily with the formation of high purity ADN [6–9]. The fuel source such as methanol and nitrogen containing compounds has been considered in which methanol was preferred because of low boiling point [8]. Using the proper composition of ADN–methanol–water or ammonium hydroxide solution, the monopropellant system can be constructed using high temperature stable catalyst based on hexaaluminate instead of Ir catalyst, which is the state of art catalyst for chemical propulsion using hydrazine [10,11]. Successful application of the monopropellant system using ADN based liquid propellant for satellite attitude and altitude control has been reported elsewhere [1,10].

However, the information on the preparation of ADN which can be scalable easily maintaining high purity above 98-99% is limited and also their decomposition characteristics of liquid propellant containing methanol and ammonium hydroxide are not well known [12,13]. Therefore, the condition for large scale synthesis should be investigated including the purity and the solubility of reactant and product. Further the information on the stability of ADN blend with fuel for long term storage are not well known, though the decomposition of solid or condensed ADN has been investigated extensively through theoretical and experimental method [1,2,14–17].

Previously, it was reported that there are three decomposition pathway, Eqs. (1)–(3) for solid ADN as follows [14]:

$$NH_4N(NO_2)_2 \rightarrow NH_3 + HNO_3 + N_2O \quad (1)$$

$$NH_4N(NO_2)_2 \rightarrow NH_3 + HN(NO_2)_2 \quad (2)$$

$$12NH_4N(NO_2)_2 \rightarrow 3NH_3 + 10N_2O + 6NO_2 + 15H_2O + 2NO + 6N_2 + HNO_3 + 2NH_4NO_3 + HNO_3 + 2NH_4NO_3 \quad (3)$$

On the other hand, two decomposition pathway were proposed from the investigation of condensed thermal decomposition: the first one is the formation of ammonium nitrate by elimination of N_2O and the other one is NO_2 formation through N–N scission. In theoretical point of view, the dimer of ADN was suggested in order to explain the role of hydrogen bond by water for the stabilization

* Corresponding author.
E-mail address: sjcho@chonnam.ac.kr (S.J. Cho).

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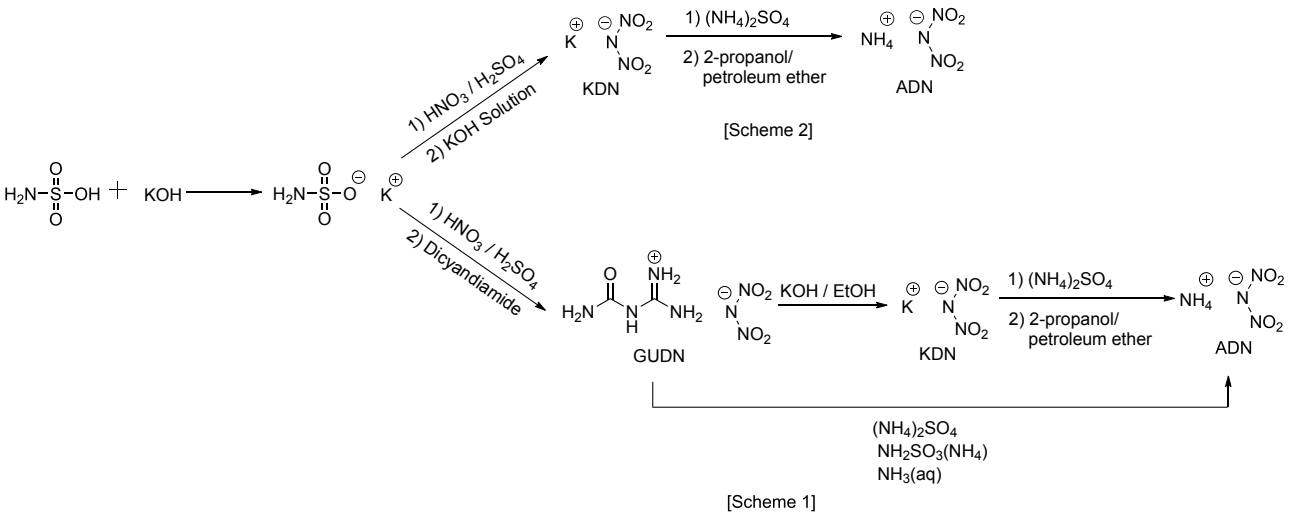

Fig. 1. Reaction scheme for the synthesis of ADN: scheme 1: GUDN-KDN-ADN; scheme 2: KDN-ADN.

of ammonium dinitramide. Thereby, it was claimed that the decomposition of ADN is initiated through surface chemical processes involving twisted dinitramides of low stability that has shorten N-N bond distance due to distortion. Under ambient condition, the rate-determining step for the decomposition of these dinitramide salts is believed to be the dissociation into NO_2 and NNO_2^- radicals. The decomposition product was consistent with the experimental observation on condensed ADN phase [2,14–16].

In the present work, we prepared the and in large scale up to a few hundred grams using the scheme 1 in Fig. 1 in which the additional crystallization process has been included to increase the purities and minimize the use of solvent, which can be utilized to prepare the blended ADN with the fuel sources, methanol, dimethylformamide(DMF) and monomethylformamide(MMF), respectively with or without ammonium hydroxide solution as stabilizer. The obtained solid and liquid blend has been characterized with differential scanning calorimetry and differential thermal analysis, X-ray diffraction, UV–vis and FT-IR. The corresponding decomposition characteristics of liquid blend has been studied under various conditions. Thereby, the scalable synthesis method for ADN has been explored and the resulting decomposition characteristics of liquid blend with and without the catalyst has been revealed.

Experimental

ADN preparation

For the synthesis of guanylurea dinitramide (GUDN), a portion of 1080 mL (25.716 mol) of 98% nitric acid to a 3 L triple jacketed reactor is added and combined with 384 mL (0.3 mol) of 98% sulfuric acid slowly. Using a circulator, the temperature of the reaction solution is maintained to −40 to 45 °C. While the temperature of the reaction solution is maintained at −35 to −40 °C, 408 g (3.018 mol) of potassium sulfamate is added. The reaction proceeds for 40 min further.

After dissolving 288 g (3.426 mol) of dicyandiamide in 2880 mL distilled water, the solution is added to a double jacketed reactor while the temperature was maintained to 15 °C using a circulator. After the nitrification reaction is completed, the reaction solution is poured into the partially dissolved cyanoguanidine solution, and the temperature is raised to 70 °C and reacted for a short time. When the reaction is complete, the resulting solid is recovered.

For the conversion into potassium dinitramide (KDN), 240 g (5.217 mol) ethanol and 120 g (6.667 mol) water are mixed in a beaker. 40 g (0.714 mol) potassium hydroxide is added to the mixed solution. The mixed liquid is added to a 1 L double jacket reactor and the reaction temperature is raised to 50 °C. 110 g (0.526 mol) of GUDN is added at a temperature of the reaction liquid at 50 °C. After the addition is completed, the reaction is carried out at 50 °C for 15 min and then cooled. When cooling is complete, the resulting solid is filtered, washed and dried at 70 °C for 3 h.

For the synthesis of ADN, 40 g (0.276 mol) of KDN and 40 g (0.303 mol) of ammonium sulfate are dissolved in 80 mL of distilled water, respectively. After mixing the two solutions, 800 mL 2-propanol was added to yield a white precipitate, potassium sulfate. This was removed by filtration and subsequently the filtrate was concentrated to obtain the solid through distillation. After the recrystallization using 2-propanol and petroleum ether, the obtained solid was filtered and washed and then dried at 50 °C for 3 h. The amount of the solid product was shown to be increased from 30 g to ~100 g scale maintaining the high purity.

For direct conversion of GUDN to ADN as shown in the scheme 1 in Fig. 1, 150 mL of distilled water was added to the 1 L double jacketed reactor and subsequently 10 g (0.0478 mol) GUDN and 7.58 g (0.0574 mol) of ammonium sulfate were also added. After completion of the addition, the reaction solution was heated to 100 °C and the reaction was allowed to proceed for 5 min. After the addition of 1500 mL 2-propanol the resulting solid is filtered and distilled. Again, 2-propanol is added in a second step and the remaining solid is filtered. The resulting liquid phase after filtration is distilled again to obtain the solid ADN.

ADN characterization

The morphology of the samples was examined using scanning electron microscopy (SEM, S-4700, Hitachi). Thermogravimetric and differential thermal analysis (TG/DTA) of the used catalysts was carried out with a thermogravimetric analyzer (DTG-60H, Shimadzu). The weight loss was measured as the temperature was increased to 400 °C at 5 °C min^{-1} under an air (Sinil, 99.9%) flow of 50 mL min^{-1}. UV–vis spectrum of the liquid blend was obtained using UV–vis spectrometer (OPTIZEN POP, ECASYS) and also FT-IR spectrum was measured with FT-IR spectrometer (IR Prestige-21, Shimadzu). In order to quantify the purity, the ion chromatography (ICS-5000, Dionex) equipped with AS19 anion exchange column

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