

Research on the synthesis process and properties of dinitramide compounds for applications in propellants and explosives

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ABSTRACT

Dinitramide compounds are characterized by a high oxygen and nitrogen content and the absence of halogens in their molecular structure, making them suitable for environmentally friendly new-generation propellants and explosives. This study outlines the optimization of the synthetic pathways for these compounds, including the preparation of guanylurea dinitramide (GUDN) via nitration and the synthesis of potassium dinitramide (KDN), ammonium dinitramide (ADN), and guanidinium dinitramide (GDN) through ion-exchange reactions. Additionally, the resulting dinitramide compounds were systematically evaluated for their physicochemical properties, ballistic characteristics, and spectral features. The findings demonstrate that these compounds exhibit high synthesis efficiency and possess properties conducive to their effective application in propellant and explosive formulations.

Keywords: Dinitramide compounds; Ammonium dinitramide; GDN; KDN; Nitration reaction.

1. INTRODUCTION

High-energy materials are essential in both civilian and military domains, serving as key components in propellants, explosives, and pyrotechnics. Over the years, new generations of propellants and explosives have been developed, focusing on optimizing performance and reducing environmental impact [1-4]. Desired characteristics of these materials include high nitrogen and oxygen content, the absence of halogens, and high density.

Among the notable high-energy materials are dinitramide compounds containing the dinitramide anion ($(\text{NO}_2)_2\text{N}^-$). These compounds exhibit high oxygen and nitrogen content, are halogen-free, and offer high energy efficiency and stability. This makes them promising candidates for environmentally friendly high-energy applications [5].

Important dinitramide compounds include ADN, KDN, GUDN, GDN, silver dinitramide (AgDN), sodium dinitramide (NaDN), and lithium dinitramide (LiDN) (figure 1). These dinitramide compounds have diverse applications ranging from basic chemistry to advanced engineering. Notably, they are often used in the development of high-performance solid and liquid propellants, next-generation explosives, and pyrotechnic formulations. Extensive research has focused on ADN as a potential oxidizer for composite solid rocket propellants and as a primary component for high-performance green propellants [6-10].

Additionally, GUDN (or FOX-12) is a low-sensitivity dinitramide compound with significant potential for use as a propellant or insensitive explosive [11]. Other dinitramide compounds, such as GDN, are used in propellants and pyrotechnic formulations [12]. Mixtures of KDN and ADN with certain energetic additives form thermally stable explosives with promising properties [13]. Some nitramide compounds, like LiDN, can be used as electrolyte components in batteries. Furthermore, dinitramide salts can also function as surfactants [14]. Currently, various synthetic

2.2.6. Vacuum stability (VST)

Evaluated using the vacuum stability test method on a Stabil Vacuum tester at 100 °C for 40 continuous hours. Each sample is tested 3 times, and the average value is recorded.

2.3. Preparation of guanylurea dinitramide

GUDN was synthesized according to the method described in reference [15], with the specific synthesis process as follows: Fuming nitric acid and sulfuric acid 98% were placed into the IKA reactor system reactor vessel. Ammonium sulfamate (AS) was placed slowly into the acid mixture at a temperature of -40 ± 2 °C. The nitration reaction mixture was then poured into an open glass bowl containing a suspension of guanylurea sulfate ((GU)₂S) at 10 ± 5 °C under constant stirring. Then, the mixture was cooled at a temperature of 15 °C. The formed white precipitate was then filtered off with a Büchner funnel, and washed with cold water. The obtained GUDN was dried at 50 °C to constant weight.

2.4. Preparation of potassium dinitramide

5 g of KOH was dissolved in a mixture of 30 g of ethanol and 15 g of water. This mixture was heated to 50 °C. Then, 18 g of GUDN was added and stirred for 30 minutes. The mixture was cooled in an ice-water bath, resulting in the formation of a white solid. The solid was filtered and washed three times with ethanol, then dried at 50 °C until its weight remained constant.

2.5. Preparation of ammonium dinitramide

10 g of KDN and 11.5 g of ammonium sulfate were each dissolved separately into 10 mL of water. The solutions were mixed and stirred for 30 minutes. 100 mL of 2-propanol was added to the solution, resulting in the formation of a white precipitate. The mixture was cooled in an ice-water bath and the precipitate was filtered and washed with 2-propanol. The desired product AND was obtained as a white solid and dried at 50 °C to constant weight.

2.6. Synthesis of guanidinium dinitramide

7.7 g of guanidine hydrochloride was dissolved in 25 mL of distilled water and 10 g of ADN was dissolved in 5 mL of distilled water. The solutions were mixed and a precipitate immediately formed. The precipitate was filtered off with a Büchner funnel, washed 3 times with ice-water and dried at 50 °C to constant weight. The desired product GDN was obtained as a white solid salt.

3. RESULTS AND DISCUSSION

3.1. Optimization study and development of the synthesis process for dinitramide compounds

Dinitramide compounds are synthesized through various pathways, primarily involving nitration reactions to produce dinitramic acid (HDN), which is subsequently converted into stable compounds such as KDN or GUDN. Ion exchange reactions are then employed to synthesize other dinitramide compounds. For instance, ADN is synthesized from the ion exchange reaction between KDN and ammonium sulfate; GDN is synthesized from the ion exchange reaction between ADN and guanidine hydrochloride; and AgDN is synthesized from the ion exchange reaction between ADN and silver nitrate.... Essentially, dinitramide compounds are synthesized through ion exchange reactions between the sulfate (or chloride, carbonate...) salts of these compounds and ADN or KDN. Thus, the primary synthesis pathway for dinitramide compounds involves the synthesis of KDN or ADN.

KDN is synthesized through the nitration of starting compounds such as sulfamate salts, ammonia, and ethyl carbamate... to produce HDN [16-19]. Among these methods, the synthesis of KDN via the nitration of ammonium sulfamate (AS) or potassium sulfamate (KS) using a HNO₃/H₂SO₄ acid mixture provides the highest yield and the easiest method to perform. However, directly synthesizing KDN from HDN is time- and energy-intensive due to the need to remove water after the nitration step. Therefore, the indirect synthesis of KDN *via* GUDN is more efficient (figure 2).

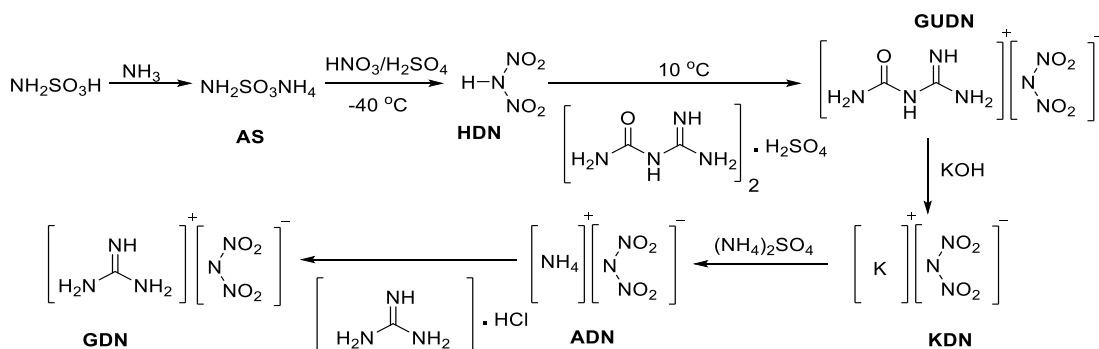


Figure 2. Synthesis process of dinitramide compounds.

Optimizing the synthesis process of dinitramide compounds involves improving the nitration reaction for the synthesis of GUDN, as well as optimizing the synthesis of KDN and ADN. The synthesis process of GUDN has been detailed in the literature [15]. To study the optimal conditions for synthesizing KDN from GUDN, reactions between GUDN and KOH were conducted at various temperatures and reactant molar ratios. The specific results are shown in figures 3 and 4.

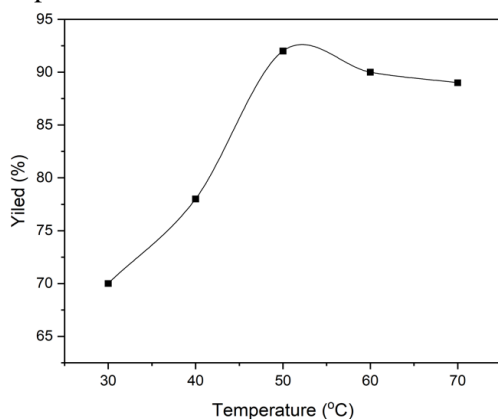


Figure 3. Effect of temperature on KDN synthesis efficiency.

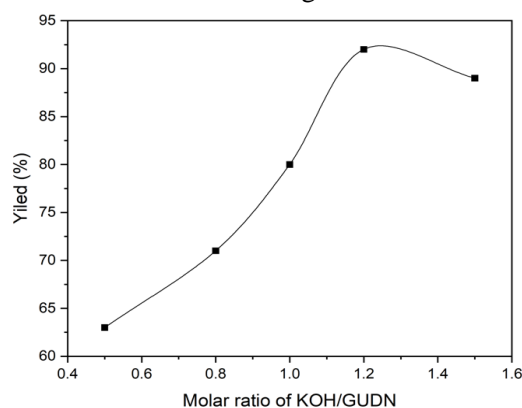


Figure 4. Effect of molar ratio of KOH/GUDN on KDN synthesis efficiency.

From the data in figure 3, it can be seen that increasing the reaction temperature to 50 °C increases the reaction yield. However, further increases in temperature slightly decreases the yield. As the temperature increases, the solubility of GUDN in the solvent mixture increases, enhancing the contact between GUDN and KOH, thereby increasing the reaction yield. Above 50 °C, the solubility of GUDN remains constant, but a small amount of ethanol evaporates, slightly reducing the amount of KDN crystallized. Therefore, the optimum temperature for this reaction is 50 °C.

When the molar ratio of KOH to GUDN increases, the reaction yield also increases (figure 4). However, if the ratio continues to increase, the yield does not change significantly and may even decrease slightly. With an increase in the amount of KOH, GUDN fully reacts with KOH. However, adding too much KOH can affect the quality of the obtained KDN. Therefore, the optimal molar ratio of KOH to GUDN is 1.2:1.

Additionally, the synthesis of GDN from ADN through an ion-exchange reaction was investigated. This reaction was conducted in an aqueous solvent, resulting in a yield of 94% for GDN.

Based on the optimal conditions for synthesizing dinitramide compounds, we have established a basic laboratory-scale synthesis procedure for dinitramide compounds under domestic conditions. The schematic diagram of the synthesis process for dinitramide compounds is shown in figure 5.

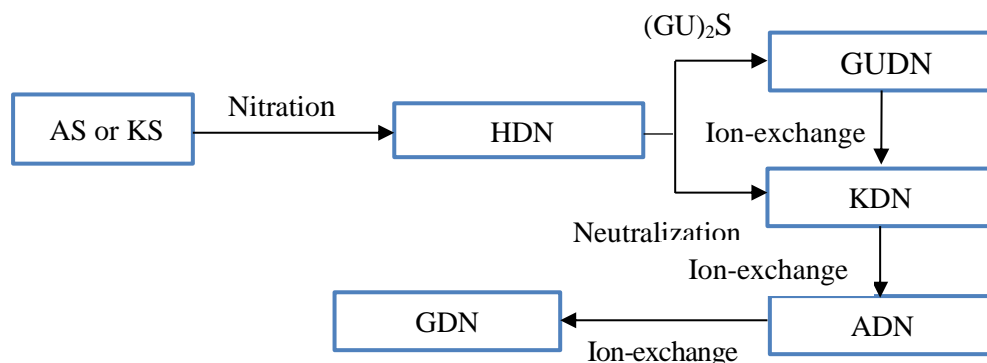


Figure 5. Diagram of the synthesis process of dinitramide compounds.

3.2. Evaluation of the characteristic properties of dinitramide compounds

Basic dinitramide compounds are energy materials used in propellants and explosives, making it crucial to evaluate their thermal properties, impact sensitivity, and vacuum stability.

Table 1. Properties of dinitramide compounds.

Properties	GDN	GUDN	KDN	ADN
Density (g/cm ³)	1.44	1.75	2.21	1.82
Impact sensitivity (%)	60	16	60	64
Vacuum stability (ml/g)	1.2	1.02	1.5	2.1

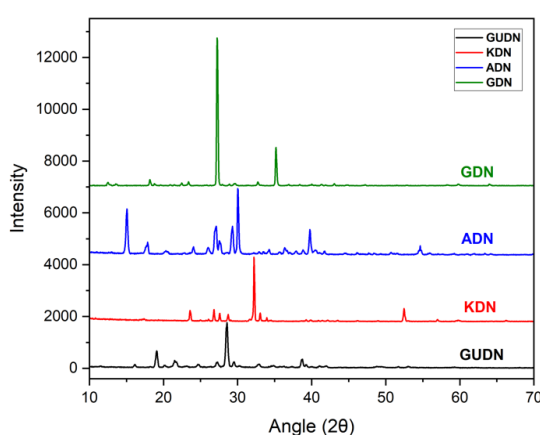
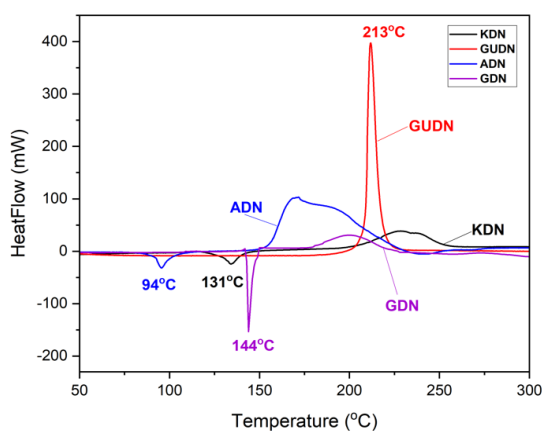


Figure 6. DSC of dinitramide compounds. Figure 7. XRD pattern of dinitramide compounds.

From the DSC graph (figure 6), it is observed that all basic dinitramide compounds exhibit thermal stability. Specifically, ADN has a melting point of 94 °C and begins to decompose at temperatures above 150 °C. GUDN is the most thermally stable compound in this group, decomposing at 213 °C. KDN melts at 131 °C and decomposes around 210 °C. GDN melts at 144 °C and decomposes around 195 °C. Additionally, the vacuum stability of the synthesized dinitramide compounds is within the permissible limits for the chemical stability of energetic materials (table 1). From the data in table 1, GUDN has a low impact sensitivity of 16%, making it suitable for use in insensitive munitions. In contrary, ADN, KDN, and GDN have impact sensitivities comparable to that of RDX.

3.3. Spectral characteristics of dinitramide compounds

The synthesized dinitramide compounds, after drying, were analyzed using IR, NMR, and XRD

spectroscopy. The specific results are presented in the following figures and tables.

The synthesized dinitramide compounds are all crystalline, as demonstrated by their XRD patterns (figure 7).

The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of GUDN have been presented in reference [15]. The $^1\text{H-NMR}$ spectrum of GDN displayed a single at δ 6.89 ppm (6H) corresponding to six protons of three $-\text{NH}_2$ groups (figure 8.b). $^{13}\text{C-NMR}$ spectra showed a distinct signal at δ 157.91 ppm corresponding to carbon atoms of the $-\text{C}=\text{N}$ group (figure 8.d).

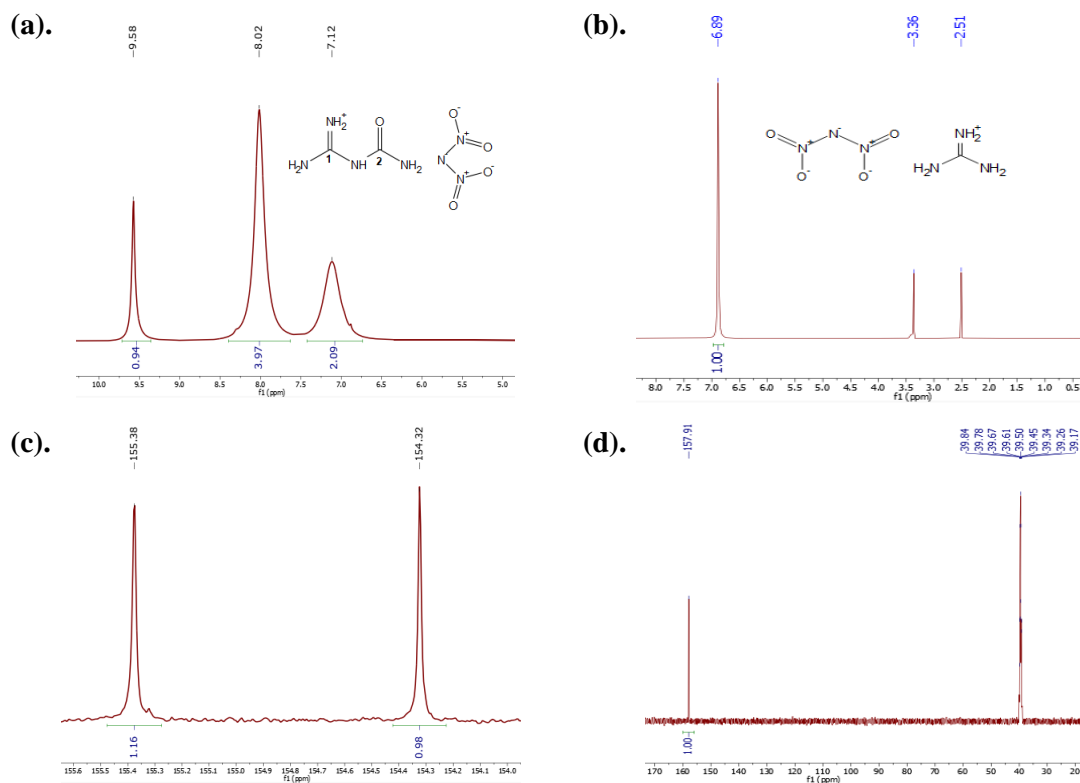


Figure 8. NMR spectrum of GUDN and GDN ($^1\text{H-NMR}$: (a). GUDN and (b). GDN; $^{13}\text{C-NMR}$: (c). GUDN and (d). GDN).

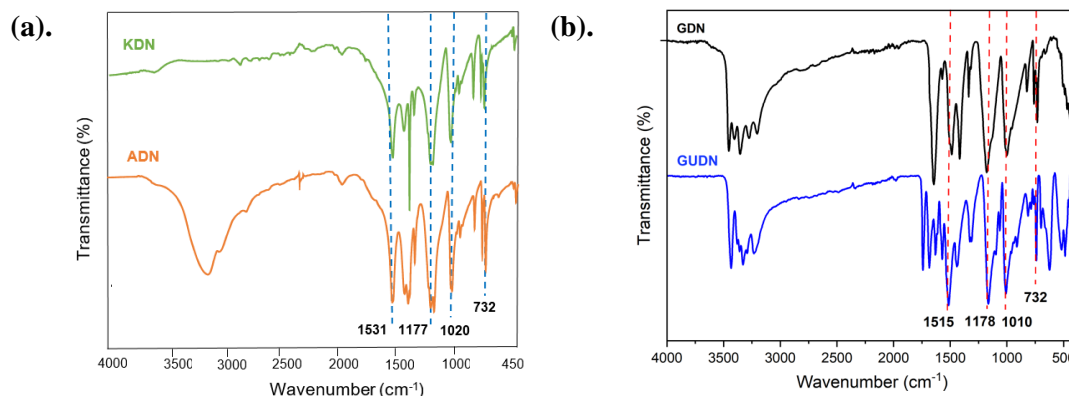


Figure 9. IR spectrum of dinitramide compounds ((a). KDN and ADN; (b). GDN and GUDN).

The FTIR spectrum of dinitramide compounds confirmed the presence of the $-\text{N}(\text{NO}_2)_2$ group. Specifically, the stretching vibrations of the NO_2 group are observed at wavenumbers 1515-1531 cm^{-1} , 1131-1145 cm^{-1} , and 1165-1178 cm^{-1} . The bending vibrations of the NO_2 group appear at

wavenumbers 468-489 cm^{-1} , 732 cm^{-1} , 761 cm^{-1} , and 817-828 cm^{-1} . The stretching vibrations of the N_3 bond occur at wavenumbers 915-951 cm^{-1} and 1002-1020 cm^{-1} (figure 9).

4. CONCLUSIONS

In summary, this study has established a synthetic route for various dinitramide compounds through nitration and ion exchange reactions. Specifically, KDN was synthesized from GUDN with a yield of 92%, while GDN was obtained from ADN with a yield of 94%. The optimal synthesis conditions for KDN were determined, with a reaction temperature set at 50 °C and a molar ratio of KOH to GUDN of 1.2:1. The properties of these dinitramide compounds were evaluated, including thermal stability, impact sensitivity, and vacuum stability. Furthermore, the FTIR, NMR, and XRD spectral characteristics of these compounds are presented in detail, providing comprehensive insights into their structural and functional attributes.

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TÓM TẮT

Nghiên cứu quá trình tổng hợp và tính chất của một số hợp chất dinitramide ứng dụng trong thuốc phóng, thuốc nổ

Các hợp chất dinitramide được đặc trưng bởi hàm lượng oxy, nitơ cao và không có halogen trong cấu trúc phân tử. Do đó, chúng được ứng dụng trong nhiên liệu tên lửa, thuốc phóng và thuốc nổ thế hệ mới thân thiện với môi trường. Nghiên cứu này trình bày quá trình tối ưu hóa con đường tổng hợp cho các hợp chất dinitramide, bao gồm việc điều chế guanylurea dinitramide (GUDN) thông qua quá trình nitro hóa và tổng hợp kali dinitramide (KDN), amoni dinitramide (ADN) và guanidine dinitramide (GDN) thông qua các phản ứng trao đổi ion. Các hợp chất dinitramide tổng hợp được đã được đánh giá các tính chất lý hóa, tính chất xạ thuật và các đặc trưng quang phổ. Các kết quả nghiên cứu chứng minh rằng, các hợp chất này thể hiện hiệu quả tổng hợp cao và sở hữu các tính chất có lợi cho ứng dụng hiệu quả của chúng trong các công thức thuốc phóng, nhiên liệu tên lửa và thuốc nổ.

Từ khóa: Hợp chất dinitramide; Ammonium dinitramide; GDN; KDN; Phản ứng nitro hóa.