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Process Optimization for Synthesis of Guanylurea Dinitramide (GUDN)

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Abstract: Guanylurea dinitramide (GUDN), a stable salt of dinitramidic acid has good thermal stability and is a potential candidate for insensitive munitions. The synthesis process involves nitration of the ammonium salt of sulfamic acid with conc. HNO_3/H_2SO_4 at $-20\,^{\circ}C$ to $-50\,^{\circ}C$ and further treatment with an aqueous suspension of guanylurea sulfate to obtain GUDN as white crystalline solid in 50% yield. In order to optimize the process parameters to get the product in higher yield and greater purity, a systematic study with variation of different parameters like molar ratio of nitrating mixture, conditioning time, and temperature was carried out.

Keywords: Dinitramides · GUDN · Insensitive explosive · Nitration · Process optimization

1 Introduction

The use of powerful, safe, and ecofriendly explosives is the main criteria of ammunitions for propellant formulations. To meet the requirements, energetic compositions with low sensitivity, which should provide safety to ammunitions, are used [1]. Ammonium dinitramide (ADN) is a relatively new solid oxidizer with high performance that combines a high burning rate with the advantageous oxygen balance and the clean burning properties of ammonium nitrate (AN) [2]. ADN has been replacing AP in composite propellants [3]. Guanylurea dinitramide (GUDN) is an important precursor for the synthesis of ADN via potassium dinitramide (KDN).

In continuing the research on insensitive high explosives the synthesis of GUDN has been optimized. GUDN is a white crystalline solid and a stable salt of dinitramidic acid with good thermal stability, low water solubility, and non-hygroscopic properties [4]. It has low vulnerability to impact and friction stimuli and is a potential candidate for insensitive munitions [5]. Its thermal stability is similar to that of RDX and superior to that of ammonium dinitramide (ADN). GUDN may find applications in LOVA propellants [6] as well as melt cast and PBX high explosives formulations [7–9]. Besides its advantageous low sensitivity, GUDN burns with an extremely low temperature, which is important in automatic guns, where barrel erosion is often encountered as a problem. GUDN was prepared by an ion exchange reaction between dinitramidic acid (DNA) and *N*-guanylurea sulfate.

Herein, the synthesis, characterization, and process optimization of GUDN is reported. The effect of reaction parameters like temperature, conditioning time, and amount of nitrating mixture were studied and optimized to achieve a better yield of GUDN.

2 Experimental

2.1 Materials and Analytical Methods

The chemicals used were of analytical reagent grade (AR). Guanylurea sulfate was synthesized from dicyandiamide by treatment with aqueous H_2SO_4.

2.1.1 UV/Vis Spectroscopy

The UV/Vis spectrum of GUDN (Figure 1) was recorded using water as solvent in the range of 200–400 nm using quartz cell. The absorption spectrum was obtained as a plot of the intensity of the transmitted or absorbed light vs. wavelength. Absorption maximum (λ_{max}) was obtained from the spectrum. GUDN shows UV maxima in water at 222 nm and 283 nm. The absorbance at 283 nm is characteristic of the $(-NNO_2)^-$ ion caused by low energy $n-\pi^*$ transitions, whereas the absorption maximum at 222 nm is attributed to high energy $\sigma-\sigma^*$ transition.

2.1.2 Differential Scanning Calorimetry (DSC)

Thermal analysis of GUDN was carried out by using DSC and DTA measurements. The DSC curve of GUDN (Figure 2) shows a sharp exothermic peak at 214.12 °C. The DTA curve of GUDN (Figure 3) shows a two-stage mass loss. The first stage started at about 200 °C with 80% mass loss, whereas the second stage with 19% mass loss is completed at

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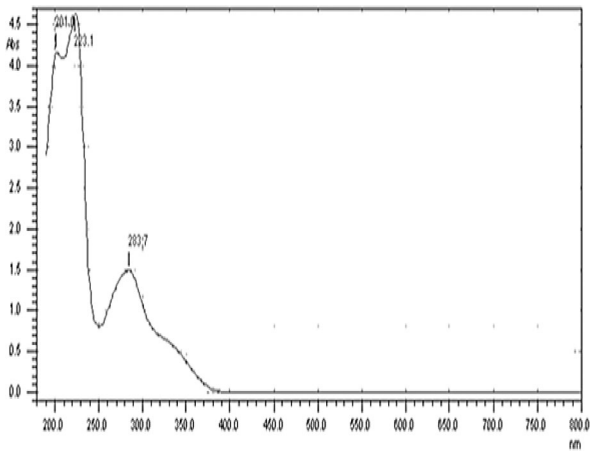


Figure 1. UV/Vis spectrum of GUDN.

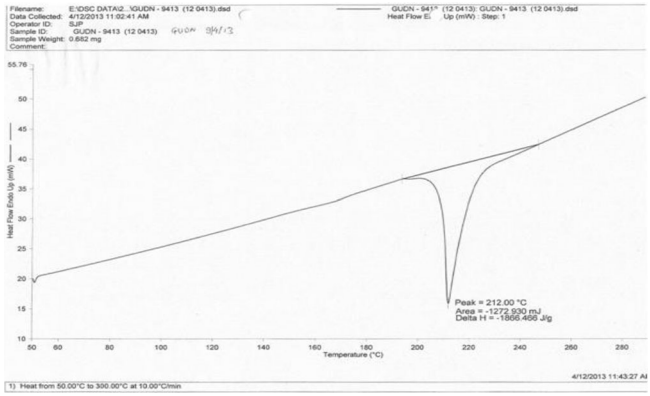


Figure 2. DSC curve of GUDN.

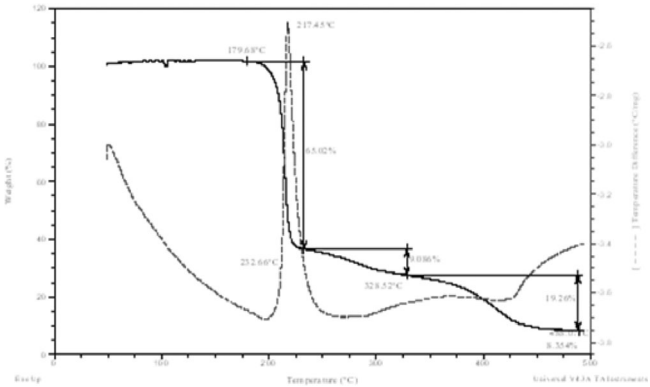
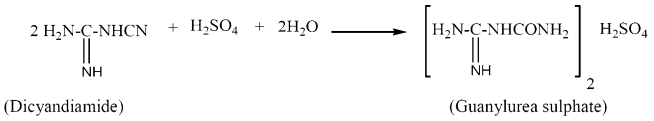


Figure 3. DTA curve of GUDN.

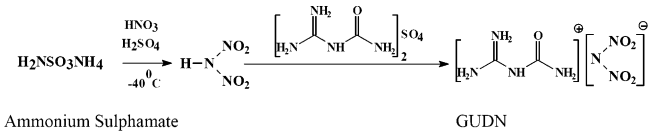
490 °C. The DTA curve indicates that the decomposition of GUDN is almost complete.

2.2 Preparation of Guanylurea Sulfate

Dicyandiamide (16.8 g, 0.2 mol) was treated with aqueous sulfuric acid (9.8 g, 0.1 mol in 50 mL H_2O) and kept over a hot water bath for 3–4 h. The resulting solution was placed in an ice bath for 1 h and the thus formed white crystals were filtered off. The remaining filtrate was concentrated over a hot water bath and cooled in ice. The resulting crystals were filtered, washed with 2-propanol and dried in an oven at 60 °C (Scheme 1). Melting point 200 °C, yield 95 %.



Scheme 1. Synthesis of guanylurea sulfate.



Scheme 2. Synthesis of guanylurea dinitramide (GUDN).

2.3 Synthesis of Guanylurea Dinitramide (GUDN)

A three-necked glass flask with mechanical stirrer assembly was fitted over a cryobath with a thermometer and an addition funnel. Conc. HNO_3 (98 %, 110 mL) was put into the flask and the cryobath was cooled to -45 ± 15 °C and conc. H_2SO_4 (98 %, 40 mL) was added dropwise whilst stirring (300 ± 25 rpm). Ammonium sulfamate (48 g, 0.42 mol) was added in small portions to the nitrating mixture for a period of 20 ± 5 min whilst stirring (300 ± 25 rpm) with constant monitoring the temperature (-20 to -50 °C), during the addition of ammonium sulfamate (Scheme 2).

Ice cold water (100 mL) was given in an open glass bowl fitted with a mechanical stirrer. *N*-Guanylurea sulfate (24 g, 0.212 mol) was suspended in ice cold water (100 mL) and the temperature was maintained at 10 ± 5 °C. The nitration mixture was quenched with the aqueous suspension (containing *N*-guanylurea sulfate) under constant stirring (300 ± 25 rpm). The reaction was robust. The color of the mixture turned to yellow and the suspension was allowed to attain ambient temperature under constant stirring (300 ± 25 rpm). After cooling, a crystalline white solid (GUDN) separated from the reaction mixture. GUDN was filtered under vacuum and washed with ice cold water and dried at 40 ± 5 °C for about 2 h. The amount of GUDN obtained was 25 g (yield 50 %). UV/Vis (λ_{max}, nm), 222 and 283 nm. FT-IR: $\tilde{\nu} =$ 3441, 3335, 3237 (NH_4^+), 1524, 1329, 1179, 814, 745 (NO_2) and (=N–N–N=) 1019, 915 cm^{-1} (Figure 4). DSC (dec. temperature) 212 °C (Ref. [7]: 212 °C).

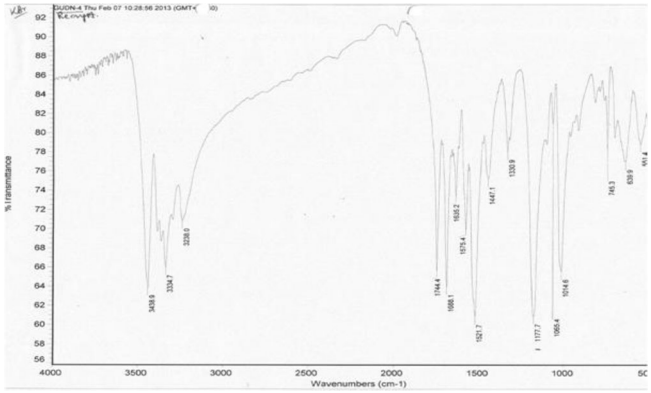


Figure 4. FT-IR spectrum of GUDN.*((<=Author: Fig. 1–4 are in very low resolution, text is almost illegible, especially fig.3. Can you provide figures in higher resolution?))*

3 Results and Discussion

This study describes the synthesis, characterization, and process optimization of GUDN, an insensitive energetic material, which finds application in insensitive munitions (IMs). The synthesis process involves nitration of the ammonium salt of sulfamic acid with conc. HNO_3/H_2SO_4 at $-20\,^{\circ}C$ to $-50\,^{\circ}C$ for about 30–40 min. Treatment of an aqueous suspension of guanylurea sulfate with the nitration mixture affords GUDN as insoluble white crystalline solid. The main advantage of this method is direct preparation of GUDN from ammonium sulfamate as solid product in high yield (50%) with high purity of $>98\%$ (as indicated by UV/Vis spectroscopy). The synthesis requires a low temperature in the range of -35 to $-45\,^{\circ}C$ during formation of dinitramidic acid. The formation of dinitramidic acid (DNA) is one of the crucial steps in the synthesis of guanylurea dinitramide. During quenching of the reaction mixture containing DNA by adding it to an aqueous solution of guanylurea sulfate, the temperature raised up to 60–70 °C forming acidic fumes. It is essential to maintain the temperature during the quenching of dinitramidic acid at about 10–15 °C to control the exothermicity of the reaction. The optimized reaction conditions are listed in Table 1.

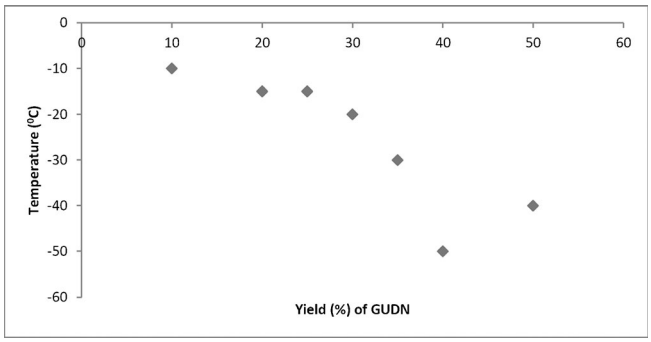


Figure 5. Effect of temperature on the yield of reaction.

3.1 Effect of Temperature on the Yield of GUDN

For the synthesis of energetic materials at higher batch size or for scaling up, it is necessary to determine the optimum reaction conditions to obtain the best yield of the product. Optimized parameters such as reaction time, temperature, and amount of nitrating mixture play a crucial role to achieve the product in high yield. The synthesis of GUDN involves nitration of ammonium sulfamate at $-20\,^{\circ}C$ to $-50\,^{\circ}C$ with a nitrating mixture. The nitration reaction is fast and highly exothermic and hence temperature optimization is one of the important factors to obtain a high yield. After addition of ammonium sulfamate to the nitrating mixture stirring was continued for a maximum of 1 h. As the temperature increased from $-20\,^{\circ}C$ to $-50\,^{\circ}C$, the yield of GUDN also varied. The optimized temperature for the synthesis of GUDN at which the highest yield was obtained is $-40\,^{\circ}C$ (Figure 5).

3.2 Effect of the Nitrating Mixture on the Reaction Yield

The crucial stage in the preparation of GUDN is the synthesis of dinitramidic acid (DNA), which involves nitration of ammonium sulfamate with a nitrating mixture in the temperature range $-35\,^{\circ}C$ to $-45\,^{\circ}C$. This step was modified by varying the quantity of the nitrating mixture. The progress of the reaction was monitored by UV/Vis spectroscopy. Figure 6 shows the effect of the amount of HNO_3 in the nitrating mixture on the yield of GUDN. In this study, the effects of nitrating mixtures with different ratios of the amount of sulfuric acid to nitric acid (1:2, 1:2.6, 1:3, and

Table 1. Effect of conditioning time, temperature and amount of nitrating mixture on the yield of GUDN.

Sr. No.	Amount of nitrating mixture (conc.H_2SO_4/HNO_3) [mL]	Temperature [°C]	Conditioning time [min]	Yield of GUDN [%]
1	50/100	−10	10	10
2	50/105	−15	15	20
3	55/110	−15	20	25
4	45/115	−20	25	30
5	40/120	−30	30	35
6	40/120	−40	40	50
7	40/130	−50	50	40

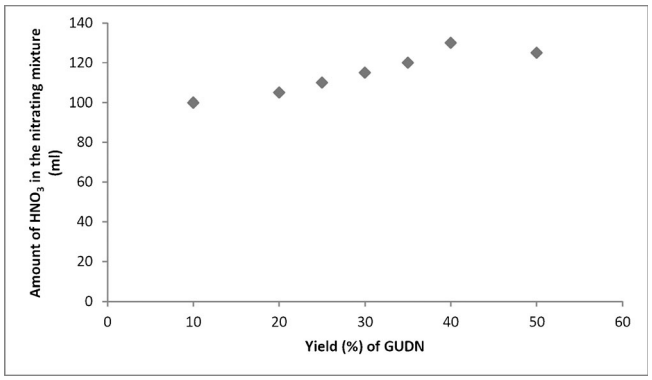


Figure 6. Effect of the amount of HNO_3 in the nitrating mixture on the reaction yield.

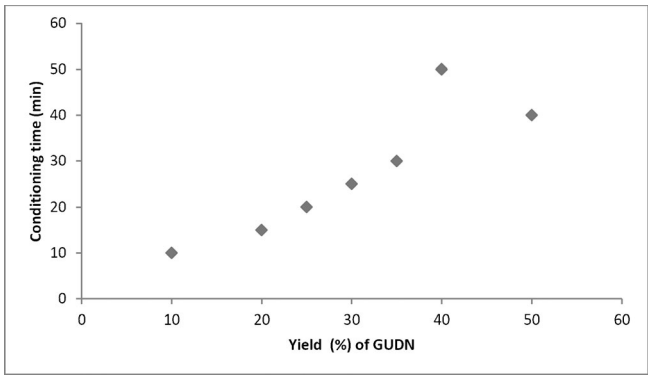


Figure 7. Effect of the conditioning time on the reaction yield.

1:3.25) were investigated. It was found that the best yield of GUDN (50%) was obtained with a nitrating mixture with 1:3 ratio (Figure 6).

It was also tried to use lower amounts of nitrating mixtures but this resulted in a decrease of the yield. Additionally, using an excess amount of nitrating mixture causes decomposition of the reaction mixture resulting in poor yield. After formation of dinitramidic acid, the solution was quenched with an aqueous solution of guanylurea sulfate at 10–15 °C. At this stage, an exothermic reaction with large acidic fumes occurred and the white crystalline solid GUDN formed. During this stage, maintaining the appropriate temperature is crucial otherwise a decrease in the yield and decomposition of the reaction mixture might occur.

3.3 Effect of Time on the Reaction Yield

The formation of dinitramidic acid is one of the key steps in the synthesis of GUDN. The yield of GUDN is mainly dependent on the conditioning time during addition of ammonium sulfamate using a nitrating mixture in the temperature range −25 °C to −50 °C. During the addition of ammonium sulfamate to the nitrating mixture, maintaining the temperature of the reaction mixture was necessary. Besides, after complete addition of ammonium sulfmate, the reaction mixture was further stirred for 20–45 min. By employing different conditioning times a better yield of dinitramidic acid could be achieved, which resulted in an improved yield of GUDN at −40 °C. The maximum yield was obtained after 40 min conditioning time as shown in Figure 7.

4 Conclusions

GUDN is one of the most important precursors for the synthesis of ADN via potassium dinitramide (KDN). GUDN was prepared by an ion exchange reaction between dinitramidic acid (DNA) and *N*-guanylurea sulfate. This study describes the synthesis, characterization, and process optimization of GUDN. The optimized reaction conditions for the synthesis of GUDN were: conditioning time of 40 ± 5 min, nitrating mixture in 1:3 molar ratio, and an optimized temperature of −40 °C ± 5 °C. Thus, GUDN could be obtained in a yield of 50%.

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