Synthesis of Ammonium Dinitramide by Nitration of Potassium and Ammonium Sulfamate. The Effect of Sulfamate Conterion on ADN Purity

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ABSTRACT: *Nitration of potassium sulphamate was carried out using a mixture of sulphuric and nitric acid at -30 °C. The reaction time was optimized at the mole ratio of sulphuric to nitric acid of (1:3.5). The difference in product yield by changing the potassium to ammonium sulphamate was studied throughly. It was found that both the yield and purity of the product is better starting with potassium sulphamate.*

KEY WORD: *Potassium sulphamate, Dinitramidic acid, Nitration, Ammonium dinitramide, Potassium dinitramide.*

INTRODUCTION

Dinitramide salts, a uniquely stable oxyanion of nitrogen, were first discovered in 1988 [1,2]. The dinitramide salts have high oxygen content and are prepared with different counterions including potassium cesium, ammonium and hydrazinium salts. The ammonium salt of dinitramide anion, ($NH_4N(NO_2)_2$) or ADN is thermally more labile and impact sensitive than ammonium nitrate, but considerably more stable than the related covalenty bounded, N-N-dinitro derivatives such as alkyldinitramines ($R\text{-}N(NO_2)_2$) or nitramide.

The ability of dinitramide anion to form stable oxygen rich salts with a variety of cations makes it a promising candidate for the development of energetic oxidizers in solid propellants. A potential practical use for this compound is as a replacement for ammonium perchlorate (AP) to give an environmentally benign solid rocket propellant system [3]. It is expected that the combustion of propellants containing halogen-free ADN instead of ammonium perchlorate (AP) will show a significant reduced plume signature and atmospheric ozone destruction caused by the emission of hydrochloric acid. With respect to ammonium nitrate, ADN has higher energy content. The exothermic decomposition takes place already under low pressure.

ADN is prepared generally by two methods:

- From dinitramines possessing the following pattern:

$XCH_2CH_2N(NO_2)_2$ which during decomposition in ammonia/water solution liberate ADN and a vinylic compound $CH_2 = CHX$ (X = NO_2, CHO, COR, COOR, CN) [4].

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- By nitration of deactivated amines (H_2NX) with strong nitrating agent like N_2O_5, NO_2BF_4, NO_2F, $NO_2HS_2O_7$, HNO_3/H_2SO_4, and $HNO_3/SO_3/H_2SO_4$ [2,4].

$$KSO_3NH_2 + 2HNO_3 \xrightarrow[-30\,^{\circ}C]{H_2SO_4} KHSO_4 + NH_4N(NO_2)_2 + H_2O$$

Recently dinitration of ammonia, with relatively good yield is also described. ADN is obtained in this case after neutralization of the reaction mixture with ammonia (gas) or ammonia solution (NH_3/H_2O). In any case, the nitration reactions are highly exothermic and need temperatures below 0 ^{o}C to run with good yields.

In the present paper, we report on the effect of sulfamate counterion on ADN purity. The effect of reaction temperature and agitation speed on the ADN yield will be discussed in a forthcoming paper.

EXPERIMENTAL PROCEDURE

ADN synthesis is carried out according to the following procedure:

Preparation of potassium sulfamate

Sulfamic acid (H_2NSO_3H) (70.35 g) is suspended in 50 ml water. 44 g potassium hydroxide is dissolved in a small amount of water (50 ml) and added to the suspended sulfamic acid.

70 ml of the neutral solution were poured into 100 ml ethanol. The potassium salt of the sulfamic acid precipitated. The salt was filtered off on a paper filter, washed with alcohol and dried in oven at 70 ^{o}C. When dry, the salt is ground to a very fine powder [8].

Nitration

Potassium sulphamate (17 g) was added in small portion of 0.5-1 g during vigorous agitation to a mixture containing 16 ml H_2SO_4 (98 %) and 45 ml fuming HNO_3. The nitration mixture was kept cool to about -35 to -45 ^{o}C, with a mixture of dry ice and dichloromethane. The viscosity increased significantly as the reaction proceeded and $KHSO_4$ precipitated. The amount of dinitramidic acid formation was followed a UV spectrophotometer at λ_{max} = 284 nm of the $n \rightarrow \pi^*$ transition of acid. Since the acid is not stable in acidic media, the acid content of the reaction mixture begins to decrease after a certain reaction time.

To determine the yield of acid, the reaction was interrupted in different time intervals. The reaction mixture was poured into a bath containing 150 g of crushed ice and 150 ml of water and neutralized immediately by a cold solution of potassium hydroxide.

Neutralization

A solution of cold potassium hydroxide was added to the reaction mixture with a vigorous agitation, while the mixture was kept cool with dry ice and dichloromethane. The temperature was not allowed to rise above 0 ^{o}C. When the neutralization approaches its terminal point, the solution becomes a characteristic green-yellow color. The neutralization continued until the solution was weakly basic (pH = 8).

The reaction mixture was evaporated to dryness powder. The dry powder was extracted with acetone, then 100 ml of 2-propanol was added to the acetone solution, and the mixture was evaporated.

Acetone dissipated first and potassium dinitramide (KDN) having a low solubility in 2-propanol precipitates. The crystals were filtered off and dried in an oven at 70 ^{o}C. KDN is obtained with 60 % yield (10.7 g) and the melting point of 130.5 ^{o}C [9].

Preparation of ADN from KDN

KDN (0.5 g) and 0.5 g $(NH_4)_2SO_4$ were each dissolved separately in 1 ml water. The solutions were mixed with each other; a white precipitate of K_2SO_4 was obtained. 10 ml of 2-propanol was added to the solution and K_2SO_4 was filtered off, the solvent was evaporated under reduced pressure. The slightly moist product from the evaporation was dissolved in 2-propanol and poured into petroleum ether, ADN precipitated. The precipitate was filtered off and dried at 50^{o}C. ADN (0.34 g) is obtained in 80 % yield with a melting point of 91 ^{o}C.

The nitration procedure was repeated by starting from ammonium sulfamate. The reaction mixture was neutralized with ammonia solution. ADN was obtained in 40 % total yield, with melting point of 86 ^{o}C. Recrystallization of ADN obtained by starting from ammonium sulfamate by dissolving crude ADN in 2-propanol and adding petroleum ether while diminishing the total yield to 30 %, increased the melting point to 89 ^{o}C. It seems that the very small amount of ammonium nitrate will remain in the sample in this case even after

the recrystalization step. Therefore, it is recommended that ADN should be prepared and purified carefully to avoid any ammonium nitrate contamination.

RESULTS AND DISCUSSION

The covalently bound alkyldinitramines have been well studied [5-7]. All covalently bound alkyldinitramines suffer instability problems that presumably originate from a combination of the steric hindrance between the two nitro groups and the high electonegativity of N-N-dinitro group. A N-N-dinitro group leaves the alkyldinitramine electron deficient, especially at the central nitrogen; these effects destabilize alkyldinitramines and the instability can be observed in their thermal properties; all known alkyldinitramines decompose thermally at temperatures less than 70 ^{o}C and are highly shock and impact sensitive.

The relative stability of nitrogen oxides, as ammonium (NH_4^+) salts measured by thermal analysis is NO_3^->$N(NO_2)_2^-$>NO_2^->>alky-$N(NO_2)_2$.

According to the Fig. 1, the corresponding dinitramide salts have less steric hindrance between the nitro groups (at least partial sp^2 hybridization at the central nitrogen and a higher N-N bond order due to the overall negative charge).

The best method to prepare the dinitramidic acid is by nitration of sulfamic acid (NH_2SO_3H) and its salts. The nitration has been carried out with a common nitrating mixture like nitric acid/sulphuric acid (HNO_3/H_2SO_4). No aprotic solvent for the nitrating agent is required when nitrating with the nitrating acids. Potassium, or ammonium sulfamate is used as starting material. For the neutralization step, neutralizing the formed dinitramidic acid to dinitramide salt, potassium hydroxide or ammonia solution is used respectively. For the nitration, the nitrating acid is cooled to low temperature, -25 ^{o}C or below, and the initial substance, the sulfamic acid salt, is added with vigorous stirring. The reaction is carried out in a reaction vessel, where a high dissipation of heat can be ensured, as the reaction mixture becomes relatively viscous when the reaction proceeds. As the reaction proceeds, dinitramidic acid, $HN(NO_2)_2$ or HDN is formed. HDN is not stable in acidic environment, once the acid content of the reaction mixture rises to a maximum, the reaction should be stopped and immediately should be diluted and neutralized by KOH.

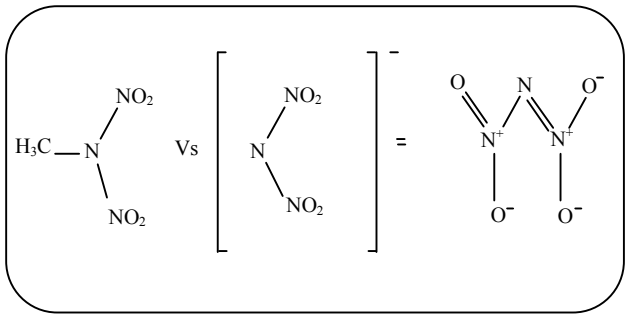

Fig. 1: Bonding in an alkyldinitramine versus dinitramide.

Since the product yield during nitration depends on important parameters like viscosity of the medium, temperature, agitation speed and rate of addition of the reactant; the formation of the dinitramidic acid and its decomposition in acidic medium becomes a critical factor, determining the yield of the product. These factors can be overcome by increasing the rate of agitation of the reaction mixture, cooling the reactor at much faster rate and also by making the system less viscous, so that the transfer of nitronium ion to the substrate takes place effectively. The viscosity of the medium can be decreased when more nitric acid is taken in the system [8].

Experiments were carried out for different periods of time with sulfuric/nitric acid ratio of 1:3.5 (Fig. 2). Fig. 2 shows that, the product yield reaches a maximum at 25 min and then decreases. These results can be explained based on the stability of the dinitramidic acid formed in the reaction mixture.

Elemental Analysis

Elemental analysis was run on a CHN-O-rapid model Fossheraeus at Petroleum Research Center, Shahre Ray, Iran. Elemental analysis of the product agrees well with calculated values, nitrogen 44.3 % (45.1 %), hydrogen 3.1 % (3.2 %).

DSC measurements

DSC was recorded in Malek Ashtar University. The thermal stability of ADN was measured by recording a DSC diagram. A typical DSC curve is shown in Fig 3. The samples were heated from room temperature with a heating rate of 10 ^{o}C/min. the synthesized ADN has an endothermic minimum at 87.56 ^{o}C and an exothermic maximum at 183.31 ^{o}C.

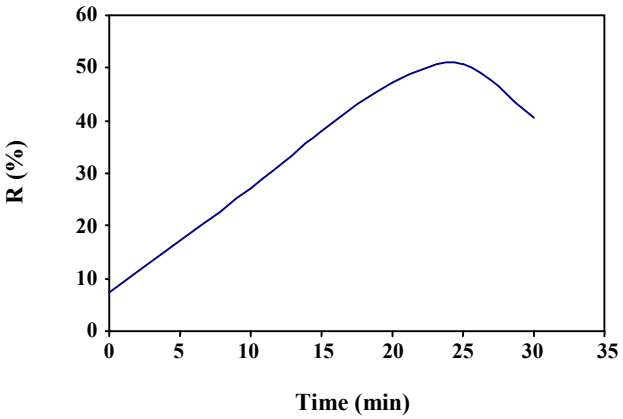

Fig. 2: Plots of total yield vs. time of nitration for ADN.

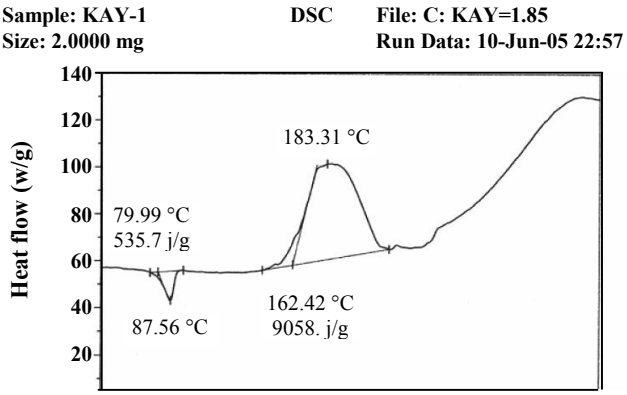

Fig. 3: DSC diagram of purified ADN by ethyl acetate.

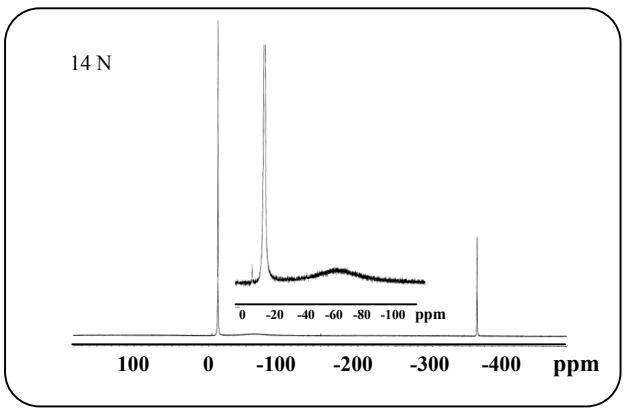

Fig. 4: The ^{14}N-NMR Spectrum of AND.

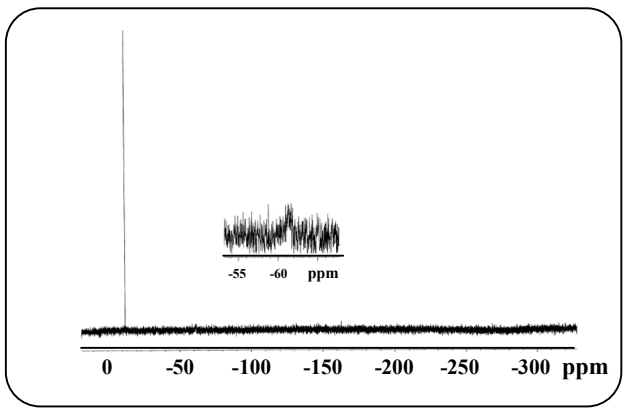

Fig. 5: The ^{15}N-NMR spectrum of AND.

^{14}N and ^{15}N-NMR Spectroscopy

The ^{14}N and ^{15}N-NMR spectrum were run on a Brucker Avance 500MHz-NMR Spectrometer at Tarbiat Moddaress University. The ^{14}N NMR spectrum of ADN (Fig. 4) shows there signals at δ = -12.0, -60.2 and -360.1 ppm. The signal at δ = -12.0 ppm is assigned for the nitrogen in the nitro group of the dinitramide. Signal at δ = -60.2 ppm is assigned for the central nitrogen atom of the dinitramide and at δ = -360.1 ppm the nitrogen atom of the ammonium ion is assigned.

The ^{15}N NMR spectrum of ADN (Fig. 5) shows three signals at -12.2, -60.8 and -360.1. The chemical shifts (in ppm) are based on the ^{14}N and ^{15}N chemical shifts of nitromethane as external reference.

UV-VIS spectroscopy

UV-VIS spectrum was recorded by the Shimadzu UV - VIS spectrophotometer. λ (ε) 214 (6680), 284 (5.329×10^3) Fig. 6 (λ = nm ε = Lmole^{-1} cm^{-1})

Infrared spectroscopy

FTIR Spectrum was recorded on Perkin Elmer, 1710 spectrophotometer. Infrared vibrational frequencies and the FT.IR spectrum of ADN are shown in table 1 and Fig. 7.

CONCLUSIONS

Nitration of potassium sulphamate using sulphuric acid/ nitric acid mixture results in the formation of dinitramidic acid. The excess acid present in the reaction mixture affects the stability of the formed dinitramidic acid, bringing down its overall yield. Maximum yield of dinitramidic acid (50.8 %) was obtained in 25 minutes when the mole ratios of sulphuric acid to nitric acid is 1:3.5.

To obtain a pure ADN product, it is recommended that KDN is prepared and purified. ADN is obtained from KDN and ammonium sulphate by cation exchange.

Table 1: Infrared vibrational frequencies of ADN.

assignt	Approx mode description	Observed freq. (cm^{-1})
A ν_1	ν as NO_2 in phase	1526 s
ν_2	ν s NO_2 in phase	1344 w
ν_3	ν s N_3	954 sh
ν_4	δ sciss NO_2 in phase	828 mw
ν_5	δ rock NO_2 in phase	738 vw
ν_6	δ wag NO_2 in phase	490 w
B ν_9	ν as NO_2 out of phase	1455 sh
ν_{10}	ν s NO_2 out of phase	1238 sh; 1181 vs
ν_{11}	ν as N_3	1025 s
ν_{12}	δ sciss NO_2 out of phase	761 m
ν_{13}	δ rock NO_2 out of phase	727 m; 722 m
ν_{14}	δ wag NO_2 out of phase	490 w

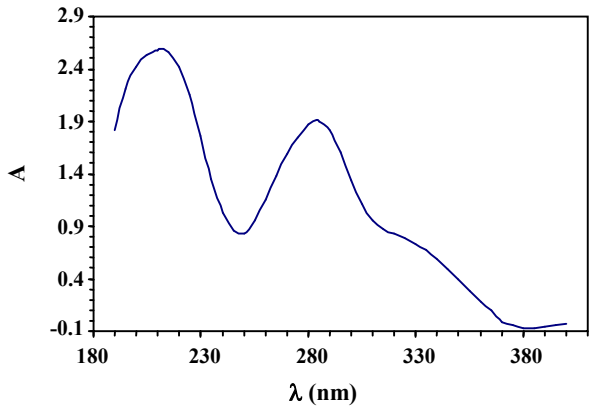

Fig. 6: UV spectrum of ammonium dinitramide aqeous solution.

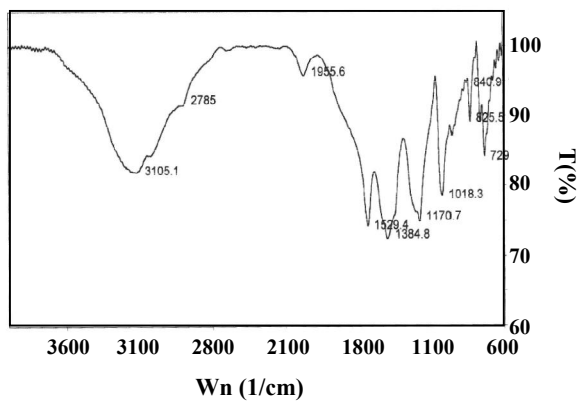

Fig. 7: FT-IR spectrum of purified ADN by ethyl acetate.

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