Study on the formation of dinitramide using mixed acid nitrating agents

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Nitration of ammonium sulphamate was carried out using a mixture of sulphuric acid and nitric acid at -30 to -40°C. The mole ratio of sulphuric acid to nitric acid was varied from 0 to 4 and the extent of formation of ammonium dinitramide (ADN) was measured. The initial yield of ADN increases with increase of sulphuric acid content in the acid mixture and starts decreasing as the reaction time is increased. The variation of product yield with change in reaction time and total acid concentration was studied.

There has been a lot of interest in recent years for the development of new high energy halogen-free oxidizers like ammonium dinitramide (ADN), hydrazinium nitroformate (HNF), hexanitrohexaaza-iso-wurtzitane (CL-20), 1,3,3-trinitroazetidine (TNAZ) etc., having high density and heat of formation. Ammonium dinitramide (ADN) is the ammonium salt of the nitramide salt of 1,1,3,3-tetraoxo-1,2,3-triazapropene anion. Dinitramide salts are useful oxidizers for high energy materials such as propellants, pyrotechnics and gas generating formulations. Russians at the Zelinsky Institute of Russia in 1971 invented a method for synthesizing dinitramide anion. Subsequently Bottaro and co-workers in USA invented methods in 1989 for the synthesis of both inorganic and organic dinitramides which could provide a new class of energetic materials. They are generally prepared by nitration of deactivated amines like NH₂NO₂ using exotic nitrating agents namely NO₂BF₄ or N₂O₅. Langlet et al., have reported that dinitramide and its salts can be prepared by nitration of ammonia-sulfate derivatives such as NH₄SO₃NH₂, NH₂SO₄(NH₄)₂ etc., using a mixture of HNO₃/H₂SO₄. The ability of dinitramide anion to form stable oxygen rich salts with a variety of cations to make compounds of high densities makes it a promising candidate for the development of energetic oxidisers in solid propellants. The present paper gives a detailed investigation on the formation of dinitramide using mixed acid nitrating agents under different conditions.

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Experimental Procedure

Materials

Ammonium sulphamate AR (SRL, Bombay) was powdered well in a mortar and pestle and was further dried in vacuum.

Conc. H₂SO₄ 98% (Qualigens, Bombay) was used as received.

Fuming HNO₃ > 98% was distilled in the laboratory from a mixture of 1:1 by weight of fuming HNO₃ (92%) with conc. H₂SO₄. The fraction between 83-85°C was used.

Liquor ammonia AR, about 25% NH₃ (Qualigens, Bombay) was used as received.

Methods

Ammonium sulphamate (5.7 g, 0.05 M) was added in small portions to a mixture containing H₂SO₄ (98%) and fuming HNO₃ at a temperature range of -35°C to -45°C in a 3 necked RB flask with stirring. The rate of addition was controlled in such a way that the temperature of the mixture did not exceed -35°C. The reaction mixture was then poured into about 100 g of crushed ice. The diluted acid was neutralised by ammonia solution. The pH of the solution was checked during the course of the neutralisation and was continued till the solution became alkaline (pH - 8).

The neutralised solution was diluted to a known concentration and analyzed by UV spectroscopy. The yield of the product was calculated by measuring the absorbance at 284 nm using the calculated molar extinction coefficient (ε). The neutralised solution was then vacuum evaporated and dried. The dried solids were then extracted with isopropanol, concentrated and dried. This was purified further by
Extraction with ethyl acetate to get ammonium dinitramide (ADN).

UV spectrum of the sample was recorded on CARY 5E UV-VIS-NIR spectrometer as water solution in the range of 200-400 nm.

Infrared spectrum of the product was recorded on Nicolet 510P FTIR spectrometer in the range of 4000-400 cm⁻¹.

Thermal study of the product by DSC was carried out using DSC-TA Instruments model DSC - 2920 at a heating rate of 5 °C per minute.

Results and Discussions

In the nitration, the first step is the formation of nitronium ion (NO₂⁺) by ionisation of HNO₃ by strong acids such as HF, HClO₄, H₂SO₄ or solid acid catalysts. The latter compounds promote ionisation of HNO₃ to NO₂⁺. H₂SO₄ is one of the most frequently employed reagents during nitration.

In a mixture of different ratios of HNO₃/H₂SO₄, the mole percent of NO₂⁺ present have been measured and well-documented. For a given concentration of HNO₃/H₂SO₄, the maximum concentration of NO₂⁺ is obtained when the mole ratio of H₂SO₄/HNO₃ is about 2. During aromatic nitration using mixed acid nitrating agents it is necessary that the nitronium ion concentration is as high as possible and the attack of the latter with the aromatic substrate is the slow rate determining step. In the case of aliphatic nitrations the attack of nitronium ion is much faster. For the conversion of ammonium sulphamate (AS) to dinitramide acid (HN(NO₂)₂), the stoichiometric ratio of the nitronium ion to reactant AS is 2 as per Eq. (1).

\[
\text{NH}_2\text{SO}_3\text{NH}_2 + 2\text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_2\text{O} \rightarrow \text{HN(NO}_2)_2 + 2\text{H}_2\text{SO}_4^- + \text{NH}_4\text{HSO}_4 \quad (1)
\]

The neutralization step is given in Eq. (2).

\[
\text{HN(NO}_2)_2 + 2\text{H}_2\text{SO}_4^- + \text{NH}_4\text{HSO}_4 + 6\text{NH}_3 \rightarrow 2\text{NH}_4\text{N(NO}_2)_2 + 3(\text{NH}_4)_2\text{SO}_4 \quad (2)
\]

Experiments were carried out using different ratios of nitric acid (NA) and sulphuric acid (SA) for different period of time. A control experiment was performed using nitric acid alone and the results were given in Table 1.

When experiments were carried out, using the stoichiometric ratio of 2, a maximum yield of 45% of the product was obtained in 20 min, and as the reaction time was increased to 30 min, the product yield decreased to 35% due to the decomposition of the product with excess acid present in the system.

The acid mixture with SA/NA in the mole ratio of 2:1 is very viscous at -40°C and hence fast addition of the reactant (AS) at a controlled rate and vigorous stirring becomes very difficult.

As the molar concentration of the acids increases, the NO₂⁺ concentration also would increase correspondingly. When equimolar mixture of acids were taken, the product yield increased with increase of the total acid concentration (i.e., sulphuric acid and nitric acid). An yield of 34% was obtained in 30 min when equimolar mixture of acids were taken.

It is seen from Table 1. that as the sulphuric acid to nitric acid mole ratio increases from 2:2 to 4:2 the yield of the product increases. When the mole ratio of SA to NA is 2:6 the yield of the product decreases. This is because the excess acid present in the system reacts with the dinitramide acid formed, thereby decreasing the yield. When SA/NA mole ratios are 1:1 and 2:1, the reaction mixture becomes very viscous at temperatures below -30°C. Since the product yield during nitration depends on important parameters like viscosity of the medium, temperature, agitation speed and rate of addition of the reactants, the formation of the dinitramide acid and its decomposition in acid 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 could be decreased when more nitric acid is taken in the system. In order to reduce the viscosity of the reaction medium and to promote effective stirring, experiments were carried out with sulphuric acid to nitric acid in the mole ratio of 1:3. The product yield increases as the reaction time is increased. An yield of 30% is obtained in 30min for SA/NA mole ratio 1:3 and 14% for SA/NA mole ratio 0:4.

Experiments were carried out for different mole ratios of sulphuric acid to nitric acid (from 0 to 4) and the yields of the product obtained for different periods of time are shown in Fig. 1.
Fig. 1 shows the product yield plotted against the reaction time for the reactions carried out with mole ratios of SA/NA 1:3, 1:1 and 2:1. From the figure it is seen that when the sulphuric acid to nitric acid mole ratio is 2:1 the product yield reaches a maximum at 20 min. When the mole ratio is 1:1 it reaches a maximum at 10 min. When the mole ratio is 1:3 the product yield is low at 10 min and gradually increases when the reaction time is increased. These results can be explained based on the stability of the dinitramidic acid formed in the reaction mixture. These results indicate that the extent of decomposition of the product is much lower when SA/NA mole ratio is <1 compared to the case with the acid mixture having SA/NA mole ratio > 1.

Spectral and thermal analysis of ammonium dinitramide

The product obtained was characterized by means of UV, IR spectroscopy, and differential scanning calorimetry.

Ammonium dinitramide shows UV maximum in water at 212 and 284 nm \(^3\). UV spectrum of ammonium dinitramide in water is given in Fig. 2. The absorbance values at 284 nm were measured for solutions of different concentrations and plotted against the concentration. The extinction coefficient \(E_{284}\) (obtained from concentration versus absorbance) is \(5.248 \times 10^3 \text{ Lmol}^{-1}\text{cm}^{-1}\) and this value is comparable with the value reported by Bottaro et al., \(E_{284} = 5.207 \times 10^3 \text{ Lmol}^{-1}\text{cm}^{-1}\). Tartakovsky et al., however, reported a value\(^5\) of \(E_{285} = 5.640 \times 10^3 \text{ Lmol}^{-1}\text{cm}^{-1}\).

Infrared spectrum of the product shows characteristic peaks\(^4\) at 3136 cm\(^{-1}\) (v N-H of NH\(^+\)), 1531 cm\(^{-1}\) (asymmetric in phase of NO\(^2\)), and 1344 cm\(^{-1}\) (symmetric in phase of NO\(^2\)). A typical IR spectrum is shown in Fig. 3.

Thermal study of the product by DSC\(^5\) shows endotherm at 92°C corresponding to the melting of...
the sample, followed by an exotherm in the range of 140°C-230°C. A typical DSC of the product is given in Fig. 4.

Conclusions
Nitration of ammonium sulphamate using sulphuric acid/nitric acid mixture results in formation of dinitramide and the product yield depends on the mole ratio of ammonium sulphamate to total acids. The excess acid present in the reaction mixture affects the stability of the formed dinitramide acid, thereby bringing down its overall yield. Maximum yield of dinitramide acid 45% was obtained in 20 mts when the mole ratios of sulphuric acid to nitric acid is 2:1 and ammonium sulphamate to total acids is 1:6.

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