Safety of Ammonium Dinitramide Synthesis *vs.* Size of a Commercial Production Scale

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Abstract: Ammonium dinitramide (ADN) is an ecological oxidizer suggested as a substitute for ammonium chlorate(VII) in solid rocket fuels. Three ADN synthetic methods were studied in order to estimate process safety under increased production scale, *viz.:* from ammonia (Method I), from urea (Method II), or from potassium sulfamate (Method III). The intermediates formed in these processes were identified and their thermal stability was examined. DSC analysis showed that the intermediates in Method II are unstable, they readily decompose and pose an explosion hazard. The intermediate in Method III is more thermally stable and less hazardous than its counterparts in Method II. The most suitable methods for large-scale processes are Methods I and III. The preferred method for commercial ADN production, in terms of safety, is Method III.

Keywords: ADN synthesis, safety, explosion potential, increased production scale

1   Introduction

Ammonium dinitramide (ADN) is employed as an oxidant in solid rocket propellants [1] and as a component in explosive mixtures to improve their oxygen balance [2]. As a result of the combustion of an ADN-based rocket fuel, no condensation trail is formed which otherwise facilitates the tracking of the rocket trajectory and the site it had been fired from [3]. Replacement of ammonium chlorate(VII) in a rocket fuel by ADN allows its specific impulse to

be increased [4]. A few synthetic routes to ammonium dinitramide are reported in pertinent literature [5-10]. Some of these are feasible on a small-scale only, as the required reactants are expensive (*e.g.* nitronium salts) [5, 6]. In order to assess the process safety and the feasibility of large-scale ADN synthesis, three synthetic methods were chosen, *viz.*: from ammonia (Method I) [7], from urea (Method II) [8] and from potassium sulfamate (Method III) [9, 10]. The ammonium dinitramide synthesis from ammonia (Method I) is a single-stage process. The reaction consists of nitration of ammonia by means of dinitrogen pentoxide in an inert solvent. The ammonium dinitramide formed is isolated by extraction or absorption. The *N,N'*-dinitrourea obtained in stage one from urea (Method II) is subsequently hydrolyzed to *N*-nitroamine. This second intermediate product is then nitrated to *N,N'*-dinitroamine. The reaction mixture is finally neutralized with ammonia. The ammonium dinitramide formed is isolated by extraction or absorption. ADN synthesis from potassium sulfamate (Method III) is a two-stage process. Stage one involves the preparation of potassium dinitramide (KDN), and stage two involves the exchange of the cation in this salt, either using a cationic exchanger or by a double replacement reaction with ammonium sulfate.

The safety of the syntheses can be assessed by analyzing the hazards connected with the properties of the intermediates formed and with the process reactions. One of the parameters that characterizes the compounds (intermediate products) formed is the maximum safe temperature of the manufacturing processes involving their use, T_{max}. The simplest method for this assessment is "the 100-deg rule" [11]. According to this rule, the maximum safe temperature of a manufacturing processes is the temperature 100 °C lower than the temperature corresponding to the maximum of the decomposition peak of the intermediate or final products recorded by DSC and DTA techniques while heating at 10.0 °C/min, or 70 °C lower than the temperature of the decomposition peak recorded on heating at from 0.5 to 2.0 °C/min. The parameter that classifies hazardous materials is the explosion potential (EP). Materials for which EP values are greater than zero are believed to be potentially hazardous and capable of exploding. Two empirical equations are reported in the literature [12, 13] that describe this parameter, notably:

$$EP = \log(-\Delta H_D) - 0.38 \cdot \log(T_0 - 298.15) - 1.67 \qquad (1)$$
$$EP' = \log(-\Delta H_D) - 0.44 \cdot \log(T_0 - 298.15) - 2.11 \qquad (2)$$

where: ΔH_D – enthalpy of decomposition (J/g), T_0 – onset temperature of decomposition (K). The method identifies two groups of materials: potentially safe and potentially hazardous. Hazards related to the reaction progress are

connected with self-heating of the reaction mixture. In the event of the rapid progress of the reaction resulting from elevated temperature, the reaction mixture will quickly become heated, which may result in a thermal explosion [14, 15]. The original temperature rise may be due, for instance, to a failure of the cooling or stirring system. The maximum possible temperature rise ΔT_{ad} (known as the adiabatic temperature rise) may be found experimentally [16]. This rise may also be estimated from the heat of reaction (ΔH) and the heat capacity of the reaction mixture (c_p) [17] using the following equation:

$$\Delta T_{ad} = \frac{|\Delta H|}{\bar{c}_p}$$
(3)

The purpose of the present study was a comparison of the ADN synthetic methods with respect to their commercial application. Attention was directed to the process safety, the yield, and the price of the starting materials. For the intermediates isolated from the process, the explosion hazard index was determined, as was the maximum safe temperature at which the manufacturing processes could be conducted.

2   Experimental

2.1 Materials and analytical instruments

The starting materials used in the syntheses were of at least 98% purity grade. Calorimetric measurements were carried out using a Unipan DSC 605 M microcalorimeter. The measurements were made using vacuum-closable aluminum holders. Decomposition tests were performed on samples of mass not greater than 1.0 mg. Sample masses for purity determination were about 10 mg. The rate of temperature rise in all measurements was 2.0 °C/min. The ammonium dinitramide content in solution and in the solid product was determined using a UV-VIS spectrophotometer Evolution 60, at 285 nm.

2.2 Adiabatic temperature rise

The adiabatic temperature rise was estimated from the heat of reaction and the heat capacity of the reaction mixtures. For the computations, typical values of the heat of reaction for nitration 200 kJ/mol, neutralization 55 kJ/mol, as well as values for the mean heat capacity of the reacting substances, chlorinated hydrocarbons 1.0, sulfuric acid 1.4 and nitric acid 1.7 J/g °C [17, 18] were used. For the remaining substances of a lesser mass, an average value of 2.0 J/g °C was assumed.

2.3 ADN synthesis

2.3.1. *ADN synthesis from ammonia (Method I).*

Dichloromethane (85 mL) and chloroform (85 mL) were added to the reaction vessel. Dinitrogen pentoxide (7 g) was then added, the vessel was tightly closed and the whole was cooled to ca. −80 °C with vigorous stirring. As soon as the system reached the required temperature, ozone was passed through the solution until it acquired a bluish tint. Subsequently, gaseous ammonia was passed for ca. 1 hour at a rate of 4 L/h, until an alkaline pH value had been achieved in the mixture. During the ammonia feed the temperature was monitored and maintained within −80 to −70 °C. Cooling and vigorous stirring were maintained for a further 120 min. After that time the reaction mixture was allowed to stand until it had attained ambient temperature. The precipitate formed was separated by filtration and the filter cake was washed with a dichloromethane/chloroform mixture (1:1 by volume, 50 mL). The product was analyzed by UV-VIS spectrophotometry. The reaction yield was 16%.

2.3.2 *ADN synthesis from urea (Method II)*

N,N'-Dinitrourea synthesis: Fuming nitric(V) acid (36 mL) and 20% fuming sulfuric acid (22.4 mL) were added to a 250-mL three-necked round-bottom flask, equipped with a mechanical stirrer and thermometer. The resultant nitrating mixture was cooled to −5 °C. Previously dried and powdered urea (15.5 g) was added portionwise to this mixture during 7 min, while maintaining the temperature within −3 to +5 °C. Stirring was continued for 30 min. The *N,N'*-dinitrourea (DNU) suspension in the post-nitration acids was cooled to −5 °C and filtered off. The filter cake was washed 3 times with dichloromethane. About 40 g of moist *N,N'*-dinitrourea was obtained.

   Nitroamine synthesis: Water (100 mL) was placed in a beaker and cooled to 0 °C. Subsequently, the *N,N'*-dinitrourea obtained was added portionwise with constant stirring while maintaining the temperature within 0 ° to +2 °C. When the addition was complete, the stirring of the solution was continued for about 20 min until the solution became clear. The *N*-nitroamine solution obtained was extracted with ethyl acetate. The organic layer was concentrated in an evaporator at 35 °C. *N*-Nitroamine (MNA) was obtained in 74% yield (against the starting urea).

   ADN synthesis from N-nitroamine: Fuming nitric(V) acid (23.9 mL) and 96% sulfuric(VI) acid (8.5 mL) were placed in a three-necked round-bottom flask, equipped with a thermometer and a mechanical stirrer. The nitrating mixture thus prepared was cooled to −30 °C and then the previously prepared

N-nitroamine (5.5 g) was added, while maintaining the temperature of the mixture between −28 and −26 °C. The solution was stirred for 20 min while maintaining the temperature in the specified range. On completion of the reaction, the contents were poured into ice/water and neutralized with ammonia to pH = 7. Ammonium dinitramide was obtained in 87% yield, as determined by UV-VIS spectral analysis.

2.3.3   *ADN synthesis from potassium sulfamate (Method III)*

Potassium dinitramide synthesis: Fuming nitric(V) acid (106.0 mL) and 95% sulfuric(VI) acid (26.4 mL) were poured into a three-necked round-bottom flask. Stirring was commenced and, as soon as a temperature of -40 ± 2 °C had been achieved, finely ground and dried potassium sulfamate (40.0 g) was added. The reactant was added in 4-g portions for 10 min. After the addition of the last portion of the sulfamate salt, vigorous agitation was continued for 30 min. As the reaction progressed, the viscosity of the mixture increased and potassium sulfate precipitated. After the required time, the reaction mixture was poured onto finely crushed ice (400 g). A cooled 50% potassium hydroxide solution was added stepwise to the post-reaction mixture. The temperature was maintained in the range of −10 to 0 °C. As the neutralization point was being approached, the reaction mixture assumed a characteristic yellow-green colour. The neutralization process was stopped when the pH of the mixture became slightly basic (pH $\approx$ 7 to 8), the precipitate formed was filtered off on a Schott funnel under reduced pressure and washed with water (60 mL). The filtrate was concentrated on a rotary evaporator to about one fourth of its volume, whereupon the mixture was cooled to room temperature. The precipitated salts were filtered off and washed with water (40 mL). The filtrate was evaporated to dryness to obtain a mixture of the potassium salts of sulfuric acid, nitric acid and dinitramide. The dried salt mixture was extracted with acetone (130 mL) with vigorous agitation. On filtration of the precipitate on a Schott funnel, the solid was washed with acetone (50 mL). The extraction process was then repeated using the same quantities of acetone. The combined filtrates were evaporated to dryness in a rotary evaporator. The KDN obtained was dried to a constant weight at 60 °C. KDN (20.8 g, 48.8% yield) was obtained and was of 99.3 mol% purity, as determined cryometrically [19].

ADN synthesis from potassium dinitramide: Ion exchange of the salt was carried out on an ion-exchange resin, Dowex 50W. The resin was allowed to swell in distilled water for 24 hours. Then the ion-exchange resin was transferred to a column, washed with hydrochloric acid of concentration 1 mol·dm^{-3}, and then several times with distilled water until neutral. KDN (4.2 g) was dissolved in

distilled water (20 mL) and the solution was transferred to the column. Once all of the solution had been introduced onto the column, elution with distilled water was commenced and continued until the eluate became neutral. The dinitramide solution obtained was neutralized with 25% ammonia solution to pH ≈ 7. Water was removed by evaporation on a rotary evaporator at 50 °C. Towards the end of the evaporation process, anhydrous ethyl alcohol (50 mL) was added and evaporated to dryness. ADN (3.5 g, 97% yield) was obtained.

3   Results and Discussion

Three synthetic methods for the synthesis of ADN were studied in order to estimate the safety of the various production processes, viz.: Method I, from ammonia, Method II, from urea, and Method III, from potassium sulfamate. The effect of the reaction temperature on the yield of the product was examined. The thermal stability of the intermediate reaction products was studied by DSC and the effect of these intermediates on the safety of the process was considered. The reagents used in Method I of the ADN synthesis were ammonia and dinitrogen pentoxide [6]. The reaction was carried out in an inert solvent in the temperature range -20 to -80 °C. The relation between yield and conditioning temperature is illustrated in Figure 1. Conditioning involved maintaining the reaction mixture at a specified temperature for a given period of time.
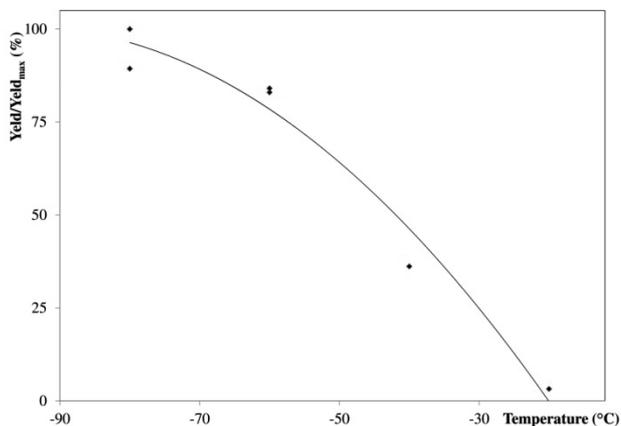
Figure 1.   Reaction yield *vs.* reaction temperature for the nitration of ammonia with dinitrogen pentoxide.

The yield from the ammonia nitration reaction depends markedly on temperature; the lower the temperature, the higher the yield. The recommended reaction temperature is −80 to −70 °C. The reaction is safe, as the temperature range for this process is about 20 °C and no unstable intermediate products are formed. One advantage of Method I for ADN synthesis is the use of inert solvents, which enhance the heat capacity of the system and thus prevent temperature oscillations. Additionally, in the event of the failure of the cooling or stirring system, boiling of the solvent will absorb the heat of reaction.

Method II for ADN synthesis is a two-stage process. In stage 1 urea is nitrated by means of a nitrating mixture composed of fuming sulfuric acid and fuming nitric acid at a temperature from −10 to +5 °C. The yield *vs.* conditioning temperature is illustrated in Figure 2.
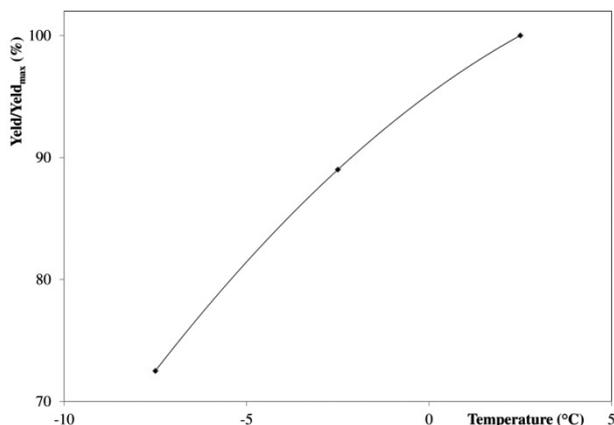

Figure 2. Reaction yield vs. conditioning temperature for the nitration of urea with a nitrating mixture composed of fuming sulfuric and nitric acids.

The highest yield from the nitration reaction was found when the process was conducted at 3 °C ±2 °C. Running this process under such conditions is hazardous, as even minor overheating of the reaction mixture was found to lead to uncontrolled product decomposition and caused the mixture to boil over. If the reaction is conducted at −10 °C, the viscosity of the reaction mixture is significantly increased, which poses problems with stirring and filtration of the intermediate *N,N'*-dinitrourea (DNU). The filtration is highly hazardous, as heating of the separated product, containing residues of the nitrating mixture, will result in its violent decomposition. The washing of crude DNU with dichloromethane improves its stability. The DNU thus washed decomposes

after ca. 30 min on heating to room temperature. Pure DNU can be obtained by washing with trifluoroacetic acid. The *N,N'*-dinitrourea (DNU) thus purified is safe to handle. Its decomposition is noticeable only after storing for several days.

Stage 2 of the ADN synthesis by Method II involves DNU hydrolysis in water, leading to *N*-nitroamine. This reaction may be performed by hydrolysis of the DNU separated by filtration from the reaction mixture at the end of the previous stage. In the former procedure yields in this reaction were ca. 50% (against the starting urea). The use of DNU in the reaction, with post-nitration acids present, causes the yield to drop to ca. 12%.

N-Nitroamine was then nitrated using a fuming nitric/sulfuric acid mixture. The reaction was performed at −28 to −26 °C. The course of the reaction depends strongly on temperature. If the reaction mixture is cooled below −28 °C, the reaction stops and unreacted reactant accumulates in the flask. In the event of the temperature rising, the reaction may suddenly accelerate. Too high a temperature causes dinitramide to decompose. If the reaction mixture is heated to −22 °C, in most cases the mixture boils over. The optimal conditions would be if the reaction were conducted at the lowest temperature at which the reactant nitration exotherm was still observed. This is the most hazardous stage of ADN synthesis by Method II.
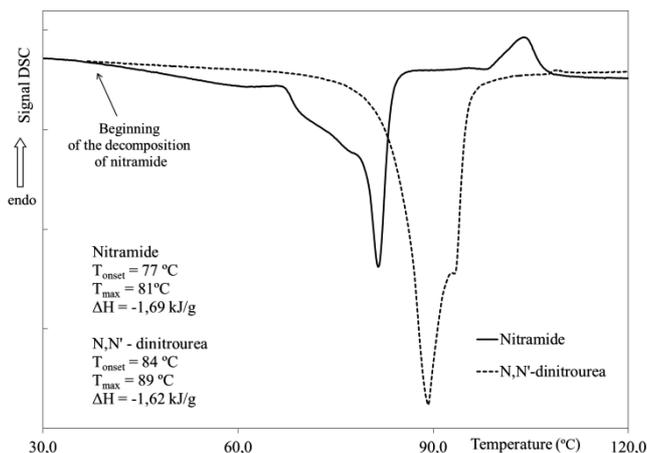

Figure 3. DSC curves of the thermal decomposition of *N,N'*-dinitrourea (DNU) and *N*-nitroamine, the intermediate compounds isolated in ADN synthesis from urea.

The intermediates in Method II are *N,N'*-dinitrourea (DNU) and *N*-nitroamine (MNA). To determine the stability of these intermediate products they were

examined by DSC analysis. The results of these analyses are shown in Figure 3.

During analysis, the *N,N'*-dinitrourea sample decomposed at 84 °C (T_{max} = 89 °C) with an exotherm of −1.62 kJ/g. The N-nitroamine onset temperature of decomposition was 77 °C (T_{max} = 81 °C), with a decomposition exotherm of −1.69 kJ/g. *N*-Nitroamine decomposition is a three-stage process, and the start of the exothermal decomposition is already visible at ca. 37 °C. These compounds are of low thermal stability; all operations with these compounds should be performed with the utmost care. If the 100-deg rule is applied [11], the maximal safe temperature for performing these processes lies within 11 to 19 °C. Under destabilizing conditions (*e.g.* contamination with acids) the temperature should be lower still. Using formulae (1) and (2), the explosion potential values were evaluated for DNU and MNA as, EP_{DNU} = 0.87, EP'_{DNU} = 0.32, and EP_{MNA} = 0.89, EP'_{MNA} = 0.35, respectively. According to these criteria, the intermediate compounds isolated in Method II should be considered as explosible and potentially hazardous materials that are prone to explosion. Dinitramide synthesis from urea is a multi-stage and time-consuming process. It proceeds with a yield of ca. 25%. Inexpensive and generally available materials are used in this method. ADN synthesis by Method II on a larger scale, however, would be hazardous.

ADN synthesis from potassium sulfamate (Method III) is a two-stage process and proceeds with a yield of ca. 50%. Optimization of KDN synthesis by this method was reported in [10]. Reaction yield *vs.* conditioning temperature for the nitration of potassium sulfamate is shown in Figure 4.
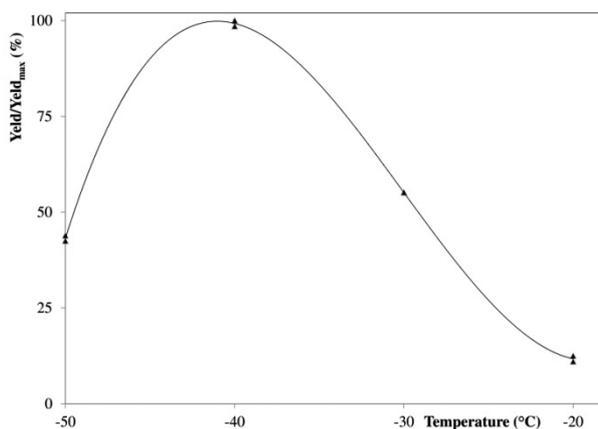
Figure 4.   Reaction yield *vs.* conditioning temperature for potassium sulfamate nitration.

The yield from the nitration of potassium sulfamate depends on temperature. The recommended reaction temperature is −40 °C±5 °C. The reaction was rated as a little time consuming. However, it is safe, as the temperature range in which it can be run with minor loss in yield is ca. 10 °C. The isolated intermediate product here is potassium dinitramide (KDN). DSC analysis of this intermediate was performed and the results compared with the analysis of ammonium dinitramide. The results are shown in Figure 5.
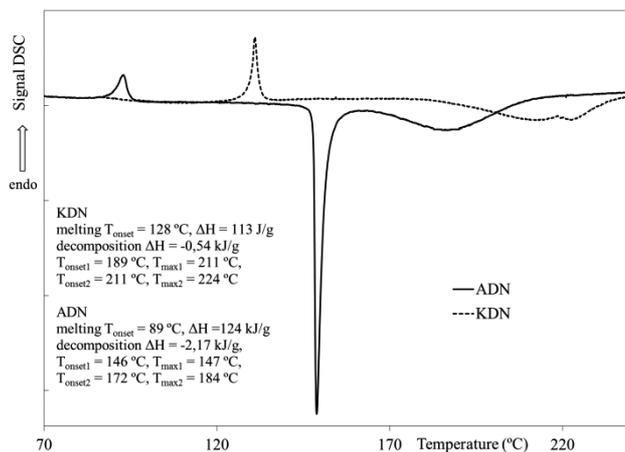
Figure 5. The DSC curves for the thermal decomposition of potassium and ammonium dinitramide.

On the DSC curve for KDN, an endothermic peak due to melting appears at 128 °C. The enthalpy of melting is 113 J/g. Decomposition of the KDN sample occurred in two stages. The onset temperatures were T_{onset1} = 189 °C, T_{onset2} = 211 °C. The temperatures of the maximum decomposition rates were: T_{max1} = 211 °C, T_{max2} = 224 °C, respectively. The first peak corresponds to KDN decomposition to potassium nitrate(V), while the second one corresponds to thermal decomposition of the potassium nitrate(V) formed. The total enthalpy of KDN decomposition was found to be −0.54 kJ/g. To emphasize the thermal stability of KDN, the decomposition of an ADN sample is also shown in Figure 5. The sample fused at 89 °C with an enthalpy of melting of 124 J/g. Decomposition of the ADN sample proceeded in two stages. The onset temperatures were T_{onset1} = 146 °C, T_{onset2} = 172 °C. The first peak corresponds to the decomposition of ADN to ammonium nitrate (AN), while the second corresponds to the thermal decomposition of AN. The total enthalpy of ADN decomposition was −2.17 kJ/g. Using the 100-deg rule for the maximum safe temperature for manufacturing

processes, this was found to be 119 °C for KDN. The maximal safe temperature for the manufacturing process where KDN is used is higher by ca. 100 °C in comparison to the intermediate products isolated in Method II, and higher by 42 °C in comparison to the final product ADN. The EP and EP' values were determined for KDN as $EP_{KDN} = 0.22$, $EP'_{KDN} = -0.35$. The corresponding values found for ADN were $EP_{ADN} = 0.87$, $EP'_{ADN} = 0.31$ [20]. The much lower EP and EP' values found for KDN indicate that this compound poses a reduced hazard relating to thermal decomposition and explosion. DSC analysis of the stability of the intermediate products formed in Methods II and III indicate that Method III is the safer method for ADN synthesis. Table 1 gives a comparison of the values of the adiabatic temperature rise for the nitration reactions, ΔT_{ad}, the reaction conditions and quantities of the reactants required to produce 1 kg ADN by the three synthetic methods.

Table 1. Comparison of the adiabatic temperature rise for the nitration reactions, ΔT_{ad}, conditions for the reactions and the quantities of the reactants required to produce 1 kg ADN by any of the three synthetic methods: from ammonia (Method I), urea (Method II), or potassium sulfamate Method III)

For 1 kg ADN	Method I	Method II	Method III
Reactant, [kg]	3.7	0.4	2.3
Dinitrogen pentoxide, [kg]	10.9	0	0
Nitric acid, [dm³]	0	3.4	6.1
Sulfuric acid, [dm³]	0	0.9	2.3
Fuming 20% sulfuric acid, [kg]	0	0.5	0
Nitration temperature, [°C]	−80	−30	−40
Temperature rise ΔT_{ad}, [°C]	71	564 (Stage 1) 191 (Stage 2)	284
Time Consumption	low	high	low

Method I features high safety. In this method, the most chemicals have to be used for the conversion to ADN and the process is conducted at the lowest temperature. By increasing the yield of the method and by developing a continuous process for this synthesis, a low-cost and simple commercial-scale ADN synthesis process could be created. A remarkable advantage of this method is the significantly minor adiabatic temperature rise ΔT_{ad}, for the reaction. For stage 1 of ADN synthesis by Method II, a significantly higher adiabatic temperature rise was noted. This has to be of particular concern, as the admissible nitration temperature range for this reaction is exceptionally narrow. Still more

troublesome is the next stage of the synthesis, in which the temperature range recommended for the reaction is ca. 4 °C. In Method III for ADN synthesis, the consumption of starting chemicals is high. The method is relatively safe and characterized by a short reaction time. When performing the nitration process in Method III, stable absorption of the heat of reaction is desirable. On a larger commercial scale, ADN could be made by Methods I or III. For safety reasons, Method III is the recommended method for commercial implementation.

4   Summary

Three methods for the synthesis of ammonium dinitramide were investigated: Method I, which consists in nitration of ammonia, Method II which starts from urea, and Method III where the substrate is potassium sulfamate. ADN synthesis by Method I proceeds with a yield ca. 16%. The reaction is run at the lowest temperature, −80 °C. The reaction is less hazardous because of the wide range of nitration temperatures and low adiabatic rise in reaction temperature ΔT_{ad}. ADN synthesised by Method II proceeds with a yield ca. 64%, and requires inexpensive starting materials. The reaction is run at a temperature of ca. −30 °C. The reaction is fraught with hazards because of the narrow range of nitration temperatures and the very large adiabatic rise in reaction temperature ΔT_{ad}. ADN synthesis according to Method III gives a yield of ca. 50%. The reaction is conducted at ca. −40 °C. ADN synthesis according to Method III creates a much smaller hazard than ADN synthesis by Method II. In Method II the intermediate products are *N,N'*-dinitrourea and *N*-nitroamine, whilst in Method III potassium dinitramide is the intermediate product. DSC analysis has demonstrated that the intermediate products formed in Method II are unstable, they readily decompose and present an explosion hazard. Potassium dinitramide, the intermediate formed in Method III, is more thermally stable, its decomposition begins at ca. 100 °C higher and its use offers the least explosion risk. Comparing the three methods for the preparation of ammonium dinitramide, it can be concluded that ADN synthesis from the potassium salt of sulfamic acid is the most promising for industrial use.

5   References

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