Transformation and Stability of N-Nitrodiethanolamine Dinitrate Nitrination Liquid System under Thermal and Mechanical Stimulation

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To obtain a deeper understanding of the process involved in the synthesis of N-nitrodiethanolamine dinitrate (DINA), in this work we carried out systematic studies on the transformation and stability of the N-nitration liquid and DINA. The thermal decomposition processes and dynamic characteristics for both the N-nitration liquid and DINA were carried out by thermal analysis methods and the mechanism for the decrease of stability of the N-nitration liquid was proposed according to experimental results. Mechanical stimulation of the N-nitration liquid and DINA were also studied by friction and impact sensitivity testing. The experimental results showed that the N-nitration liquid is highly sensitive to temperature and can decompose easily when the reaction temperature increases. However, mechanical sensitivity of the N-nitration was demonstrated to be much lower than that of DINA. Therefore, precise thermal control is the key factor to ensure safety during the preparation of DINA.

1. Introduction

N-Nitrodiethanolamine dinitrate (DINA) is a secondary high explosive containing both a nitrate and a nitrate ester functionality. It can be melt-cast into charges and has been widely used as a high energy plasticizer in propellants and as an excellent gelatinizing agent for nitrocellulose.[1] In Europe and the US, research on the application of DINA in propellants started early in the Second World War.[2, 3] The efficient synthesis of DINA was usually achieved through O-nitration[4, 5] followed by N-nitration[6, 7] of N,N-diethanol-amine (DEA; Scheme 1). The most classical approach for the preparation of DINA was from the nitration of DEA with nitric acid/acetic anhydride in the presence of zinc chloride.[8] The product of DINA is precipitated by dilution of the mixture and the nitration liquid was treated as waste nitrating acid (after DINA separation). In recent years, the synthetic method for the preparation of DINA in Russia and China has been improved by applying MgO as dehydrating agent rather than Ac₂O and using NaCl as the catalyst. The synthetic procedure is as follows: DEA was added into the HNO₃-MgO system (O-nitration liquid system) to achieve O-nitration; then NaCl was added and the temperature of the mixture (N-nitration liquid system) was raised (the heat preservation process requires about 30 min to finish the N-nitration step). Although the O-nitration and N-nitration processes were carried out under different reaction conditions, the synthetic process was actually an “one-pot” procedure without any purification. The first step is the formation of dangerous diethanolamine dinitrate (DIA) by adding DEA into the HNO₃-MgO mixture and the nitramine moiety was further achieved by the addition of NaCl as catalyst.[9] The “one-pot” process was originally designed to reduce the explosion risk in the purification procedures; however, after the addition of NaCl and increasing the temperature, the N-nitration liquid system (before precipitation of DINA) itself has also been proven to be an unstable system which has caused several serious accidents in recent years. Therefore, it is urgent to carry out thorough stability studies of this N-nitration liquid system.

Scheme 1. The synthetic process involved in the preparation of DINA.
the heat preservation stage is the key step for the overall process safety. In this paper, a series of analysis experiments were designed to study the transformation and stability of the N-nitration liquid for the first time to reduce the risk in the synthesis process of DINA. The studies of thermal decomposition processes and dynamic characteristics for both the N-nitration liquid and DINA were carried out systematically by thermal analysis methods and a mechanism for the decrease of stability of the N-nitration liquid was proposed according to the experimental results. The mechanical stimulations of the N-nitration liquid and DINA were also studied by friction and impact sensitivity testing to further avoid explosion risks as part of the agitator and transfer processes. This work obtaining the thermal safety parameters on the stability of the N-nitration liquid and DINA could be important to acquire a better understanding of the nitration reaction and to be used as the reference to improve safety levels in the synthesis of DINA.

2. Results and Discussion

2.1. Thermal Behavior of the N-Nitration Liquid and DINA

In order to study the thermal stability of the N-nitration liquid, differential scanning calorimetry (DSC) measurements with a heating rate of 10 °C min⁻¹ were applied. According to the DSC curve of the N-nitration liquid (Figure 1), decomposition of this nitration liquid consists of two exothermic processes. The first and larger exothermic peak occurred at 143.92 °C, while the second one occurred at 202.01 °C. For the sake of contrast, the thermal behavior of DINA was also studied and showed in Figure 1. The DSC curve of DINA exhibits a major exotherm at 214.57 °C, which is obviously higher than that for the N-nitration liquid under same experimental conditions. The larger exothermic peak of the N-nitration liquid occurred at 143.92 °C, which may be caused by the formation of certain intermediates or by-products.¹⁰ The experimental results demonstrate that the N-nitration liquid is much more sensitive to the temperature than DINA itself and can decompose easily when the temperature rises, indicating clearly that the temperature should be controlled strictly during the synthesis process of DINA.

To further explore the factor which causes the decrease in the thermal stability of the N-nitration liquid, samples at different stages of the synthetic process of DINA were collected and studied. According to the literature,⁹ the major compound in the O-nitration liquid was diethanolamine dinitrate (DIA) as the N-nitration reaction was not able to carry out and the DINA cannot be formed before the addition of chloride ion salt. However, we suppose that the formation of the nitrate salt of DIA may also occurred along with the N-nitration transformation such a strong acid environment. With this in mind, we set out to attempt the synthesis the nitrate salt of DIA and obtained the sample of MNDIA successfully. Figure 2 showed the structural formulae of DIA, MNDIA and DINA. The structure of MNDIA and DINA were characterized by NMR (500 MHz) and elementary analysis. As a result of the fact that the skeleton structures of the MNDIA and DINA are similar, their ¹H NMR, ¹³C NMR signals and peak shapes are also similar. The calculated data of MNDIA (C₆H₁₀N₃O₇): C 18.69, H 4.06, N 21.70 %; the elementary analysis found: C 18.69, H 4.06, N 21.98 %. The calculated data of DINA (C₈H₁₄N₄O₇): C 20.01, H 3.36, N 23.33 %; the elementary analysis found: C 19.95, H 3.43, N 23.62 %. Through NMR and elementary analysis, structures of MNDIA and DINA were identified and the samples were further used for thermal analysis studies.

The studies of thermal stabilities of the O-nitration liquid, the N-nitration liquid, MNDIA and DINA were all carried out through DSC measurements and the experimental results were showed in Figure 3. According to Figure 3, the exothermic peak of MNDIA occurred at 143.00 °C at heating rates of 10 °C min⁻¹, which is extremely close to the first and larger exothermic peak of the N-nitration liquid. This result indicated that the lower thermal stability of the N-nitration liquid compared with DINA is more likely to be caused by the formation of MNDIA. In addition, the exothermic peak of the O-nitration liquid occurred at 167.20 °C, which is higher than that of the N-nitration liquid and lower than that of DINA, indicating that the stability of DIA is higher than MNDIA but lower than DINA.

Based on the thermal experiment studies, it can be proposed that chloride catalyst is crucial for the N-nitration of DIA.¹¹ A small amount of chlorination of DIA may also be applied as trigger for the formation of MNDIA, which can also be further transfer into DINA through a dehydration reaction (Scheme 2). The existence of MNDIA may be the main reason for the decrease of the stability of the N-nitration liquid.

To find out whether the thermal stability of fresh DINA product will be influenced by different nitration temperatures, a series of experiments were carried out by changing the temperature of the N-nitration liquid and holding the other reaction conditions unchanged. All of the fresh DINA products were obtained by a “one-pot” synthetic process. Four kinds of fresh DINA products under different holding temperature (65.0 °C, 76.5 °C, 70.0 °C, 72.5 °C) were obtained and the results were showed in Figure 4. It can be seen that the decomposition temperatures are almost unchanged when the holding temperature of the N-nitration liquid is increased from 65.0 °C to 72.5 °C, which indicates that thermal stability of fresh DINA products will not change with holding temperature in a certain

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Figure 1. DSC curves of the N-nitration liquid and DINA.
range. Therefore, it is concluded that the holding temperature has great impact in the synthetic process but has very little influence on thermal stability of the final fresh product system.

2.2. Thermal Decomposition Kinetics of the N-Nitration Liquid

In order to investigate the non-isothermal kinetics of thermal decomposition of the N-nitration liquid, DSC curves at different heating rates were employed (Figure 5). The characteristic temperatures of the N-nitration liquid at the heating rates of 2.5, 5, 10 and 20 °C min⁻¹ were obtained and listed in Table 1, where $\beta$ is the heating rate (°C min⁻¹); $T_0$ is the initial decomposition temperature (°C); $T_{p1}$ is the decomposition peak temperature of the first peak (°C); $T_{p2}$ is the decomposition peak temperature of the second peak (°C). Obviously, $T_{p1}$ and $T_{p2}$ moved to high temperature with the increase of heating rates.

The heat can be transformed into reaction progress ($\alpha$) by an integration method. The reaction progress versus temperature under different heating rates were obtained and are shown in Figure 6. For the first decomposition peak, a Flynn–
Wall–Ozawa model\textsuperscript{12,13} was employed to calculate the apparent activation energy (\(E\)) of the \(N\)-nitration liquid under different \(\alpha\) values and the results were showed in Figure 7. Taking \(\alpha\) value of 0.6 as the boundary, \(E\) could be allotted into different two stages, indicating that the decomposition process of this \(N\)-nitration liquid proceeds in two stages. \(E\) in the first stage is about 55 kJ mol\(^{-1}\), which is obviously lower than those for RDX (177 kJ mol\(^{-1}\))\textsuperscript{14}, HMX (201 kJ mol\(^{-1}\))\textsuperscript{15} and CL-20 (143–168 kJ mol\(^{-1}\))\textsuperscript{16} under the same experimental condition.

DSC measurements of DINA at different heating rates (Figure 8) were also studied so that they can be compared with the thermal behaviors of the \(N\)-nitration liquid. The Kissinger model\textsuperscript{17,18} and the Flynn–Wall–Ozawa model were both employed to calculate the kinetic parameters (apparent activation energy (\(E\)) and pre-exponential constant (\(A\))) of the decomposition reaction of DINA and the DINA nitration liquid. The results were showed in Table 2. The agreement between these two methods is excellent. Taking the Kissinger model as an example, the calculation result of \(E\) and \(A\) of DINA were 138.54 kJ mol\(^{-1}\) and \(1.02 \times 10^{3}\) s\(^{-1}\), respectively. The activation energy was 52.79 kJ mol\(^{-1}\) for the \(N\)-nitration liquid, much lower than that of DINA (138.54 kJ mol\(^{-1}\)). Compared with that of DINA, the low activation energy can partly explain the easier decomposition behavior of the \(N\)-nitration liquid.
2.3. Thermal Safety of the N-Nitration Liquid

Thermal safety parameters analysis of DINA and the N-nitration liquid were carried out according to GJB772A-97. Extrapolated onset temperatures ($T_{eo}$) at heating rate of 0 °C·min$^{-1}$ can be forecasted by a polynomial method. Based on the $T_{eo}$ obtained, the self-ignition temperature was calculated using the Zhang–Hu–Xie–Li method.\[19, 20\] The formula for calculation is as follows: The calculated results of $T_{eo}$ and $T_{beo}$ were listed in Table 3 [Eq. (1)]:

$$T_{beo} = \frac{E - \sqrt{E^2 - 4ERT_{eo}}}{2R}$$

where $T_{beo}$ is self-ignition temperature, $E$ is the apparent activation energy (kJ·mol$^{-1}$), $R$ is the gas constant (8.314 J·K$^{-1}$·mol$^{-1}$) and $T_{eo}$ values are extrapolated onset temperatures at heating rate of 0 °C·min$^{-1}$.

### Table 3. Thermal safety parameters of DINA and the N-nitration liquid.

| Sample          | $T_{eo}$ (°C) | $T_{beo}$ (°C) |
|-----------------|---------------|----------------|
| DINA            | 196.91        | 199.29         |
| N-nitration liquid | 84.70        | 85.86         |

As can be seen from Table 3, $T_{eo}$ and $T_{beo}$ of the N-nitration liquid were 84.70 °C and 85.86 °C, respectively. The thermal safety parameters of the N-nitration liquid are comparatively lower than those of DINA. The result was indicative of a poor thermal safety of the N-nitration liquid and temperature is an important factor affecting safety in the synthetic process of DINA.

2.4. Mechanical Sensitivity of the DINA Nitration Liquid

The friction sensitivity and impact sensitivity of DINA and the N-nitration liquid were both detected. The results were showed in Table 4, where the impact sensitivity date $H_{50}$ and friction explosion rate $P$ were the average result of four parallel experiments.

The results demonstrated that the mechanical sensitivity of the N-nitration liquid is relatively low. The friction sensitivity and impact sensitivity of the N-nitration liquid were much lower than those of DINA. Overall, upon analysis of the thermal sensitivity and mechanical sensitivity of the N-nitration liquid, it is clear that temperature is one of the most important factors influencing the whole synthetic safety of DINA.

### Table 4. Results of mechanical sensitivity tests.

| Sample       | Impact sensitivity | Friction sensitivity |
|--------------|--------------------|---------------------|
|              | $H_{50}$ [cm]      | $P$ [\%]            | Confidence intervals |
| N-nitration liquid | 53               | 16                  | (4, 36)              |
| DINA         | 92                 | 88                  | (69, 98)             |

3. Conclusions

The stabilities of the N-nitration liquid under thermal and mechanical stimulation were systematically studied by comparison with DINA. The results demonstrate that the N-nitration liquid is much more sensitive to temperature than DINA which may be caused by the formation of MNDIA during the N-nitration step. The calculation activation energy for the N-nitration liquid was much lower than that for DINA, which partly explained the easier decomposition behavior of the N-nitration liquid. In contrast to thermal sensitivity, mechanical sensitivity of the N-nitration liquid was comparatively lower than that of DINA and temperature control should be treated as the key safety factor in the synthesis of DINA.

### Experimental Section

#### Samples

The O-nitration liquid and N-nitration liquid were taken out at different stages of the synthetic process (before and after the addition of NaCl, respectively). O-nitration liquid, N-nitration liquid and DINA (99.0%) were all supplied by Xi’an Modern Chemistry Research Institute.

#### Apparatus and Measurements

The thermal analysis experiments were performed with a model DSC Q200 instrument (TA, America). The sample was encapsulated in an Au crucible under a closed atmosphere. Measurements were performed from 40 °C to 500 °C under similar conditions. Operation conditions: Sample mass, 6.0 mg (DINA esterification liquid), 6.0 mg (DINA nitration liquid), 0.6 mg (DINA); atmosphere: dynamic nitrogen.

Friction sensitivity test is performed according to method 602.1 in GJB 772A-1997. Operation conditions: sample mass, 20 mg; gauge pressure, 1.65 MPa; Swing angle, 67°. Impact sensitivity test is performed according to method 601.2 in GJB 772A-1997. Operation conditions: sample mass, 50 mg; drop hammer, 5 kg.

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Conflict of Interest

The authors declare no conflict of interest.

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