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Molecular Modeling as a Complementary Approach of Experimental Evaluation of Incompatibilities of Ammonium Nitrate

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The serious potential consequences of the hazards posed by ammonium nitrate (AN) incompatibility (as the increase of explosive properties) provide motivation for a deeper understanding of the mechanisms of the reactions involved in these phenomena. Complementary to experimental methods, commonly employed to describe incompatibilities between substances, molecular modeling was used in this work to understand the mechanism through which the explosive reaction takes place, to identify which molecules can be really generated from this process and to estimate the energy involved. In a first step, a study of all the available mechanisms of AN decomposition was conducted at DFT (Density Functional Theory) level of theory (Cagnina et al., 2013). Then, this method was applied to identify reaction mechanisms of major ammonium nitrate's incompatibilities (chlorinated compounds such as the sodium salt of dichloroisocyanuric acid and sodium salts). The good coherence between theoretical and experimental results observed, encourage the use of molecular modeling as a *a priori* tool for the comprehension and prediction of chemical incompatibilities.

1. Introduction

Ammonium nitrate (AN) is an important and widely used product in the chemical industry. It is commonly used as a fertilizer component and as an ingredient in explosive mixtures. It is described in the scientific literature as a strong oxidizer and as a weak and insensitive explosive and it is considered to be a relatively safe substance, due to its high stability in standard temperature and pressure ranges. However, during the manufacturing process, storage, transport, and use, AN may be contaminated by impurities, and autoignition and explosion may take place, caused by their catalytic effects on the decomposition of AN (Marlair and Kordek, 2005). Chlorinated compounds, such as the sodium salt of dichloroisocyanuric acid (SDIC, see Figure 1) and sodium nitrite (NaNO_2) are well-known as hazardous contaminants of AN.

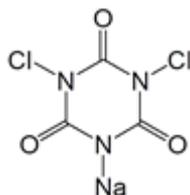


Figure 1: Chemical representation of the sodium salt of dichloroisocyanuric acid (SDIC).

Concerning the sodium salt of dichloroisocyanuric acid, calorimetric analysis revealed that pure AN and pure SDIC do not show any exothermic activity below 200 and 175 °C, respectively. However, a 1:1 mixture of these two components shows a first exothermic peak in the temperature range of 60–90 °C and a second

larger peak at 110–125 °C (Badeen et al., 2005). This clearly indicates that the mixture is less thermally stable than its pure components but it does not explain the reaction mechanism through which the reaction takes place between the two chemicals. Sodium nitrite (and sodium nitrate) is used in the manufacture of water-in-oil ammonium nitrate emulsion (ANE) explosives (Xuguang, 1994) and large quantities of these salts may be present in the industrial environment. In particular, NaNO_2 represents a very inexpensive source to produce nitrogen gas bubbles via a nitrosation reaction when mixed into a solution of ammonium nitrate. In an ANE explosive, the presence of such evenly dispersed small voids enhances the ignitability and the ability of the explosive to undergo steady detonation. The real danger of powdered NaNO_2 coming into contact with AN emulsion explosive at a manufacturing site has been reported anecdotally (FACTS, 1995). Despite the similarity, no industrial accident has been reported in the literature concerning a chemical incompatibility between AN and sodium nitrate (NaNO_3).

Calorimetric test results of the pure salts and the effect of the addition of NaNO_2 or NaNO_3 to AN showed that an incompatibility is highlighted between AN and NaNO_2 but not between AN and NaNO_3 and that the mixtures showed varying thermal behaviours depending on the amount of water present. Again this result extremely interesting and useful is not enough to understand the chemistry hidden behind this behaviour.

Indeed, they can indicate consequences of the incompatibility, allowing users to apply adequate mitigation measures, but they do not explain exactly how the incompatibility drives the undesired reaction scheme. Attempts using molecular modelling, described in literature, showed that the theoretical approaches represent a viable complement to identify the reaction pathways (Di Tommaso et al., 2011) and provide a deep level of understanding of the phenomenon important for a wider and global overview on chemical incompatibilities.

In this work we applied the molecular approach to the study of the major ammonium nitrate's incompatibilities (SDIC and NaNO_2), to understand the different behaviour between NaNO_2 and NaNO_3 and the role played by water (or moisture) in the incompatibility reactions.

2. Computational details

The reaction mechanisms are investigated using the Density Functional Theory (DFT). The DFT energy has the following expression:

$$E[\rho] = T_s[\rho] + V_{\text{ext}}[\rho] + J[\rho] + E_{\text{xc}}[\rho] \quad (1)$$

Where $T_s[\rho]$ is the kinetic energy term for non-interacting particles, $V_{\text{ext}}[\rho]$ is the external potential, $J[\rho]$ is the classical energy term for the electron-electron repulsion and $E_{\text{xc}}[\rho]$ is the exchange and correlation functional which is not exactly known and needs to find a consistent approximation having good performance to the target study. Over the years, a lot of different exchange and correlation functionals were developed and therefore a DFT benchmark study on the decomposition reaction of ammonium nitrate has been undertaken in our previous work (Cagnina et al., 2013) to determine the most efficient combination of functional and basis set (M06-2X/6-311+G(2d,2p)) to describe accurately the chemical reaction analysed. The stationary points were identified as minima (no imaginary frequency) or as transition states (one imaginary frequency) by performing a frequency calculation with the same method and basis set. Intrinsic reaction coordinate (IRC) calculations were also carried out to verify that the identified products and reactants were correctly connected to the proposed transition states. All open shell systems were calculated within a spin-unrestricted formalism and spin contamination, monitored by the expectation value of S^2 , was found to be negligible. All of the calculations were performed using the Gaussian 09 software package (Frisch et al., 2009).

3. Results and discussion

It is expected that actual reaction conditions play a major role in chemical incompatibilities, making complex the clear identification of the reaction mechanism at experimental level. Several recent studies have shown that theoretical approaches represent a viable complement to identify the reaction pathways, especially when complex reaction mechanisms giving unstable and short-living intermediates are concerned (Di Tommaso et al., 2011). In order to achieve a wider and global overview on chemical incompatibilities, molecular modelling results obtained in this study were used as a complement and enrichment of existing experimental data.

3.1 Decomposition of pure ammonium nitrate

The decomposition mechanism of the pure ammonium nitrate in the gas phase was studied in detail in our previous study and five main reaction channels were identified. It was found that the reaction is globally exothermic, but its initiation depends on overcoming an energy barrier of 40.2 kcal/mol involved in the homolysis of the nitric acid (the rate determining step of the reaction) coming from the decomposition of

ammonium nitrate in NH_3 and HNO_3 ($\Delta G^\ddagger = 4.9$ kcal/mol). The stability of the pure ammonium nitrate, at standard conditions, is due to the presence of this high energy barrier.

3.2 Reaction mechanism of ammonium nitrate and the sodium salt of dichloroisocyanuric acid

The first system of incompatibility that we have studied is the one formed by AN and the sodium salt of dichloroisocyanuric acid due to the possible involvement of such mixtures in the accident that took place in Toulouse in September 2001 (Dechy et al., 2004). Until now, the thermal hazards of such a mixture have been investigated only by laboratory experiments, such as DSC, TG, FTIR, MS and several species have been detected as N_2 , NO , HCl , NO_2 , Cl_2 , H_2O , CO_2 , N_2O and NCl_3 . Nevertheless a clear and unambiguous explanation of the incompatibility between these two substances was not found. As proposed by the experimental study of Paul et al. (2004) the first reaction for the AN–SDIC adduct that we have characterized is the hydrolysis of SDIC followed by the reaction of the hypochlorous acid with ammonia from the decomposition of ammonium nitrate. For this reaction, the rate-determining step is the hydrolysis of SDIC that presents an important activation energy, ΔG^\ddagger , of 78.4 kcal/mol. Consequently, this mechanism is not energetically favoured with respect to the decomposition of pure ammonium nitrate ($\Delta G^\ddagger = 45.1$ kcal/mol). Therefore, this hypothesis was discarded, and a direct reaction between AN and SDIC was considered.

Since AN is easily decomposed in NH_3 and HNO_3 , SDIC is susceptible of reacting with both molecules. However if the reaction between ammonia and SDIC leads to the formation of exothermic products, the other one gives endothermic products. Therefore only the reaction paths starting from the first reaction (SDIC and NH_3) will be retained in the following, because it is strongly irreversible (large energy difference between products and transition state) and exothermic. The contact between SDIC and ammonia gives, passing through a transition state, $\text{TS}_{\text{SDIC}+\text{NH}_3}$, of 58.0 kcal/mol, the sodium salt of monochloroisocyanuric acid (SMIC) and the monochloroamine (NH_2Cl). It is in the decomposition path of monochloroamine that we have found a possible explanation for the incompatibility between these two substances. Starting from NH_2Cl , the decomposition can be separated into two different paths, labelled A and B that are sketched in Figure 2.

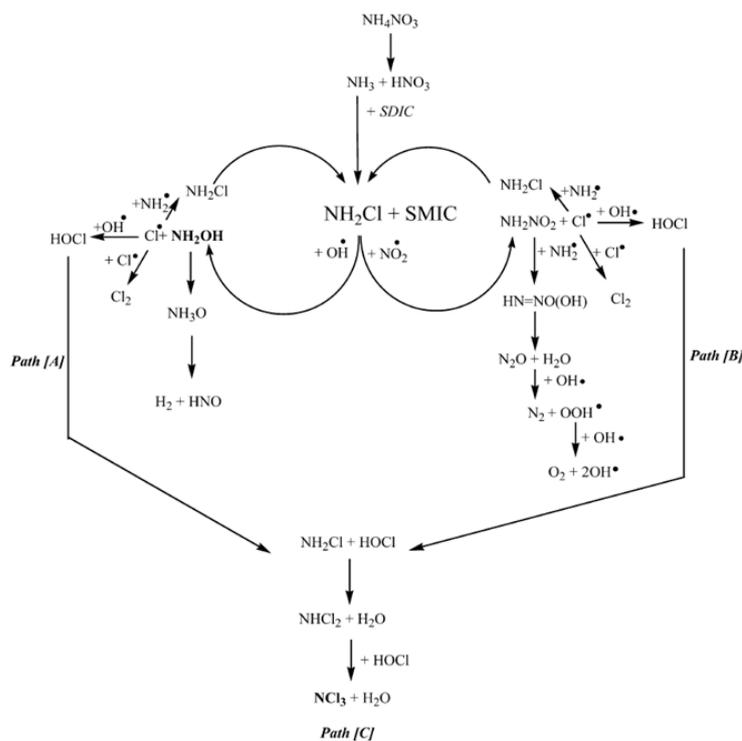


Figure 2: Reaction path for the decomposition of monochloroamine, resulting from the reaction between the ammonia and the dichloroisocyanuric acid (Cagnina et al., 2014).

In path A, the monochloroamine reacts with the hydroxyl radical (OH^\bullet), present in the reactive environment, to form hydroxylamine (NH_2OH) and chlorine radical. The chlorine radical reacts with amidogen radical (NH_2^\bullet), hydroxyl radical, and another chlorine radicals, all present in the reactive environment after the decomposition of HNO_3 or formed from the previous reaction, to form monochloroamine, hypochlorous acid, and a chlorine

molecule. The relative Gibbs free energies of these three molecules are respectively -53.1 , -46.6 , and -49.4 kcal/mol. It is interesting to note that all of these reactions are very exothermic, and the energy stored from these reactions allows the energy barrier of decomposition of nitric acid (40.2 kcal/mol, discussed in the previous section dedicated to ammonium nitrate decomposition) to be overcome. It should be also remarked that monochloroamine is formed during the mechanism, so that the decomposition of NH_2Cl becomes autocatalytic. Hydroxylamine, instead, undergoes isomerization and a hydrogen elimination gives molecular hydrogen and the nitroxyl radical ($\text{HNO}\cdot$) passing by energetically high transition states.

Following pathway B, the monochloroamine reacts with the nitric oxide radical, previously produced by the homolytic decomposition of nitric acid, to form the nitramide (NH_2NO_2) and chlorine radical. NH_2NO_2 , already characterized as one of the intermediates of ammonium nitrate decomposition, decomposes in N_2O , N_2 , and O_2 while chlorine radical gives rise to the same reactions (with amidogen radical, hydroxyl radical, and chlorine radical) described above.

Since both paths A and B lead to the formation of hypochlorous acid, a reaction between the hypochlorous acid and the monochloroamine was characterized, as shown in Figure 2 (path C). This reaction forms a stable molecule of dichloroamine (NHCl_2) and water. The dichloroamine molecule is able, in turn, to react with the hypochlorous acid molecule and to form trichloroamine (NCl_3) and water.

These theoretical results allow the characterization of the direct decomposition mechanism of AN with SDIC and of all the experimentally observed products (N_2 , NO , HCl , NO_2 , Cl_2 , H_2O , N_2O), via paths A, B, and C. The rate-determining step of the direct reaction between AN and SDIC is represented by the reaction of NH_3 with SDIC, leading to NH_2Cl and SMIC (58.0 kcal/mol). At this point of the study, direct decomposition is energetically favored with respect to the SDIC hydrolysis hypothesized by Paul et al. (2004) (58.0 vs 78.4 kcal/mol, respectively). Nevertheless it should be recalled that the rate determining step in the AN decomposition requires 40.2 kcal/mol, and it is therefore still favoured with respect to both reactions.

3.3 Role of water in the reaction between AN and SDIC

Other effects should be, therefore, considered. In particular, ammonium nitrate is a highly hygroscopic substance that can easily collect water molecules from the environment. Moreover the presence of water or moisture in the AZF plant in Toulouse has not been excluded, and experimental papers reporting data obtained in humid air indicate that the presence of moisture decreases the thermal stability of the mixture significantly (Li and Koseki, 2005). Therefore, the effect of the presence of water was investigated, for the rate-determining steps of the AN-SDIC decomposition (reaction involving hydrogen and chlorine transfer). The inclusion of one water molecule in the rate-determining step of the reaction AN-SDIC reduces the reaction barrier by 25.9 kcal/mol (from 58.0 to 32.1 kcal/mol), because it catalyzes the transfer of the hydrogen atom between SDIC and NH_3 in the transition state (see Figure 3).

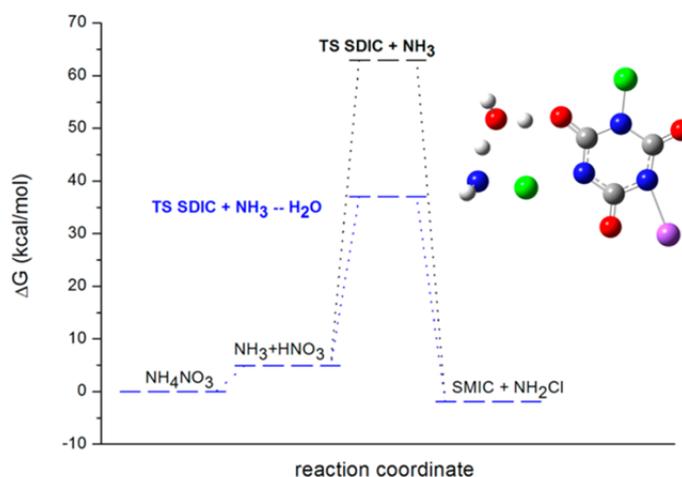


Figure 3: Comparison of Gibbs free energy profiles for the reaction between AN and SDIC in the gas phase and with a water molecule (Cagnina et al., 2014).

The water molecule is regenerated at the end of the reaction so that a true catalytic effect is observed. These results clearly indicate that in the presence of a water molecule, the reaction between AN and SDIC becomes competitive with respect to the decomposition of pure AN, the difference being 8.1 kcal/mol (32.1 vs 40.2

kcal/mol, respectively). Therefore, it could be hypothesized that the presence of water, even in small quantities, could ignite the incompatibility reaction between AN and SDIC.

3.4 Reaction mechanism of ammonium nitrate and sodium salts (NaNO₂ and NaNO₃)

Following the procedure defined to study the incompatibility between AN and SDIC, in this section, the attention is focused on the identification of the reaction mechanism of AN-NaNO₂ and AN-NaNO₃ mixtures, with a particular attention to the rate determining step: the direct reaction between the products of the first decomposition of ammonium nitrate (NH₃ or HNO₃) and contaminants. Since AN decomposes into nitric acid and ammonia, passing through a weakly endothermic step ($\Delta G = 4.9$ kcal/mol), the reaction of sodium nitrite and nitrate with both species have been considered.

Sodium nitrite reacts preferentially with HNO₃ giving NaOH and two molecules of NO₂ passing by a transition state with a relative Gibbs free energy of 44.1 kcal/mol.



Two major points should be retained from these results. The first one is the energy barrier which is higher than the direct decomposition of AN (44.1 vs 40.2 kcal/mol), thus ruling out a simple direct incompatibility between the two species. The second relevant point concerns the difference with respect to the AN-SDIC reaction. Indeed, in this case the origin of the incompatibility is rationalized in terms of a direct reaction between ammonia and the contaminant, while in the case of sodium nitrite and ammonium nitrate, it is the nitric acid that plays a key role in the interaction with NaNO₂.

Also in the case of the reaction between sodium nitrate and ammonium nitrate the reaction involving nitric acid is favoured in comparison to the reaction involving ammonia. This reaction gives a sodium hydroxide and a dinitrogen pentoxide molecule (N₂O₅), with an activation free energy of 50.7 kcal/mol.



Comparing the energies obtained for the decomposition of pure ammonium nitrate ($\Delta G = 40.2$ kcal/mol) with the ones obtained for the reaction between ammonium nitrate and sodium nitrate ($\Delta G^\ddagger = 50.7$ kcal/mol), the study confirms experimental data: no incompatibility exists between the two chemicals.

3.5 Role of water on AN- sodium salts reactions

Since sodium nitrite-nitrate and ammonium nitrate are salts extremely hygroscopic and that samples are almost never subjected to complete drying in the experimental protocols, we have also considered the role that water and moisture can have in the reaction. To do this, a water molecule was introduced in the theoretical model to simulate the experimental conditions and to better understand the reaction mechanism between sodium salts and nitric acid (see Figure 4). In the case of sodium nitrite, the presence of a water molecule, in the geometry of the transition state, causes a decrease in the activation barrier for the reaction of 7.4 kcal/mol that makes the reaction between the ammonium nitrate and sodium nitrite ($\Delta G^\ddagger = 36.7$ kcal/mol) competitive in comparison to the decomposition of the pure ammonium nitrate ($\Delta G = 40.2$ kcal/mol). This result, consistent with experimental data, evidenced the incompatibility between the two substances. However, unlike the reaction between the AN and SDIC, the water does not have a catalytic role in the AN-NaNO₂ mixture incompatibility because it is not directly involved in the reaction but facilitates the reaction by promoting the formation of a complex network of non-covalent interactions between the atoms involved in the transition state.

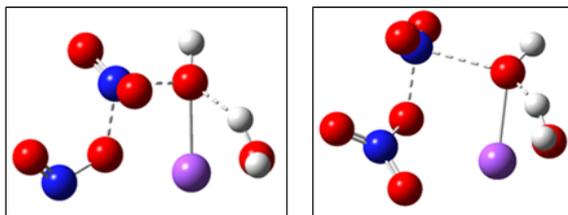


Figure 4: Molecule of water introduced into the modeling of the transition state of the reaction between the sodium nitrite (right)- sodium nitrate (left) and ammonium nitrate. The dotted lines indicate the non-covalent interactions.

In the case of sodium nitrate, the presence of a water molecule in the geometry of transition state ($TS_{\text{NaNO}_3+\text{HNO}_3}$) causes a decrease in the activation barrier of the reaction of 9 kcal/mol that is not enough to justify an incompatibility between the two substances, even in a wet environment. In fact, the energy associated with the barrier remains higher ($\Delta G^\ddagger = 41.7$ kcal/mol) compared to the decomposition energy of pure ammonium nitrate ($\Delta G = 40.2$ kcal/mol).

4. Conclusion

The detailed DFT studies on the reaction between AN and SDIC and AN and sodium salts ($\text{NaNO}_2 - \text{NaNO}_3$) were carried out, aiming to elucidate the microscopic mechanism of incompatibility between AN and contaminants. Results of the theoretical study, always in agreement with the experimental data (SDIC and NaNO_2 are incompatible with ammonium nitrate, while NaNO_3 is compatible with ammonium nitrate) confirm the relevance of molecular modeling in the comprehension and prediction of chemical incompatibility of AN in complement with experimental analysis and the pivotal role of water in these processes.

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