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Study of Incompatibility of Ammonium Nitrate and its Mechanism of Decomposition by Theoretical Approach

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The dramatic accident involving ammonium nitrate (AN) that took place at Toulouse in September 2001 has once again focused attention to the complex hazards pertaining to this chemical. Despite the significant efforts made to increase AN safety over the whole supply chain, we are still facing insufficient knowledge of the actual mechanisms of ammonium nitrate decomposition that may take place in abnormal situations. The paper proposes a theoretical study of chemical incompatibilities of ammonium nitrate with the aim to better understand the driving mechanism(s) through which the explosive reaction takes place with the neat or contaminated substance, to identify what molecules can realistically be generated from this process and to estimate the energy involved. The results, coupled with experimental data, should allow a better understanding of ammonium nitrate hazard profile.

1. Introduction

Ammonium nitrate is not only a principal component of airborne aerosol, but it is chiefly an important and widely used product in the chemical industry. The commercially important applications are twofold: a) as a fertilizer component and b) as an explosive ingredient. Among inorganic fertilizers, AN is the most universally used because of its unique combination of nitrogen bound as both nitrate and ammonium ions that are the only two forms in which plants can efficiently absorb nitrogen from the soil. According to scientific literature (Oxley et al., 2002) pure ammonium nitrate is considered as a relatively stable chemical, since it can be preserved unaltered at ordinary temperature and pressure. Indeed even if it melts at quite low temperature (170 °C), significant thermally induced decomposition requires temperature of more than 200 °C. When fertilizer grade AN is manufactured, it is classified as an oxidising agent Class 5.1 for transportation purposes (it is also considered as an oxidiser under GHS UN Recommendations), but in extraordinary situations it may detonate as an explosive. Although pure ammonium nitrate is generally used safely, several noteworthy accidents involving AN have occurred over the years, causing a significant number of deaths and injuries (Marlair and Kordek, 2005). Table 1 summarizes some of major AN accidents.

Table 1: Some major AN accidents

Year, Place	Substances involved	Effects
1921, Oppau - Germany	(NH ₄) ₂ SO ₄ /NH ₄ NO ₃	Explosion
1947, Canada	NH ₄ NO ₃	Fire
1947, Texas City - USA	NH ₄ NO ₃ (pure)/NH ₄ NO ₃ -sulphur	Explosion
1954, Finland (ship)	NH ₄ NO ₃ /paper/copper acetoarsenite	Fire followed by explosion
1994, Sergeant Bluff - USA	NH ₄ NO ₃	Explosion
2000, Aunay-Sous-Crecy - France	NH ₄ NO ₃ /organic materials	Decomposition of AN
2001, Toulouse - France	NH ₄ NO ₃ /sodium salt of dichloroisocyanuric acid (SDIC)	Explosion

With ammonium nitrate, three major hazardous phenomena need to be considered: fire, decomposition and explosion. Whereas by itself AN is not combustible, it can thermally decompose and give off gaseous products of ammonia and nitric acid and other gases including vapours of toxic nitrogen dioxide (NO₂) when exposed to external heat. Additional factors like confinement or contamination may trigger an explosion hazard. Indeed, as can be seen in Table 1, the major accidents that have occurred over the years involved mixtures of ammonium nitrate with other substances. It has been evidenced that while combined with contaminants, the explosive sensitivity of AN may sharply increase because ammonium nitrate's stability decreases (Sun et al., 2005). As an oxidizing agent AN can intensify the development of a fire involving combustible materials (like wood or plastics). From literature, it is known that a lot of substances are incompatible with AN such as ammonia or metals, as reported in Table 2.

Table 2: Some main chemicals showing incompatibility with AN (Bretherick, 2007)

Substances	Effects
Ammonia	Free ammonia in NH ₄ NO ₃ may either stabilise, or tend to destabilise, the salt upon the situation.
Chloride salts	AN containing 0.1 % of ammonium chloride decomposes vigorously below 175 °C. Presence of 0.1 % of calcium chloride or iron(III) chloride in the nitrate lowers its initiation temperature sufficiently to give a violent or explosive decomposition.
(powdered) Metals	Al, Sb, Bi, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Sn and Zn react violently or explosively with fused ammonium nitrate below 200 °C.
Acids	Mineral acids destabilise. Concentrated acetic acid mixtures ignite on warming.
Organic fuels	Fire incidents involve AN mixed with 1% of organic fuels (confinement required). Up to 2-4 %, such mixtures are used as commercial explosives.
Ammonium sulfate	AN containing the sulfate readily explodes on contact with potassium or its alloy with sodium.
Sulfides	In presence of sulfide ores, explosives containing AN may undergo runaway reaction, leading to detonation at T < 40 °C.

Considering the serious consequences that a chemical incompatibility between substances can produce, the control of chemical hazards in industrial environments requires a rapid and accurate identification of incompatibility issues that exist between two or more chemicals. For these reasons, chemical incompatibilities with AN is a topic that has attracted a large number of scientific studies and has led to the performance of experiments designed primarily to enhance the safety of the operators of industries (Li and Koseki, 2005). Because of its complexity and despite the scientific interest aroused, the decomposition mechanisms pertaining to pure ammonium nitrate or mixtures of ammonium nitrate and contaminants are not yet unambiguously defined. Until now, the thermal hazards of AN and its mixtures have been investigated using experimental methods like differential scanning calorimetry (DSC), thermogravimetry (TG), simultaneous TG-DTA-FTIR-MS, heat flow calorimetry (HFC) (Badeen et al., 2005). Information about chemical incompatibilities is collected in the material safety data sheet of the substance or in incompatibility charts (Winder and Zarei, 2000) used for segregation of dangerous substances or mixtures to avoid the risk of accidents, but the data contained herein is often general and limited. In this context, theoretical approaches represent a viable alternative and/or complementary option to experimental investigation, especially when complex reaction mechanisms related to the production of unstable intermediates or requiring extreme experimental conditions are concerned or when only old experimental data are available. In this paper, we present a theoretical study in which molecular modelling is used as a valuable and reliable tool to identify the reaction channels involved in the decomposition of the pure and contaminated AN. The main aim of the present work is to understand the reaction mechanisms that are driving some chemical incompatibilities in which ammonium nitrate is involved. To achieve this goal, the study was done in two stages: the first step was to define the possible overall reaction mechanisms and the energy involved in the detonation of pure AN. The second step was to study the reaction pathways of the main incompatibility systems with AN. The ultimate objective is to define an overall reaction mechanisms, the energies involved, the products formed and their evolution over time. Once these results are obtained, the longer term objective of the present work, would be to assess whether it is possible to develop predictive methods that allow one to estimate *a priori* the outcome when incompatible substances are in contact with AN.

2. Computational Details

The reaction mechanisms are investigated using the *Density Functional Theory* (DFT). This theory is based on the principle that the energy of a molecule can be determined from the electron density $\rho(r)$ instead of a wave function used in other *ab initio* methods. When using DFT, the 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, an unknown term. The problem of finding accurate approximations to $E_{\text{xc}}[\rho]$ is the biggest challenge for DFT experts. Over the years, a lot of different exchange and correlation functionals were developed and, therefore, there is a list of different functionals that present advantages or disadvantages. A DFT benchmark study on the decomposition reaction of ammonium nitrate has been undertaken to determine the most efficient combination of functional and basis set to describe accurately the chemical reaction analysed. The best overall agreement with the reference methods, giving generally more accurate results, was obtained with M06-2X/6-311+G(2d,2p) method (Zhao and Truhlar, 2008). Once the energy of the molecules is defined, it is possible to characterize its variation along the reaction coordinate. The reactants, intermediates and products are identified as stable minima energy and transition states as maxima energy along this path. All the reaction mechanisms presented below were studied by the M06-2X/6-311+G(2d,2p) method and the calculations were carried out with the Gaussian-09 package (Frisch et al., 2009).

3. Decomposition path of pure ammonium nitrate

Pure ammonium nitrate is a colourless salt and it was discovered recently that the heating of the solid material produces a vapour which contains not only NH_3 and HNO_3 , but also NH_4NO_3 molecules (Hildenbrand et al., 2010). The salt melts at 169°C and at this temperature the decomposition process is already started (Kummer 1947). The first step of the decomposition mechanism of pure AN is known to be the endothermic dissociation into ammonia and nitric acid, but after this first step the rest of the decomposition mechanism is not yet defined in a unique way and different reactions can be assumed (Médard, 1999):



From the ancient work of Berthelot (1892) about the explosive nature of ammonium nitrate it seems that detonation takes place according to the third equation described above: $\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} + \frac{1}{2} \text{O}_2$.

In a recent kinetic study, performed by Park and Lin (2009), a mechanism for the decomposition reaction of AN, which is similar to that known for the other reactions of [H,N,O]-containing systems has been suggested. In the present work we studied the overall reaction of decomposition of ammonium nitrate and we analyzed the various paths that lead to the different reaction products identified experimentally by Park. Our aim is to explain the formation of products, estimate their associated energies and analyze whether a relationship exists between experimental rate constants and theoretical activation barriers.

The reaction path, proposed in this study, is shown in Figure 1. From the literature (Nguyen et al. 1997) it is known that in the gas phase the equilibrium structure of ammonium nitrate corresponds to a nitric acid – ammonia complex containing a strong hydrogen bond. Our theoretical calculations confirm this finding because this structure was the only stable minimum found on the potential energy surface. It is used as energy reference for all the stationary points along the reaction path.

The first step of the reaction is the dissociation of AN into ammonia and nitric acid, through an endothermic step of 15.3 kcal/mol. This nitric acid undergoes homolytic breaking of the NO bond (55.4 kcal/mol) and this step leads to the formation of nitric oxide and hydroxyl radicals. The hydroxyl radical reacts with the ammonia-molecule which had resulted from the initial dissociation, through a transition state (TS_1), to form the amidogen radical (NH_2) and water.

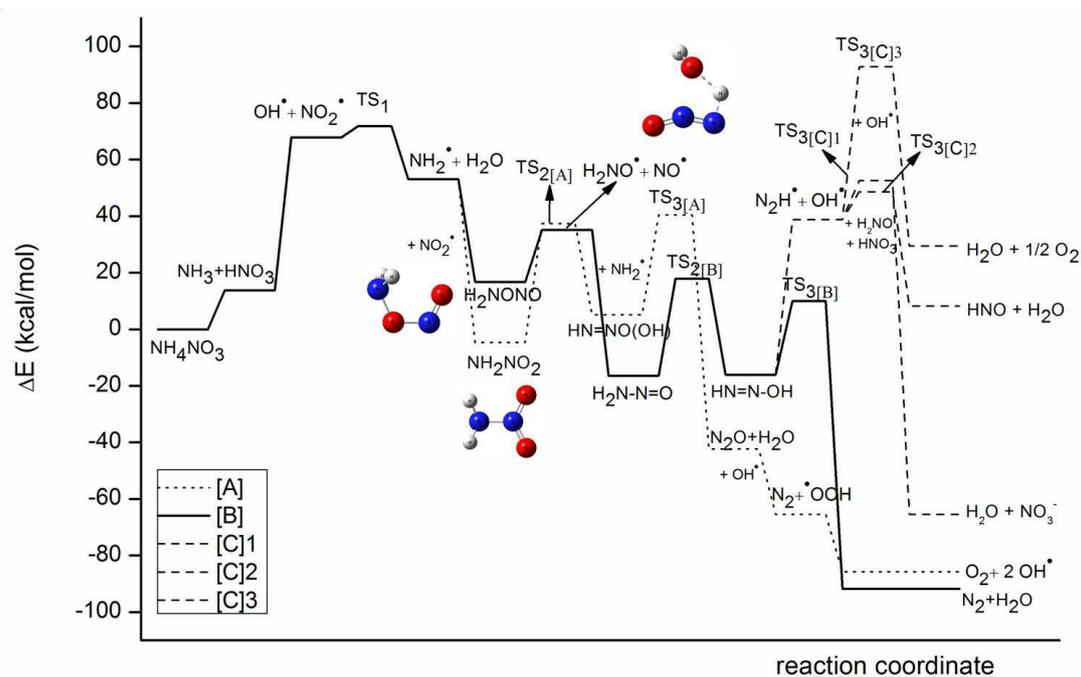


Figure 1: Reaction pathways of ammonium nitrate decomposition studied at the M06-2X/6-311+G(2d,2p) level

Two different radicals coupling between amidogen and nitrogen dioxide lead, through a barrier-less reaction, to the formation of two distinct intermediates (NH_2NO_2 and H_2NONO). Therefore from this radical coupling, the decomposition path can be separated into two different paths called [A] and [B] in the Figure 1. The first intermediate (NH_2NO_2) is more stable by approximately 24 kcal/mol compared to the second (H_2NONO). Following pathway [A], NH_2NO_2 could undergo a keto-enol isomerisation, through a transition state ($\text{TS}_{2[\text{A}]}$), to form $\text{HN}=\text{NO}(\text{OH})$. This intermediate can rearrange, passing a transition state of about 40 kcal/mol $\text{TS}_{3[\text{A}]}$, to form the dinitrogen oxide, N_2O . The subsequently decomposition of N_2O into N_2 and O_2 is promoted by the presence of species like hydroxyl and peroxy radicals. Following pathway [B], homolytic breaking of the NO bond from the H_2NONO intermediate, leads to the production of dihydronitroxide H_2NO and nitric oxide radicals. The nitric oxide radical can react with the amidogen radical, previously formed, to give the $\text{H}_2\text{N}-\text{N}=\text{O}$ intermediate. This molecule could undergo a nitro-nitrite isomerisation through a transition state, $\text{TS}_{2[\text{B}]}$, to form the $\text{HN}=\text{N}-\text{OH}$ intermediate. From this intermediate the decomposition may follow either of two further possible paths: it may remain on path [B] or pursue an alternative reaction that gives rise to the path called [C]. In pathway [B], the $\text{HN}=\text{N}-\text{OH}$ decomposes, through a transition state $\text{TS}_{3[\text{B}]}$ into N_2 and water. In pathway [C], the $\text{HN}=\text{N}-\text{OH}$ undergoes an homolytical rupture of the NO bond which leads to the formation of N_2H and OH radicals. The OH radical thus formed can react with three different molecules (paths [C]₁, [C]₂, [C]₃). In path [C]₁, it can react with nitric acid to form a water – nitrate ion complex, containing a strong hydrogen bond, passing by a transition state $\text{TS}_{3[\text{C}1]}$ of about 12 kcal/mol. This complex may then dissociate into water and nitrate ion. In path [C]₂, it can react with the dihydronitroxide radical to form a water – HNO complex (monomeric form of the hyponitrous acid), passing by a transition state $\text{TS}_{3[\text{C}2]}$ of about 16 kcal/mol. This complex may then dissociate into water and HNO. Lastly in path [C]₃, a reaction takes place between two OH radicals to form water and an oxygen atom passing by higher barriers (54 kcal/mol). Through the analysis of the potential energy surface, it was possible to identify all the reaction mechanisms involved and all the products formed in the gas phase (N_2 , H_2O , O_2 , OH, HNO, NO_3) in the experimental work of Park concerning AN decomposition. There is also a good agreement between the calculated activation barriers and the measured rate constants in this study. Our calculations show that the reaction is globally exothermic but not spontaneous since it must overcome energy barriers of approximately 40-50 kcal/mol.

4. Reaction mechanism of the mixture of ammonium nitrate and the sodium salt of dichloroisocyanuric acid (SDIC)

As shown in Table 2, numerous incompatibilities with AN that can increase the fire and explosion risks have been identified. The first system of incompatibility that we have studied is the one formed by AN and

the sodium salt of dichloroisocyanuric acid (SDIC) due to the possible involvement of such mixtures in the accident that took place in Toulouse in September 2001 (Dechy et al., 2004). Experimental studies previously conducted (Badeen et al., 2005) revealed that pure SDIC and pure AN do not display any exothermic activity below 175 °C and 200 °C, respectively. However, a 50:50 mixture of these two components shows a first exothermic peak in the temperature range of 60-90 °C and a larger exotherm at 110-125 °C. This clearly indicates that the mixture is less thermally stable than its neat components. From the decomposition of the mixture, several species have been detected as N₂, NO, HCl, NO₂, Cl₂, H₂O, CO₂, N₂O and it has been suggested that small quantities of NCl₃, a very reactive substance, may be produced during the decomposition of the mixture. NCl₃ was positively evidenced by UV/VIS spectrometry by Guengant 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. No study has been conducted using theoretical tools. We have undertaken a theoretical study using the same method M06-2X/6-311+G(2d,2p) selected for the study of the decomposition of pure AN. The aim is to confirm that one of the possible reactions between these two substances may begin from the hydrolysis of SDIC that leads to the formation of a molecule of hypochlorous acid, HOCl, as proposed by the experimental study of Paul et al. (2004). HOCl is a strong oxidant because there is a chlorine atom with an oxidation number of +1 in the molecule. We suppose that this acid reacts with AN to produce monochloroamine, dichloroamine and trichloroamine. The last one decomposes spontaneously into N₂ and Cl₂. Moreover a second reaction can occur: this is the opening of the isocyanuric cycle that leads to the formation of NH₂Cl, NHCl₂, CO₂ and NCl₃. These two reactions are shown in Figure 2:

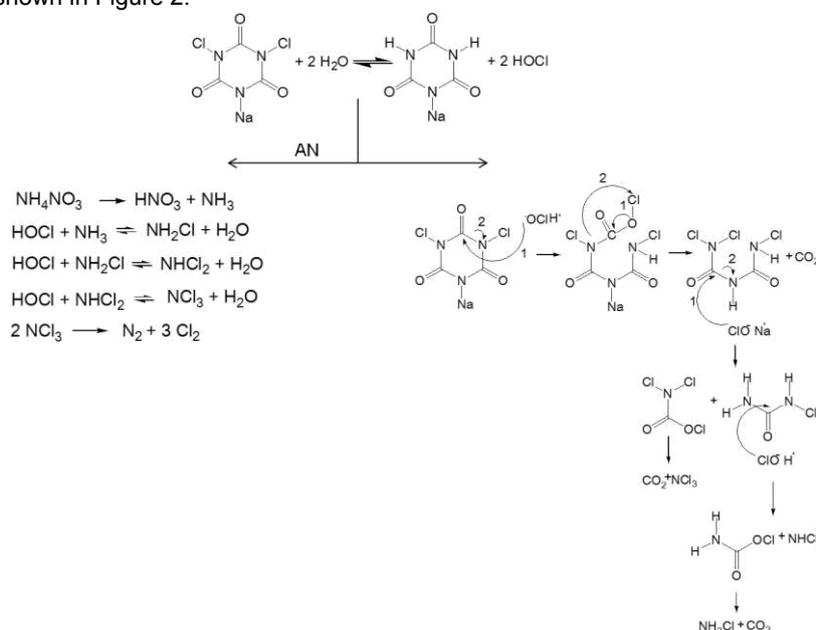


Figure 2: Two reactions that can produce monochloroamine, dichloroamine, trichloroamine

Considering the two decomposition reactions proposed and taking into account the decomposition of neat AN, we can find all the products detected experimentally by MS and FTIR (Badeen et al., 2005). Due to the complex reactions and to the high barriers involved, data from a kinetic study would be required for estimating the rate of each reaction.

5. Conclusion

Theoretical calculations have confirmed the complexity of the reactivity of AN as five competing mechanisms, through which the decomposition of AN in the gas phase can take place, were identified. It is believed that this process occurs through a multi-step radical mechanism presenting energy barriers. The first one forming radicals (55.4 kcal/mol) seems to be the rate limiting step and could explain the many experimental observations in which the process of AN decomposition occurs only under specific conditions. The simple decomposition of neat ammonium nitrate becomes considerably more complex when AN reacts with another substance. Due to the fact that some reactions are in competition with each other, that they occur with a fast radical mechanism and that they can form products too reactive to be

detected, it becomes difficult, with experiments only, to have a clear idea of the mechanism involved in these reactions. In this preliminary study on the incompatibility between AN and SDIC, three mechanisms have been identified producing highly reactive molecules such as trichloroamine, an explosive substance. Their co-existence already confirms all the products detected by experiments. Kinetic studies supported by further DFT calculations coupled with additional experimental data should allow to define more precisely the reaction mechanism of these chemicals and to provide useful information to reduce hazards.

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