

Understanding of the mechanisms of chemical incompatibility of ammonium nitrate by molecular modeling

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Summary

The serious potential consequences of the hazards posed by chemical incompatibility, especially in a large-scale industrial environment, provide motivation for a deeper understanding of the mechanisms of the reactions involved in these phenomena. In this PhD work, two incompatibilities of ammonium nitrate were studied by molecular modeling. Results, in qualitative agreement with the calorimetric experiments, show the potential of the modern computational approaches to establish a clear link between microscopic (molecular) description and macroscopic effects of incompatibilities.

Problem addressed

Numerous chemical reactants, whenever placed in contact with other products or materials, tend to lead to undesired chemical incompatibility phenomena. Ammonium nitrate (NH_4NO_3 , AN), widely used in the chemical industry as fertilizer component and as an ingredient in explosive mixtures, is known for its long list of incompatibilities (as metals, halides, and organics) [1] and often involved in major accidents (Toulouse, 2001). Indeed, such incompatibilities are known to reduce the runaway temperatures and sometimes increase the reaction enthalpies. In order to prevent the occurrence of those phenomena, which can lead to particularly dangerous situations in an industrial environment, a rapid and accurate identification of the incompatibilities is needed. Until now, experimental studies, Safety Data Sheets (SDSs), chemical compatibility charts and software were the only possible approaches used to study and prevent incompatibilities. Despite their undeniable utility, these methods do not explain exactly how the incompatibility drives the undesired reaction scheme, in terms of thermodynamic data. Therefore, complementary to these approaches, molecular modeling was used in this PhD work to ensure a deeper understanding.

The first objective of this work was thus to provide insights into the possible reaction pathways, enthalpies and products formed by incompatibility reaction between ammonium nitrate and its hazardous contaminants such as chlorinated compounds (sodium salt of dichlorisocyanuric acid, SDIC) and sodium nitrite (NaNO_2). More in general it aimed to understand the leading mechanisms of incompatibility phenomenon and to propose a modeling approach to complete and improve experimental results of these processes with the objective to enhance process safety of chemicals during use, transport and storage.

State of the art

Ammonium nitrate 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 the catalytic effects of the contaminants on the decomposition of AN [2]. Despite its importance, the mechanisms of decomposition of pure ammonium nitrate or in the presence of contaminants have not been yet unambiguously clarified and many hypotheses succeeded.

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 [1].



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

Sodium salt of dichloroisocyanuric acid, a substance belonging to the family of chloramines used as bleaching agents, disinfectants and bactericides, is the contaminant suspected to be, according to preliminary investigations, one of the likely root causes of the explosion that occurred in 2001 in the Grande Paroisse (AZF) fertilizer plant in Toulouse, France [3]. 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. Moreover, differential scanning calorimetry (DSC) results showed an important exothermic activity below 200°C for the AN–SDIC prepared in ambient conditions with a relative humidity of 70% [4]. This clearly indicates that the mixture is less thermally stable than its pure components and that the presence of moisture decreases the thermal stability of the mixture significantly. Starting from their experimental study, Paul et al. [5] advanced the hypothesis that the hydrolysis of SDIC followed by the reaction of the hypochlorous acid was the cause of the incompatibility between the two chemicals compounds.

Sodium nitrite and sodium nitrate are used in the manufacture of water-in-oil ammonium nitrate emulsion (ANE) explosives [6] and large quantities of these salts may be present in the industrial environment. The real danger of powdered NaNO_2 coming into contact with AN emulsion explosive at a manufacturing site has been reported anecdotally [7]. 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 (obtained at the Canadian Explosive Research

Laboratory) 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 behaviors depending on the amount of water present.

These results, allowing users to apply adequate mitigation measures, do not clarify the chemistry hidden behind this behavior. There is thus a huge need to identify by which mechanism the incompatibility phenomena can lead to a sudden dangerous detonation.

Computational details

Since some attempts using molecular modeling to obtain thermochemical data for reactive or hazardous materials or to predict thermodynamic data underpinning undesired reactions, proved to be fruitful [8], in this study, a theoretical approach was extended to the study of chemical incompatibilities. The reaction mechanisms were investigated using the Density Functional Theory (DFT), which can calculate the energy (Figure 2) and the electronic properties of the ground state of a molecule from the electronic density. From known energy, it is possible to define a potential energy surface on which reactivity study can be conducted. This approach allow calculating energies of reactants, transition states and products that can be represented in a energy diagram as shown of Figure 2.

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

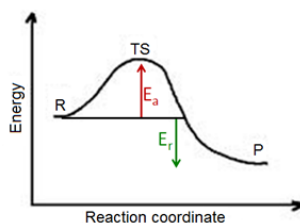


Figure 2: Principle of energy diagram.

$T_s[\rho]$ 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.

All of the calculations were performed using the Gaussian 09 software package [9].

Applications/implementations/results

DFT benchmark and ammonium nitrate decomposition

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 was performed at the beginning of this work in order to determine the most efficient combination of functional and basis set (M06-2X/6-311+G(2d,2p)) to describe accurately the chemical reaction analyzed. To do this,

17 functionals were tested including global hybrids, range-separated hybrid functionals and double hybrids. After, the decomposition mechanism of the pure ammonium nitrate in the gas phase was studied in detail by DFT and five main reaction channels, giving the experimentally characterized compounds (N_2 , H_2O , O_2 , $\cdot OH$, HNO , $\cdot NO_3$) were identified. As shown in Figure 3, the first step of the reaction is the dissociation of AN into NH_3 and HNO_3 , through an endothermic step of 4.9 kcal/mol.

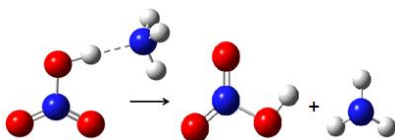


Figure 3: Chemical representation of the decomposition of AN.

The nitric acid then undergoes a homolytic breaking at high energy ($\Delta G = 40.2$ kcal/mol), giving the formation of nitric oxide and hydroxyl radicals. This is the rate determining step. The hydroxyl radical then reacts with the ammonia molecule to form the amidogen radical ($NH_2\cdot$) and water. Then, two different radical couplings can occur between amidogen and nitrogen dioxide, leading to two different intermediates (NH_2NO_2 and H_2NONO). From the first one (NH_2NO_2), N_2O is formed. It can, in turn, react with the hydroxyl radical to form N_2 , O_2 , and $\cdot OH$. Instead, the decomposition of H_2NONO leads to the formation of $\cdot NO$ that can, in turn, react with the amidogen radical to produce $N_2 + H_2O$ and $N_2H + \cdot OH$ radicals. In conclusion, it was found that the reaction is globally exothermic, but its initiation depends on overcoming an energy barrier of about 40 kcal/mol involved in the homolysis of the nitric acid. This high energy barrier explains the fact that pure AN does not decompose spontaneously at standard conditions.

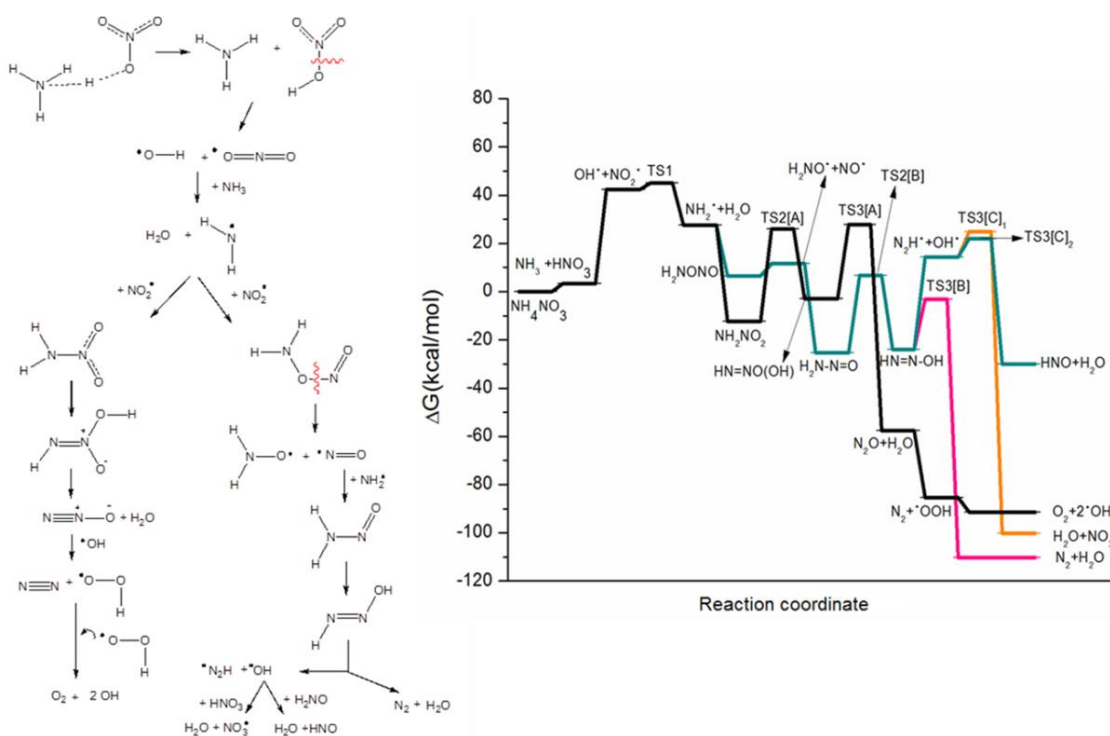


Figure 4: Reaction paths and CBS-QB3 energy profiles for the decomposition of ammonium nitrate [10]. These results (and the results of the benchmark) were published in *Phys. Chem. Chem. Phys.*, **2013**, 15, 10849-10858. [10]

Reaction mechanism of ammonium nitrate and sodium salt of dichloroisocyanuric acid

The first system of incompatibility that was studied by DFT is the one formed by AN and SDIC. As proposed by Paul et al. [5], the hydrolysis of SDIC followed by the reaction of the hypochlorous acid with ammonia was the first reaction characterized (Figure 5). Theoretical calculations showed that the rate-determining step of this reaction (hydrolysis of SDIC) presents an activation energy higher (ΔG^\ddagger of 78.4 kcal/mol) than that of the decomposition of pure AN ($\Delta G^\ddagger = 45.1$ kcal/mol).

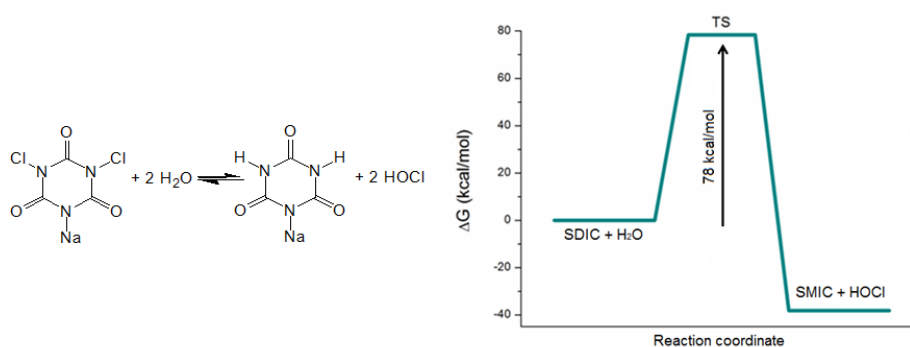


Figure 5: Reaction paths and M06/2X energy profiles for the hydrolysis of SDIC.

Consequently, this mechanism is not energetically favored with respect to the decomposition of pure ammonium nitrate and this hypothesis was discarded in favor of a direct reaction between AN and SDIC.

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) was retained in the following. The contact between SDIC and ammonia gives, passing through a transition state of 58.0 kcal/mol, the sodium salt of monochloroisocyanuric acid (SMIC) and the monochloroamine (NH_2Cl). We have found that the decomposition path of monochloroamine was 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 6.

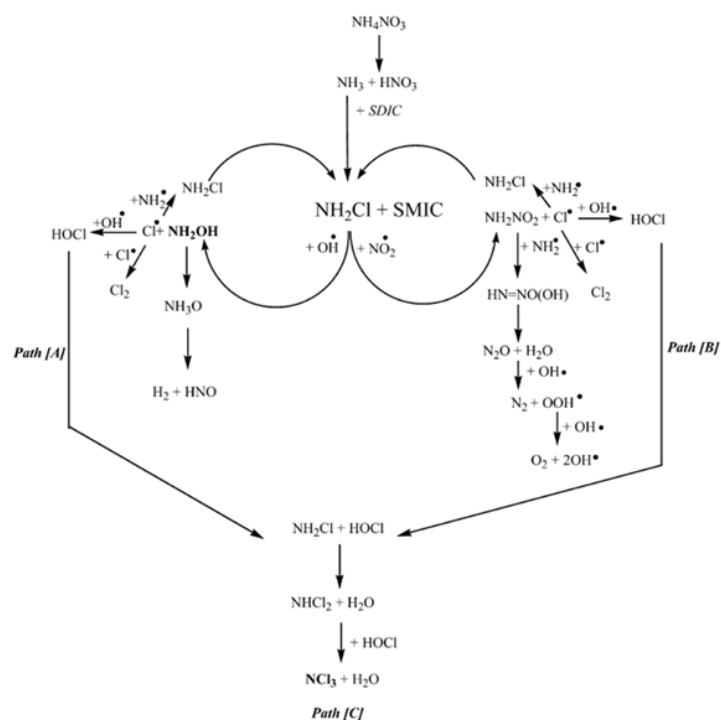


Figure 6: Reaction path for the decomposition of monochloroamine, resulting from the reaction between the ammonia and the dichloroisocyanuric acid.

In path A, the monochloroamine reacts with the hydroxyl radical (OH^\bullet), present in the reactive environment, to form hydroxylamine (NH_2OH), an explosive compound, and chlorine radical. The chlorine radical reacts with radicals (NH_2^\bullet , OH^\bullet , Cl^\bullet) 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. 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.

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 6 (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 that presents an higher energy barrier (58.0 kcal/mol) compared to the rate determining step of the decomposition of AN (40.2 kcal/mol) as can be seen on figure 7a). Nevertheless other effects, as the presence of water or humidity, should be considered since ammonium nitrate is a highly hygroscopic compound. 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 7). 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 (32.1 vs 40.2 kcal/mol, respectively). Therefore, the important conclusion of this work is that the presence of water, even in small quantities, could ignite the incompatibility reaction between AN and SDIC.

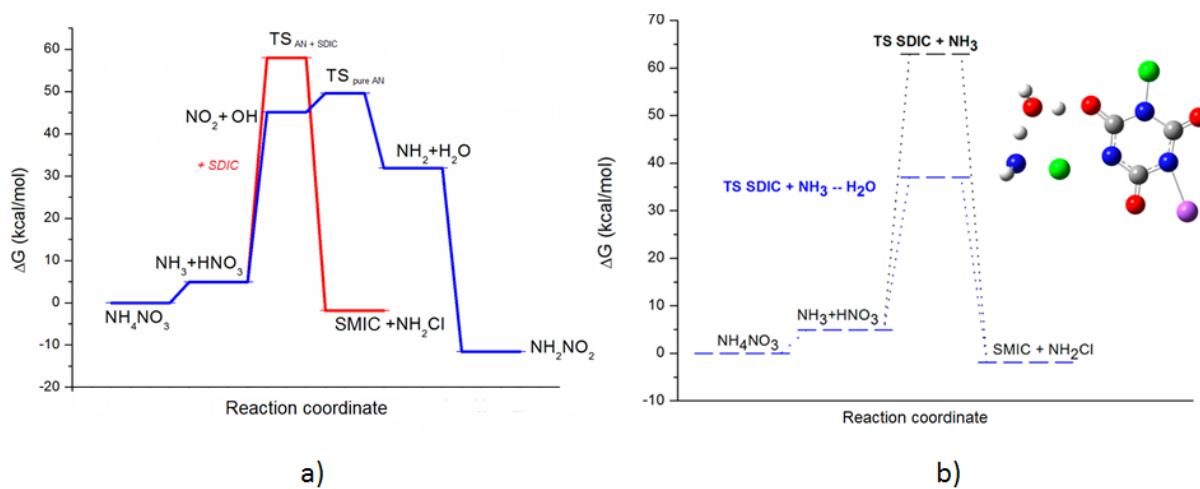


Figure 7: Comparison of Gibbs free energy profiles for the decomposition of pure AN and the reaction between AN-SDIC in gas phase (a) and between the AN-SDIC reaction in gas phase and with a water molecule (b).

Results obtained by molecular modeling are in perfect agreement with the results of Badeen et al. concerning an important exothermic activity below 200°C for the AN–SDIC prepared in ambient conditions with a relative humidity of 70% [4] and with the experimental data obtained by DSC experiments at the Canadian Explosive Research Laboratory (Figure 8).

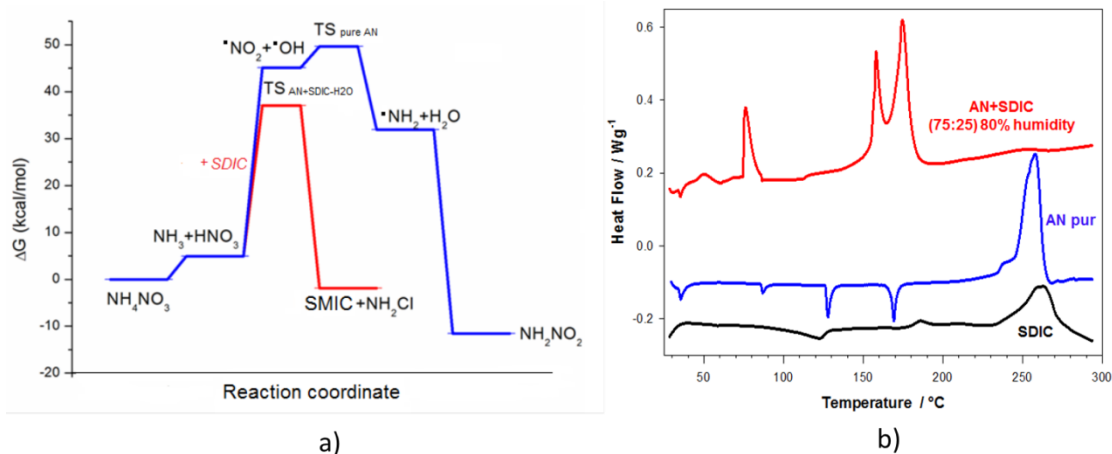


Figure 8: Agreement between DFT (a) and calorimetric (b) results for the reaction between AN and SDIC.

These results were published in *Ind. Eng. Chem. Res.*, 2014, 53, 13920–13927. [11]

Reaction mechanism of ammonium nitrate and sodium salts (sodium nitrate and sodium nitrite)

Following the procedure defined to study the incompatibility between AN and SDIC, the third part of this work was focused on the identification of the reaction mechanism of AN- NaNO_2 and AN- NaNO_3 mixtures, with a particular attention to the rate determining step: the direct reaction between the products of the first decomposition of ammonium nitrate (NH_3 or HNO_3) and contaminants. Indeed, a detailed theoretical approach was not performed to save computational time by focusing on the rate determining step.

Theoretical results indicate that the sodium nitrite reacts preferentially with HNO_3 giving sodium hydroxide (NaOH) and two molecules of NO_2 passing by a transition state with a relative Gibbs free energy of 44.1 kcal/mol. Also sodium nitrate reacts preferentially with HNO_3 giving sodium hydroxide (NaOH) and a dinitrogen pentoxide molecule (N_2O_5), with an activation free energy of 50.7 kcal/mol.

It's interesting to note that unlike the case of SDIC, here, the origin of the incompatibility is rationalized in terms of a direct reaction between nitric acid and the contaminant. However also for this reaction the energy barrier is higher than the direct decomposition of AN (44.1 vs 40.2 kcal/mol for NaNO_2 and 50.7 vs 40.2 kcal/mol for NaNO_3). If this result confirms experimental data concerning the non-existence of an incompatibility between sodium nitrate and ammonium nitrate, it cannot explain the incompatibility between sodium nitrite and ammonium nitrate: the activation barrier for the reaction between AN and NaNO_2 is higher than the decomposition energy of pure AN.

Considering the pivotal role of water in the case of the incompatibility between AN and SDIC and the hygroscopicity of AN and sodium salts, a water molecule was also introduced in the transition states of the rate determining step of the reactions. 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 as observed in Figure 9. However, unlike the reaction between AN and SDIC, the water does not have a catalytic role in the AN- NaNO_2 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.

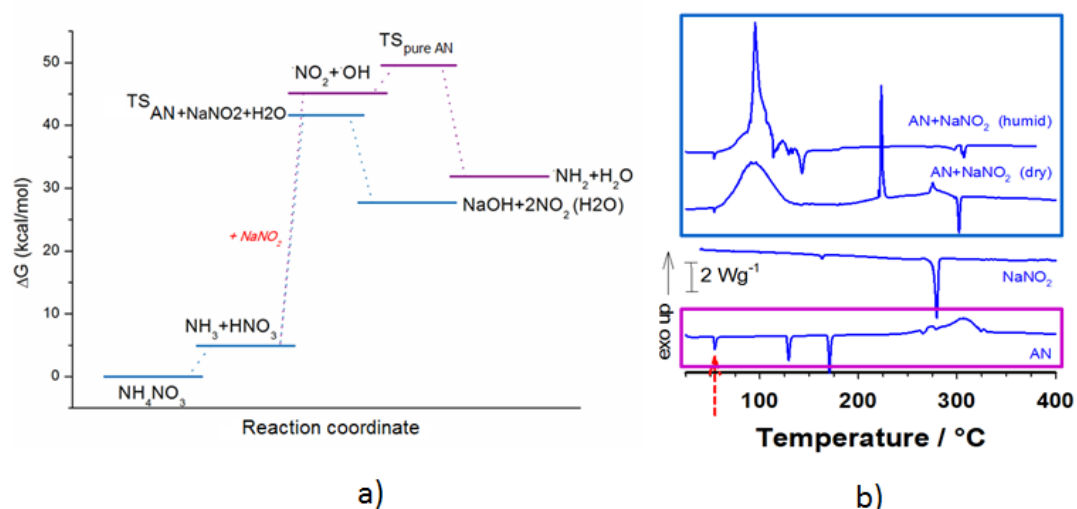


Figure 9: Agreement between DFT (a) and calorimetric (b) results for the reaction between AN and NaNO_2 .

Considering the case of sodium nitrate, the presence of a water molecule added in the geometry of the transition state causes a decrease in the activation barrier that is not enough to justify an incompatibility between the two substances, even in a wet environment. This result is in total agreement with the experimental results.

These results are the subject of a publication in progress: *A theoretical and experimental study of the reaction between ammonium nitrate and sodium salts for Ind. Eng. Chem. Res.*

Conclusions and key innovations

The strong need to be able to prevent incidents of catastrophic extent lead to implement new tools and new techniques for the study of phenomena of incompatibilities. In this PhD work, molecular modeling allowed identifying a complete path of decomposition of pure ammonium nitrate as well as a new reaction mechanism explaining the incompatibility between AN and SDIC or NaNO_2 and justifying products previously characterized experimentally. Also, the theoretical and microscopic nature of the study highlighted the significant synergistic role, often overlooked during experimental analysis, carried by water in the presence of a contaminant and revealed the autocatalytic character

of some incompatibility mechanisms. Moreover, good agreement was highlighted between theoretical and experimental results found in the literature and obtained from calorimetric analysis at the Canadian Explosive Research Laboratory.

The theoretical method employed in this thesis, a pioneer approach in the field of the study of chemical incompatibilities, has produced a thorough level of understanding of the phenomenon. This underlines the potential of molecular modeling as an *a priori* tool for investigating safety of chemicals in the field of risk assessment and management. It can be interesting to continue to test its efficiency through the study of other incompatibilities of AN (as sugar, sulphur) and complement its description by kinetics analysis. This approach could be also extended to the study of other hazardous industrial products such as organic peroxides, well known to be incompatible with several contaminants.

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