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Investigation of Ammonium Nitrate Contaminants Based on Computational Chemistry Approach

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Ammonium nitrate (AN) was involved in a number of major accidents in the last century. Safety issues related to the use of ammonium nitrate is far from being achieved: insufficient knowledge are still available about the interaction mechanisms of ammonium nitrate with contaminants despite significant efforts. This paper proposes to investigate AN's contaminants, which can be grouped into three categories depending on their action when they are in contact with ammonium nitrate: promoters, inhibitors, and inerts. The aim of this study is to identify possible common reaction pathways inside of each category to finally build a predictive tool able to determine if a contaminant may involve a chemical incompatibility with AN or not, with the help of computational chemistry approach.

1. Introduction

Ammonium nitrate is extensively used in the industry as fertilizer and propellant due to its nature of oxidizer. It is classified as an oxidizing agent according to the UN Recommendations on the Transport of Dangerous Goods (UN, 2015). AN is incompatible with a wide range of substances as chlorides like dichloroisocyanurate (SDIC), organic compounds, nitrites (e.g. $NaNO_2$) just to mention few. Besides, the identification and the prevention of incompatibility problems represent an important safety challenge in industrial context. The control of chemical risk in the industrial environment requires a quick and accurate screening. Currently, this information is mostly provided by Differential Scanning Calorimetry tests (DSC). The limitation of this approach relies on the fact that it is not possible to identify and understand the detailed mechanism involved in the reactions between two or more substances.

In the last years, INERIS, in collaboration with Chimie ParisTech, developed a molecular modeling approach to complete and improve experimental knowledge about chemical incompatibilities with ammonium nitrate. This theoretical work, based on Density Functional Theory (DFT) calculations, was intended to provide insights into the possible reaction pathways, in terms of energetics and products formed by interaction between ammonium nitrate and AN's contaminants. In a first step, the mechanism of decomposition of pure ammonium nitrate in the gas phase was characterized (Cagnina et al., 2013). Then, the reactivity in contact with SDIC was studied due to its possible role in the accident that occurred at the AZF factory in 2001 in Toulouse. The characterized mechanism involves the direct reaction of SDIC with NH_3 in presence of water that was evidenced playing a catalytic role in the reaction (Cagnina et al., 2014). The same theoretical approach was also successfully used for sodium salts in contact with AN, demonstrating the capability of the theoretical approach to predict a priori if a contaminant is experimentally compatible or not. These theoretical results were validated by comparison to experimental testing, performed by CERL's (Canadian Explosives Research Laboratory) calorimetric tools (Cagnina et al., 2016). This computational study helped to face some difficulties by clarifying the reaction mechanisms involved in these chemical incompatibilities and to identify the dangerous products generated. The work in progress now aims to extent the use of this computational chemistry approach to more generally investigate and predict the effect of the different types of AN contaminants that can be found in AN formulations: inhibitors,

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inerts, and promoters. To this aim, new contaminants were studied in view of the future development of a simplified tool to predict the behaviors of contaminants in AN formulations.

2. AN's contaminants

In general, AN is used in formulations mixed with contaminants. These contaminants can be added to improve the efficiency of the formulation (as in fertilizers) or to improve explosion effect in explosive applications. Some additives are also used as stabilizer (like carbonates, sulfates, phosphate of sodium, potassium, calcium) to avoid the decomposition during transport and storage. Moreover, AN formulations could be also accidentally subjected to contamination by impurities.

These contaminants can lower the thermal stability of AN and promote auto-ignitions and explosions, caused by their catalytic effects on the decomposition of AN. Besides, Table 1 lists a series of major disasters caused by AN during the last hundred years. Most accidents were caused by incompatibility with substances with which AN came into contact.

Table 1: Some major AN's accidents

Year, Place	Substances involved	Effects
1921, Oppau-Germany	$(NH_4)_2SO_4/NH_4NO_3$	Explosion
1947, Brest (ship)-France	NH_4NO_3-combustible	Fire followed by explosion
1947, Texas City-USA	NH_4NO_3(pure)-NH_4NO_3-sulphur	Explosion
1954, Finland (ship)	NH_4NO_3/paper /copper acetoarsenite	Fire followed by explosion
1994, Sergent Bluff-USA	NH_4NO_3	Explosion
2000, Aunay-Sous-Crecy-France	NH_4NO_3/organic materials	Decomposition of AN
2001, Toulouse-France	NH_4NO_3/sodium salt of dichloroisocyanuric acid (SDIC)?	Explosion
2013, West-USA	NH_4NO_3+organic and woody materials	Fire followed by explosion

2.1 Promoters

A promoter (or incompatible substance) is a contaminant that favors the decomposition of ammonium nitrate, lowering the temperature of decomposition compared to pure AN. This is notably the case of fuel in explosive applications but also the case of some other substances that were not introduced in the AN formulation for this purpose. To evidence this behavior, calorimetric experiments like differential scanning calorimetry (DSC) or Reactive System Screening Tool (RSST) can be performed on pure ammonium nitrate, on the suspected incompatible substances and on their mixture. In the case of a promoter, the decomposition temperature of the mixture is lower than for pure AN and the heat released can be greater.

Promoters are numerous among AN's contaminants. Inside this category, we can find various types of chemicals such as fuels, halide salts (Oxley et al., 2002), nitrates and sulfates of chromium, iron, copper, aluminum and chromium oxide (Oxley et al., 1992). DSC and RSST experiments conducted on a large series of contaminants clearly demonstrated the destabilizing effect of the such incompatible contaminants by lowering the decomposition temperature (Tmax and Tonset) when compared with neat ammonium nitrate (Han et al., 2015; 2016). Table 2 presents some of the most common promoters.

Table 2: Examples of promoters of AN's decomposition, data extracted in Oxley et al. (1992, 2002) and in Han et al. (2015, 2016).

Fuel	**Halide Salts**	**Nitrates**	**Sulfates**
carbon, mineral oil, diesel, sugar, nitrobenzene, nitromethane, aluminium sulfur	KCl, NH_4Cl, $CaCl_2$, NaCl, KBr, KI, KF	Chromium(III), Aluminum(III) and Copper(II) Nitrates	Chromium(III), Aluminum(III), Iron(II), Iron(III) and Copper(II) Sulfates

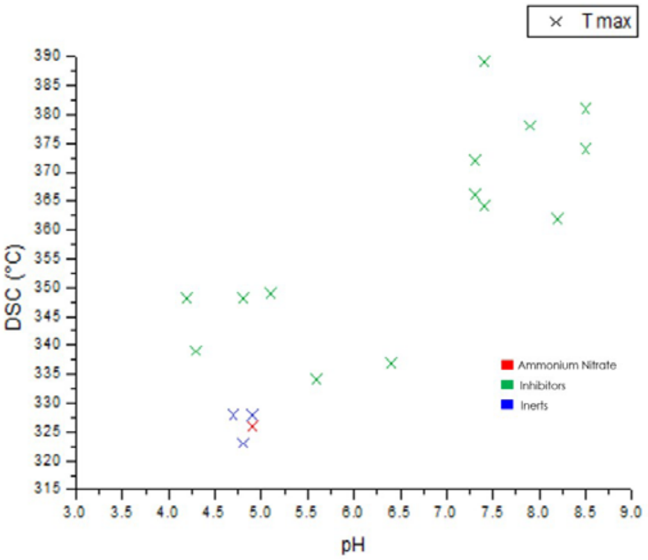
2.2 Inerts

AN inert behaves according to a dilution effect on AN. It does not change the chemical reaction itself but the conditions of the reaction due to its incorporation in the mixture, reducing the probability of an AN explosion (Oxley et al., 2002).

Inert materials ($NaNO_3$, KNO_3 and $Ca(NO_3)_2$) seem to not affect the thermal stability of AN. Indeed, no significant shift of decomposition exotherm is observed, suggesting no interaction between AN and nitrate salts (Cagnina et al., 2016). So, these contaminants are used as filler and not as stabilizers. Other inerts like KNO_3 and $Ca(NO_3)_2$ may be expected to present the same reactivity profile considering the similarity with $NaNO_3$.

2.3 Inhibitors

AN's inhibitors can be identified in calorimetric experiments, when the decomposition temperature of AN mixed with the contaminant is higher than the decomposition temperature of neat AN (Han et al., 2016). However, the heat released during the reaction is lower than that of pure ammonium nitrate decomposition. Inhibitors present the capability to make ammonium nitrate more stable. Experimentally, most of the oxyanions ($A_xO_y$likesulfates, carbonates or phosphates of sodium, potassium, ammonium and calcium) raise the decomposition exothermal peak of AN obtained by DSC experiments (Oxley et al., 2002). As shared in Figure 1, most of theoxyanions increase the temperature of the AN's exothermic maxima and it seems to exist a certain correlation between the pH of the oxyanions and their ability to inhibit the decomposition and the dangerous reactions of ammonium nitrate (represented by Tmax). When varying the cation among Na^+, K^+, NH_4^+ and Ca^{2+}, there are not great differences in the position of the exothermic peak (Oxley et al., 2002). For substances like AN, $(NH_4)_2SO_4$, $NaHCO_3$ and K_2CO_3, some RSST experiments are also available (Han 2015(a), Han 2105(b)). These values are in agreement with the previous DSC tendencies. Looking at Figure 1, oxyanions likes CO_3^{2-}, HCO_3^- and HPO_4^{2-} maintain a pH range of 7.4–8.3. DSC experiments show that they enhance the AN's exothermic maxima 40–60 °C higher than pure AN. Contaminants like SO_4^{2-} and $H_2PO_4^-$, with a pH value of 4- 5, increase the maximum by 10-20 °C.



AN +	pH	Tmax
KH_2PO_4	4.2	348
NaH_2PO_4	4.3	339
$NaNO_3$	4.7	328
KNO_3	4.8	323
$(NH_4)_2SO_4$	4.8	348
Pure	**4.9**	**326**
$Ca(NO_3)_2$	4.9	328
Na_2SO_4	5.1	349
$CaSO_4$	5.6	334
$CaHPO_4$	6.4	337
Na_2HPO_4	7.3	366
$KHCO_3$	7.3	372
K_2HPO_4	7.4	364
$(NH_4)_2HPO_4$	7.4	364
$CaCO_3$	7.4	389
$MgCO_3$	7.9	378
K_3PO_4	8.2	362
K_2CO_3	8.5	374
Na_2CO_3	8.5	381

Figure 1: Oxyanions's pH versus Tmax decomposition temperature of AN, data extracted by Oxley (2002).

3. Computational Chemistry applied to chemical incompatibility

Up to now, the only tools devoted to the study and the prevention of the phenomena of chemical incompatibility are the calorimetric tests, tables of incompatibilities, safety data sheets, analysis of the accidentology and information from chemicals regulations such as CLP. These tools despite their undisputed importance, provide only incomplete information. The difficulty of investigating chemical incompatibilities lies mainly in the complexity of the reaction paths generated in the presence of intermediates whose experimental characterization is sometimes difficult. To overcome this problem, computational chemistry studies were performed on AN. As for the calorimetric experiments, the mechanism of decomposition of pure AN was first studied. Successive tests were carried out between AN and other contaminants to see if the preferred reaction was that of pure AN or AN with the substance. The reaction path, the energy profile and all possible reaction intermediates were determined. The objective of the research is to identify physicochemical parameters that can provide useful information for predicting the behavior of substances when they enter in contact with AN. This theoretical work, based on Density Functional Theory (DFT) calculations (M06-2X functional) and the software Gaussian09, provides insights into the possible reaction pathways in terms of energetics and products formed by incompatibility reaction between ammonium nitrate and contaminants.

3.1 Decomposition of ammonium nitrate

At first, the decomposition mechanism of pure AN was studied (Cagnina et al., 2013), with the aim to define all the steps and all the intermediates involved.
Pure ammonium nitrate decomposition starts with a proton transfer to nitrate anion to give NH_3 and HNO_3 (eq.1). Then, nitric acid decomposes in two radicals that generate a sequential radical chain (eq. 2). Dissociation of nitric acid is the rate limiting step.

$NH_4NO_3 \rightarrow NH_3 + HNO_3$ (1) $HNO_3 \rightarrow OH^{\bullet} + NO_2^{\bullet}$ (2)

Based on this mechanism, a methodology was applied to study AN incompatibility. It consists in looking for reactions between a substance and NH_3 or HNO_3, generated by the decomposition of AN. In case of contaminants not compatible with AN, they can react with NH_3 and/or HNO_3 in a more favourable reaction than pure AN generating instable (dangerous) products. On the contrary, in case of compatible contaminants, either they do not react with NH_3 or HNO_3 (in the case of inerts) or they can react with NH_3 and/or HNO_3 in a more favourable reaction than pure AN but generating stable products.

3.2 Effects of contaminants

Some contaminants have been investigated to cover a wide range of chemical species that can be found in AN's formulations, (Menicacci et al., 2018) namely:

1) $CaCO_3$ which is normally used as an ammonium nitrate decomposition inhibitor,
2) $CaSO_4$ which is normally used as inert (it means that does not react with AN) and it has a diluent action,
3) $(NH_4)_2SO_4$ which has a promoter profile of the decomposition of AN.

3.2.1 AN + CaCO3

During transport and storage, calcium carbonate is used as an inhibitor of ammonium nitrate decomposition, i.e. not only compatible but even stabilizing AN's formulations. This system has already been studied experimentally and the products of the reaction are: calcium nitrate, carbon dioxide, ammonia and water (Kaljuvee et al., 2008; Popławski et al., 2016). This led to the following reaction:

$$2\ NH_4NO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + 2\ NH_3 + CO_2 + H_2O \qquad (3)$$

The study of the mechanism of decomposition between AN and calcium carbonate was performed by DFT calculations (Menicacci et al., 2018). Good agreement was obtained between calculations and experimental results. In fact, applying the methodology explained before, the products obtained experimentally were identified (eq.3). Our DFT calculation indicate that the reaction of calcium carbonate happens after the decomposition of ammonium nitrate in NH_3 and HNO_3. As seen from the figure 2, calcium carbonate can react with ammonia, forming the complex [NH_3---$CaCO_3$], or with nitric acid, to form the [NO_3---$CaCO_3H$] complex. In both cases, we have two favorable and spontaneous reactions. The one with HNO_3 is more favorable in comparison with the one with NH_3. At the end of the complete pathway of reaction, an inert stable calcium complex [$(NO_3)_2$---$CaCO_3H_2$] is formed (see Figure 3(a)). It easily decomposes giving the products identified at experimental level. This is a confirmation that this methodology well describes the behavior of ammonium nitrate.

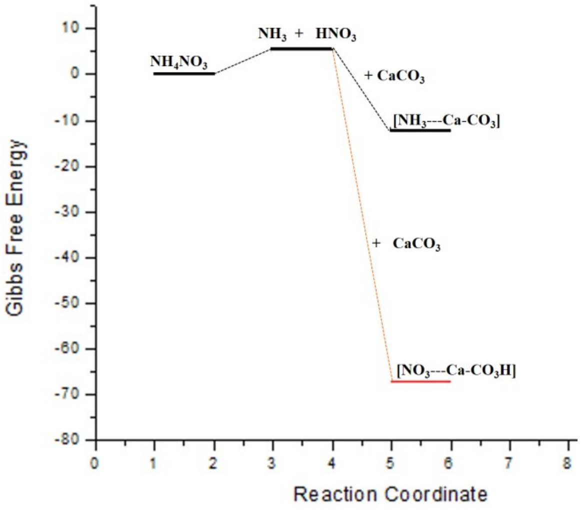


Figure 2. Gibbs free energy for the system AN + CaCO3, taking in consideration the first two step of reaction.

3.2.2 AN + CaSO4

Calcium sulfate, despite the structural similarities with $CaCO_3$, is AN-compatible but it used as an inert material rather than an inhibitor. As less experimental data are available in this case, other experimental studies were performed at CERL, in order to have more information especially on the reaction products that are formed once AN has decomposed in the presence of $CaSO_4$. However, the decomposition temperature of AN+$CaSO_4$ is not influenced by the concentration of calcium sulfate. Adding more quantity of $CaSO_4$ does not consistently affect the shift of Tmax (Oxley et al., 2002).

The study of AN + $CaSO_4$ system (Menicacci et al., 2018) was conducted by similarity with the AN + $CaCO_3$ system. As seen in the previous system, ammonium nitrate decomposes into ammonia and nitric acid, which reacts with $CaSO_4$ by two different reaction pathways. The privileged reaction channel proceeds through the reaction with HNO_3, forming cationic final complexes like [NO_3---$CaSO_4H_2$---NO_3] (Figure 3(b)). The analysis in progress suggests that the nature of the products formed during the decomposition may explain why $CaSO_4$ exhibit an inert behavior rather than an inhibitor one (like $CaCO_3$).

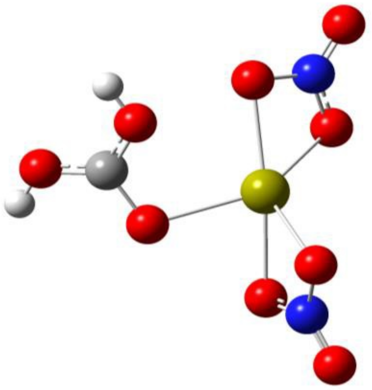


Figure 3(a). Image of the stable calcium complex complex [$(NO_3)_2$---$CaCO_3H_2$].

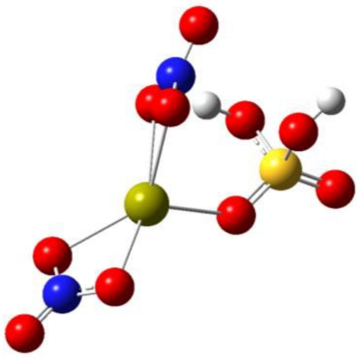


Figure 3(b). Image of the stable calcium [NO_3---$CaSO_4H_2$---NO_3].

3.2.3 AN + $(NH_4)_2SO_4$

The study of another system, AN + $(NH_4)_2SO_4$ implied in the accident of Oppau (Germany 1921), is underway. The behavior of ammonium nitrate in the presence of ammonium sulfate present a real challenge since the destabilizing capacity of $(NH_4)_2SO_4$ appeared to depend on its concentration (Kristensen 2016). The preliminary DFT results show that the cause of the incompatibility may be due to the acidity of the NH_4^+ cation. The theoretical studies in progress aim to clarify this ambiguity.

4. Conclusion and Perspectives

Computational chemistry approach allowed to identify the reactivity of carbonate and calcium sulfate with AN by describing both the thermodynamic profile and the reaction path. It seems to be possible to predict if a substance acts as a promoter, inhibitor or an inert on AN, with the total agreement with experimental studies. Therefore, considering the impossibility of testing an infinite number of substances and determine for each one the mechanism of action with AN, a simplified approach is also looked for. In fact, it could be possible, thanks to the versatility of DFT methodology, to associate a theoretical descriptor to the type of reaction that a contaminant makes with AN. The aim is to demonstrate that promoters, inhibitors and inerts have a peculiar way to react with AN. This means that potentially, it could be found some peculiar descriptors able to predict the behavior of a contaminant. The objective of our future work will be to build a simplified tool based on the identification of physicochemical parameters specific to promoters, inhibitors and inert substances that can guide the identification of the type of interaction that occurs between ammonium nitrate and a substance with which it interacts.

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