



HAL
open science

Modeling chemical incompatibility: the ammonium nitrate and sodium salt of dichloroisocyanuric acid as a case study

Stefania Cagnina, Patricia Rotureau, Guillaume Fayet, Carlo Adamo

► **To cite this version:**

Stefania Cagnina, Patricia Rotureau, Guillaume Fayet, Carlo Adamo. Modeling chemical incompatibility: the ammonium nitrate and sodium salt of dichloroisocyanuric acid as a case study. *Industrial and engineering chemistry research*, 2014, 53 (36), pp.13920-13927. 10.1021/ie502154b. ineris-01863924

HAL Id: ineris-01863924

<https://hal-ineris.archives-ouvertes.fr/ineris-01863924>

Submitted on 29 Aug 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Modeling chemical incompatibility : the ammonium nitrate and sodium salt of dichloroisocyanuric acid as a case study

Stefania Cagnina^{a,b}, Patricia Rotureau^b, Guillaume Fayet^b and Carlo Adamo^{a,c,*}

Institut de Recherche Chimie Paris CNRS Chimie Paris-Tech, 11 rue P. et M. Curie, F-75005 Paris, France ; Institut National de l'Environnement Industriel et des Risques (INERIS), Parc Technologique Alata, BP2, 60550 Verneuil-en-Halatte, France ; Institut Universitaire de France, 103 Boulevard Saint Michel, F-75005 Paris, France

Abstract

The dramatic accident involving ammonium nitrate (AN) that took place at Toulouse in September 2001 has once again focused attention on the hazards pertaining to chemical incompatibility in industrial environment. To complete the experimental results, a detailed theoretical study was performed in order to better understand the involved mechanisms, considering the reaction between ammonium nitrate and the sodium salt of dichloroisocyanuric acid (SDIC). Starting from theoretical results obtained for the pure reactants, the gas-phase decomposition mechanism of the mixture was investigated and fully characterized by means of Density Functional Theory (DFT) calculations. Beyond the complete characterization, in terms of intermediate structures and energies, of the decomposition pathways, our results evidenced as anticipated the role of water in catalyzing the decomposition reaction, through a significant decrease of the activation energy of the rate determining step. These results, in qualitative agreement with the calorimetric experiments, pointed out the instability of the AN-SDIC wet mixture and the underpinning incompatibility mechanism between these two chemicals.

a) Chimie ParisTech; b) INERIS; c) IUF

*corresponding author: carlo.adamo@chimie-paristech.fr

1. Introduction

Considering the serious consequences^{1,2}, chemical incompatibility between substances has attracted a large number of studies and has led to experiments primarily designed to improve the safety of the operators in chemical industries and laboratories.³⁻⁶ Because of the complexity of the treated subject and despite the interest aroused, a chemical incompatibility has been only defined in terms of caused effects and, until now, only experimental and empirical descriptions of chemical incompatibilities exist.⁷⁻¹⁰ Incompatibility occurs when chemicals, that are not inherently hazardous by themselves, become especially unsafe upon mixing with other substances.⁹ The term *incompatibility* is used to describe a wide range of chemical reactions that lead to self-ignition, generation of heat or toxic gases, decomposition, polymerization, formation of new and possibly more hazardous compounds. Incompatibility can lead to fire, explosion and detonation or any combination of these actions resulting from contact between two chemicals or between a chemical with air and moisture or with its container.⁷ Contamination of pure substances, even by small quantities (trace impurities)² is another potential source of chemical incompatibility.¹¹

From a practical point of view, chemical's compatibility for storage and transport can be determined by using Material Safety Data Sheets (MSDSs),¹² chemical compatibility charts¹³⁻¹⁷ and software such as CAMEO Chemicals (Computer-Aided Management of Emergency Operations)¹⁸ or WISER (Wireless Information System for Emergency Responders)¹⁹. MSDSs are documents collecting information and procedures for handling and working with chemicals such as physical and chemical properties, potential hazard information, emergency procedures and manufacturer contact information. Chemical compatibility charts indicate, sometimes by means of pictograms of hazards,²⁰ the risk that can be produced by mixing two chemicals, defined starting from chemical families, reactive groups (e.g. acids or aldehydes)²¹ or hazardous classes (e.g. flammable or oxidizer) detailed in transport of dangerous goods^{22,23} or Classification-Labeling-Packaging (CLP)²⁴ chemical's regulations. They sometimes indicate undesired consequences (eg. fire or flammable substances or gas generation).²⁵

Unlike to previous charts, software programs contain libraries of technical data with information and recommendations pertaining to specific hazardous chemicals (e.g. hydroxide peroxide or sulfuric acid) and they may be used for the prediction of reactivity.²⁶ In the last years, several enhancements have been incorporated to help with the generation and presentation of chemical compatibility charts but, even if they can potentially become standards for the chemical industry,²⁷ none of these methods is exhaustive. 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, in terms of thermodynamic data. This level of understanding of the phenomenon is important for a wider and global overview on chemical incompatibilities.

Some attempts using molecular modeling were made to obtain thermochemical data for reactive or hazardous materials^{28,29,30} or to predict thermodynamic data underpinning undesired reactions.³¹

Indeed, theoretical approaches represent a viable complement to reduce the number of experiments³² and to identify the reaction pathways, especially when complex reaction mechanisms giving unstable and short-living intermediates are concerned.³³

In this work, we aim to extend this molecular approach to the study of chemical incompatibilities, until now analyzed only by experimental techniques³⁴⁻³⁷, in order to establish a clear link between microscopic (molecular) description and macroscopic effects. In particular, we will focus our attention on the determination of hazard properties of a mixture of ammonium nitrate (AN) and sodium salt of dichloroisocyanuric acid (SDIC), an incompatibility suspected to be, according to preliminary investigations, one of the likely root causes of the explosion that occurred in the Grande Paroisse (AZF) fertilizer plant in Toulouse³⁸. This accident, promoted some experimental work to study incompatibility issues between these chemicals³⁹⁻⁴¹ but to our knowledge, no certainty has been evidenced about the actual sequence of events in the case of Toulouse.⁴² However the most recent accident that occurred on the 17th of April 2013, in a fertilizer storage and distribution in West, Texas, has still reinforced the perception of the importance of potential contaminants, among which inorganic chlorides, in AN based disasters, as shown in the Chemical advisory jointly released by EPA, OSHA and ATF US agencies as the aftermath of this new disaster.⁴³

Pure AN is considered as a relatively safe substance, due to its high stability in standard temperature and pressure ranges.⁴⁴ However, during the manufacturing process, storage, transport and use, AN may be contaminated by impurities and auto-ignition and explosion may take place, caused by their catalytic effects on the decomposition of AN.^{8,45-47} Chlorinated compounds, such as SDIC, are well known as hazardous contaminants of AN⁴⁸⁻⁵⁰. Several experimental studies were carried out on the AN/SDIC mixture. In particular, calorimetric analysis^{39,40} revealed that pure AN⁴⁰ and pure SDIC³⁹ do not show any exothermic activity below 200°C 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°C³⁹. This clearly indicates that the mixture is less thermally

stable than its pure components. Among decomposition products of the mixture, several species have been detected including N_2 , NO, HCl, NO_2 , Cl_2 , H_2O , CO_2 , N_2O .³⁹ The NCl_3 , a very reactive substance, was also characterized by UV/VIS spectrometry.⁴¹ A reaction mechanism between these two chemicals⁴⁹ has been proposed starting with the hydrolysis of SDIC that leads to the formation of hypochlorous acid, HOCl. The hypochlorous acid, a strong oxidant, is then supposed to react with ammonium nitrate to produce monochloroamine, dichloroamine and trichloroamine. Moreover a second reaction, concerning the decomposition of the isocyanuric-type cycle, can simultaneously occur also leading to the formation of monochloroamine, dichloroamine and trichloroamine (see Scheme 1, SI).

In this complex experimental framework, we want to confirm and/or identify, by theoretical approach based on Density Functional Theory (DFT), chemical reactions between the sodium salt of dichloroisocyanuric acid and ammonium nitrate taking into account previous experimental indications, dealing with identification of products and hypothesis of mechanisms. In a previous study,⁵¹ DFT calculations allowed to identify the complex mechanism of the gas-phase decomposition of isolated AN. In this work, a complete DFT study was further performed to fully characterize the mechanism of decomposition of pure SDIC and then that of the SDIC-AN adduct. In addition, the effect of water was considered, as its presence was identified as playing a major role in the underlined accidents.

2. Computational details

All the calculations were performed using the Gaussian 09 software package.⁵² Stationary point's optimizations were performed using the M06-2X functional⁵³ and 6-311+G(2d,2p) basis set^{54,55}. This level of theory has been proven to provide the most accurate energetics, among a large series of functionals and basis sets, for the decomposition of pure ammonium nitrate.⁵¹ 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.⁵⁶ 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. Total energies, enthalpies and Gibbs free energies were computed for all the

identified intermediates and products at 25°C and 1 atmosphere, but only Gibbs free energies will be discussed in details.

3. Results and Discussion

It is expected that actual reactions conditions play a major role in chemical incompatibilities, making a clear identifications of the reaction mechanism at experimental level cumbersome if not impossible. Indeed, many phenomena could happen during the explosive reactive processes, including catalysis (eventually involving external components such as reactors walls or surfaces), solvent and phase effects.⁵⁷ While some of them (as solvent effects, see *infra*) could be easily considered in modeling (albeit in an approximate way), other are more difficult to treat. In any case, as clearly evidenced in many experimental and theoretical works,⁵⁸⁻⁶⁰ valuable insights are derived by the analysis of the reaction in controllable conditions, such as in the gas phase or solution, and they are a pre-requirement to more complex analysis and models.^{60,61}

3.1 *Reminder of ammonium nitrate decomposition*

The decomposition mechanism of the pure ammonium nitrate in gas phase was studied in detail in our previous study⁵¹ and five main reaction channels, giving the experimentally characterized compounds (N_2 , H_2O , O_2 , $\cdot OH$, HNO , $\cdot NO_3$) were identified. A brief summary is given below (see Scheme S2 in SI for more details). The first step is the dissociation into ammonia and nitric acid, which requires a low energy ($\Delta G = 4.9 \text{ kcal mol}^{-1}$). The nitric acid then undergoes a homolytic breaking at high energy ($\Delta G = 40.2 \text{ kcal mol}^{-1}$), 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 that can, in turn, react with the hydroxyl radical to form N_2 , O_2 and $OH\cdot$. The decomposition of H_2NONO leads to the formation of $NO\cdot$ that can, in turn, react with the amidogen radical to produce $N_2 + H_2O$ and $N_2H + OH\cdot$ radicals.

The $OH\cdot$ radical can then react with three different molecules to form $H_2O + NO_3^-$, HNO and O_2 . In conclusion, it was found that the reaction is globally exothermic but its initiation depends on the overcoming of an energy barrier of about 40 kcal mol^{-1} 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.

3.2 Decomposition of pure sodium salt of dichloroisocyanuric acid (SDIC)

During the investigation following the disaster at the AZF plant in Toulouse, the sodium salt of dichloroisocyanuric acid (Figure 1), present on the site, was suspected to have an influence on the accident.⁴⁹ This salt is produced as a white crystalline powder or in granular form and is widely used for the sterilization of swimming pools and drinking water or for fighting against infectious diseases. It melts at about 200°C but up to this temperature, the salt is stable at standard conditions and generally used safely. Its decomposition temperature is 240°C.⁴¹ As an oxidizing agent, in certain conditions, the salt may lead to fire when in contact with combustible materials. It can cause a very vigorous reaction in contact with ammonium compounds or hydrated salts.⁸ Beside, using the *ARIA Database* 16 accidents involving SDIC were reported in France and one in the United Kingdom since 1995 (Table S1 in SI).⁶² Regarding the gas phase decomposition of pure sodium salt of dichloroisocyanuric acid no much material exists, at the best of our knowledge, in the literature. However, interesting publications⁶³⁻⁶⁵ concerning the decomposition mechanism of the cyanuric acid, a parent compound, can be useful to hypothesize its decomposition. Cyanuric acid undergoes a sublimation near 360°C and the evolved isocyanuric vapours thermally decompose in the gas phase with the formation of isocyanic acid, HNCO.⁶⁶ This latter may, in turn, undergo a new consecutive thermal reaction producing gases such as CO₂, CO, N₂, H₂ and HCN. This last reaction has been extensively studied in the literature at both experimental^{67,68} and theoretical^{69,70} levels. Starting from these results, we have characterized two decomposition reactions for SDIC, both giving two molecules of chlorine isocyanate (Cl-N=C=O) and one molecule of sodium isocyanate (Na-N=C=O). However the first path corresponds to a two steps mechanism while the second is composed by a single step. The first reaction, shown in Scheme 1, involves an initial breaking of two nitrogen - carbon bonds ($\Delta G^\ddagger = 44.1 \text{ kcal mol}^{-1}$) to form a molecule of chlorine isocyanate. The rest of the initial cycle decomposes with a low energetic barrier ($\Delta G^\ddagger = 12.6 \text{ kcal mol}^{-1}$) to form another chlorine isocyanate and a sodium isocyanate molecule. The second path involves a concerted breaking of N1-C2, N3-C4 and N5-C6 bonds of SDIC (see Figure 1) but its energy is too high to be competitive ($\Delta G = 48.0 \text{ kcal mol}^{-1}$) with the first proposed reaction.

3.3 Reaction mechanism of AN and SDIC

Starting from the proposition of Paul et al.,⁴⁹ 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 coming from the decomposition of ammonium nitrate (Scheme **S1** in SI). 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. Therefore this mechanism is not energetically favored 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. As shown in the previous study, AN is easily decomposed in NH_3 and HNO_3 ($\Delta G^\ddagger = 4.9$ kcal mol⁻¹).⁵¹ Thus, the reactions of these two species, NH_3 and HNO_3 , with SDIC have to be considered.

Reaction of sodium salt of dichloroisocyanuric acid (SDIC) with ammonium nitrate. The reaction between ammonia and SDIC presents a free energy barrier (ΔG^\ddagger) of 58.0 kcal mol⁻¹ and leads to the formation of exothermic products ($\Delta G = -6.8$ kcal mol⁻¹). The reaction between nitric acid and SDIC presents a ΔG^\ddagger of 45.9 kcal mol⁻¹ and gives endothermic products ($\Delta G = 36.0$ kcal mol⁻¹, see Scheme **S3** and Table **S2** in SI for details). Only the reactions paths starting from the first reaction (SDIC and NH_3) will be retained in the following, since it is strongly irreversible (large energy difference between products and transition state) and exothermic. The obtained results (ΔE , ΔH and ΔG) are collected in Table 1.

First, the ammonia reacts with the SDIC, passing through a transition state, $\text{TS}_{\text{SDIC}+\text{NH}_3}$, of 58.0 kcal mol⁻¹, to form the sodium salt of monochloroisocyanuric acid (SMIC, see Figure 1), and the monochloroamine (NH_2Cl). From this step, two reactions take place: the first involves the decomposition of SMIC and the second concerns the decomposition of the NH_2Cl .

Decomposition of sodium salt of monochloroisocyanuric acid (SMIC).

The SMIC could react with both NH_3 and HNO_3 (Table **S3** in SI). The first reaction (SMIC and NH_3 , see Figure 2) occurs with a ΔG^\ddagger of 32.1 kcal mol⁻¹ and leads to the formation of NH_2Cl and **I** that are two exothermic products ($\Delta G = -35.6$ kcal mol⁻¹). The reaction between nitric acid and SMIC presents, instead, a ΔG^\ddagger of 14.4 kcal mol⁻¹ and it gives endothermic products ($\Delta G = 4.9$ kcal mol⁻¹). As in the previous case, only the pathway opened by the reaction of SMIC with NH_3 (Figure 2) was explored, due to its irreversibility and favorable exothermicity.

The reaction between these two chemicals produces NH_2Cl and sodium isocyanurate (**I** in Figure 2). The intermediate **I** can react with nitric acid (but not with NH_3) to form NaOH and a new intermediate (**II**) passing through a transition state, TS_2 , of $42.3 \text{ kcal mol}^{-1}$. Then a homolytic rupture of the N-N bond ($\Delta G = 35.7 \text{ kcal mol}^{-1}$) gives the formation of $\cdot\text{NO}_2$ radical and intermediate **III**, which decomposes to **IV**, through a transition state, TS_3 , of 27.4 kcal/mol . The reaction proceeds with a ΔG^\ddagger of 30.7 kcal/mol (TS_4) and Intermediate **V** and the isocyanic acid (HNCO) are formed. HNCO in turn decomposes to form CO and NH as already suggested by previous calculations.⁶⁸ Finally, another molecule of isocyanic acid (HNCO) and the $\text{NCO}\cdot$ radical are easily formed $\Delta G^\ddagger = 19.6 \text{ kcal/mol}$ (TS_5) from **V**. In summary this path is endothermic of 49.9 kcal/mol and the rate determining step (TS_2) corresponds to the breaking of the N-O bond of nitric acid followed by the formation of the N-N bond of **II** and is characterized by a barrier of 42.3 kcal/mol .

Decomposition of monochloroamine. More complex is the reaction channel corresponding to the decomposition of monochloroamine (NH_2Cl). Starting from NH_2Cl (issued from the reaction between SDIC and NH_3), the decomposition can be separated into two different paths, labelled [A] and [B]. These paths are sketched in Scheme 2 and their energies are shown in Figure 3.

In path [A], the monochloroamine reacts with the hydroxyl radical ($\text{OH}\cdot$), present in the reactive environment, to form hydroxylamine (NH_2OH) and chlorine radical, passing through the transition state TS1_A at $14.1 \text{ kcal mol}^{-1}$. Hydroxylamine is a hazardous molecule that may explode upon heating as evidenced by the accident happened in February 1999 at the Concept Sciences Inc. (CSI) hydroxylamine manufacturing unit in Pennsylvania followed, the next year, by an explosion at the Nissin Chemical HA plant in Japan.⁷¹ The chlorine radical reacts with amidogen radical ($\text{NH}_2\cdot$), hydroxyl radical and another chlorine radical, 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 $-49.4 \text{ kcal mol}^{-1}$. It is interesting to note that all 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 reminder of ammonium nitrate decomposition) to be overcome. It should be also remarked that the monochloramine is formed during the mechanism, so that the decomposition of NH_2Cl becomes autocatalytic. Hydroxylamine, instead, undergoes isomerization into ammonia oxide (NH_3O) via a 1,2-hydrogen shift from the O to the N atom

(TS2_A of 50.5 kcal mol⁻¹). Subsequently, a hydrogen elimination gives molecular hydrogen and the nitroxyl radical (HNO•). The transition state TS3_A to overcome is also energetically high (57.8 kcal mol⁻¹). These high energy barriers come from the simultaneous breaking of two nitrogen – oxygen σ bond and the formation of a hydrogen – hydrogen σ bond and a nitrogen – oxygen π bond, as suggested by Wang.⁷²

Following pathway [B], the monochloroamine reacts with the nitric oxide radical, previously produced by the homolytic decomposition of nitric acid, to form the nitramide (NH₂NO₂) and chlorine radical, passing by the transition state, TS1_B, of 31.8 kcal mol⁻¹. The energy needed to generate the crucial NO₂• radical is released, as above mentioned, along the path [A]. The NH₂NO₂ was already characterized as one of the intermediate of ammonium nitrate decomposition.⁵¹ As it was studied in the related paper, decomposition products of the nitramide are N₂O, N₂ and O₂. Chlorine radical gives rise to the same reactions (with amidogen radical, hydroxyl radical and chlorine radical) described above.

Both paths [A] and [B] lead to the formation of hypochlorous acid. Then, a reaction between the hypochlorous acid and the monochloroamine was characterized, as shown in Scheme 2 (path [C]). This reaction forms a stable molecule of dichloroamine (NHCl₂) and water, passing through a transition state TS1_C of 68.7 kcal mol⁻¹. The dichloroamine molecule is able, in turn, to react with the hypochlorous acid molecule and to form trichloroamine (NCl₃) and water, with a transition state TS2_C of 61.4 kcal mol⁻¹. Even if minor variations in relative energies are found, mainly due to the different DFT methods chosen, our results well match those obtained for the ammonia – hypochlorous acid reaction.⁷³

These theoretical results allow the characterization of the direct decomposition mechanism of AN with SDIC, and of all the experimentally observed products³⁹ (N₂, NO, HCl, NO₂, Cl₂, H₂O, N₂O), via the paths [A], [B] and [C]. The rate determining step of the direct reaction between AN and SDIC is still represented by the reaction of NH₃ with SDIC, leading to NH₂Cl and SMIC (58.0 kcal/mol)

3.4 Role of water

At this point of the study, direct decomposition is energetically favored with respect to the SDIC hydrolysis (58.0 vs. 78.4 kcal/mol, respectively), the reaction commonly supposed to be at the origin of the SDIC and AN incompatibility.⁴⁹ It should be recall that the rate determining step in the AN decomposition requires 40.2 kcal/mol and it is therefore still favored with respect to both reactions. Other effects should be, therefore, considered.

In particular, ammonium nitrate is a highly hygroscopic substance that can easily collect water molecules from the environment⁴⁴. The presence of water or moisture in the AZF plant in Toulouse has not been excluded⁴⁹ and experimental papers report data obtained in humid air.^{39,40} Indeed, Differential Scanning Calorimetry (DSC) results showed an exothermic activity below 100°C for the AN-SDIC prepared in ambient with relative humidity of 70%³⁹ in comparison to a minimal exothermic activity at 110-125°C for the dry mixture in 50:50 proportions that indicated that the presence of moisture decreases the thermal stability of the mixture significantly. Therefore, the effect of the presence of water was investigated, following different examples of water-catalyzed reactions^{74,75}, for the rate determining steps of the decomposition reaction of pure ammonium nitrate and of the AN-SDIC decomposition (reaction involving hydrogen and chlorine transfer).

Concerning the decomposition of pure ammonium nitrate, a water molecule was added to form a hydrogen bond with the nitric acid (see Figure S1 in SI). The net effect of this water is to increase the energy required for the homolysis of the NO bond, due to the breaking of the hydrogen bond (from 40.2 to 46.2 kcal/mol). So, a water molecule does not promote the decomposition of pure AN reaction.

Considering the AN-SDIC adduct, the inclusion of one water molecule in the rate determining step reduces the reaction barrier by 25.9 kcal/mol (from 58.0 to 32.1 kcal/mol, see Table S4 in SI), since it catalyzed the transfer of the hydrogen atom between SDIC and NH₃ in the transition state (see Figure 4). In the same step, the chlorine atom moves from SDIC to the ammonia molecule to produce, at the end, the monochloramine and the sodium salt of monochlorisocyanuric acid. 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⁻¹ (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, in line with the experimental works.^{39,40}

4. Conclusion

A detailed DFT study on the reaction between AN and SDIC was carried out, aimed to elucidate the microscopic mechanism of incompatibility between these two chemicals, suspected to be potentially involved in the explosion of a fertilizer plant in Toulouse³⁸.

After a preliminary analysis of the decomposition of the two bare reactants, a detailed mechanism for the AN+SDIC reaction was characterized in the gas phase, leading to the experimentally characterized compounds. This mechanism, based on a direct reaction between NH_3 and SDIC, is energetically favored with respect to that commonly mentioned in literature, which takes place through a hydrolysis reaction of SDIC. Furthermore, our results show the pivotal role of water (even in trace) in the chemical incompatibility between the two substances, as also indicated by Differential Scanning Calorimetry (DSC) experiments. More generally, this study shows how modern computational approaches provide insights on the understanding of reaction mechanisms at the basis of chemical incompatibilities that are of great importance for the safety management of chemicals in industrial contexts.

Acknowledgements

The authors are grateful to Shanti Singh, Richard Turcotte (CERL, Canada), Guy Marlair (INERIS, France) and to Cyril Peltier (Région Ile-de-France, France) for useful discussion.

References

- (1) Grewer, T. H.; Rogers, R. L. Exothermic secondary reactions. *Thermochim. Acta* **1993**, *225*, 289.
- (2) Gustin, J. L. Influence of trace impurities on chemical reaction hazards. *J. Loss Prev. Process Ind.* **2002**, *15*, 37.
- (3) Andreozzi, R.; Marotta, R.; Sanchirico, R. Thermal decomposition of acetic anhydride – nitric acid mixtures. *J. Hazard. Mater.* **2002**, *A90*, 111.
- (4) Chi, J.-H.; Wu, S.-H.; Charpentier, J.-C.; I, Y.-P.; Shu, C.-M. Thermal hazard accident investigation of hydrogen peroxide mixing with propanone employing calorimetric approaches. *J. Loss Prev. Process Ind.* **2012**, *25*, 142.
- (5) Leggett, D. J. Identifying Hazards in the Chemical Research. *Process Saf. Prog.* **2012**, *31*, 393.
- (6) Leggett, D. J. Process safety in the future? A view from the chemistry. *Process Saf. Prog.* **2004**, *23*, 163.
- (7) Pohanish, R. P.; Greene, S.A. *Wiley Guide to Chemical Incompatibilities*, Hardcover, 2009.
- (8) Bretherick, L. *Handbook of reactive chemical hazards*, Butterworths, London, 2007.
- (9) Yoshida, T. *Safety of reactive chemicals*, Elsevier, Amsterdam, 1987.
- (10) Sax, N. I. *Handbook of dangerous materials*, Reinhold Publishing Corporation, 1951.
- (11) Eto, I.; Akiyoshi, M.; Miyake, A.; Ogawa, T.; Matsunaga, T. Hazard evaluation of runaway reaction of hydrogen peroxide – Influence of contamination of various ions. *J. Loss Prev. Process Ind.* **2009**, *22*, 15.
- (12) Leggett, D. J. Management of chemical plants using chemical compatibility information. *Process Saf. Prog.* **1997**, *16*, 8.
- (13) Winder, C.; Zarei, A. Incompatibilities of chemicals. *J. Hazard. Mater.* **2000**, *A79*, 19.
- (14) Leggett, D. J. Rapid Identification of Reactivity Hazards in a Multiuse Facility. *Process Saf. Prog.* **2006**, *25*, 108.
- (15) EPA 600/2-80-76, A Method for Determining the Compatibility of chemical mixtures, April 1980.
- (16) Compatibility of Cargoes, published in 46 CFR Ch. 1 (10-1-93 Edition) - Part 150 with changes that appeared in the Federal Register dated April 11, 1994 as a Final Rule by Coast Guard (CGD 92-100) for Bulk Hazardous Materials.
- (17) Health and Safety Executive (2009) *Chemical warehousing, the storage of packaged dangerous substances*, 23-24.
- (18) <http://cameochemicals.noaa.gov> (accessed September 24, 2013)
- (19) <http://wiser.nlm.nih.gov> (accessed September 24, 2013)
- (20) http://www.risque-chimique.fr/incompatibilites_stockage.html (accessed October 4, 2013)
- (21) http://rehs.rutgers.edu/lswaste_epachem.html (accessed October 3, 2013)

- (22) UN CETDG, United Nations Recommendations on the Transport of Dangerous Goods, 10th edn., United Nations Committee of Experts on the Transport of Dangerous Goods, New York, 1997.
- (23) FORS, Australian Code for the Transport of Dangerous Goods by Road and Rail A.D.G. Code., 6th ed., Australian Transport Advisory Council, Federal Office of Road Safety, AGPS, Canberra, Australia, 1998.
- (24) EC Regulation No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labeling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.
- (25) Gay, D. M., Leggett, D. J. Enhancing Thermal Hazard Analysis Awareness With Compatibility Charts. *Journal of Testing and Evaluation*, **1993**, *21*, 477.
- (26) Johnson, L. E.; Farr, J. K. CRW 2.0: A representative-compound approach to functionality-based prediction of reactive chemical hazards. *Process Saf. Prog.* **2008**, *27*, 212.
- (27) Gorman, D.; Farr, J.; Bellair, R.; Freeman, W.; Frurip, D.; Hielscher, A.; Johnstone, H.; Linke, M.; Murphy, P.; Sheng, M.; van Gelder, K.; Viveros, D. Enhanced NOAA Chemical Reactivity Worksheet for Determining Chemical Compatibility. *Process Saf. Prog.* **2013**, DOI: 10.1002/prs.11613.
- (28) Saraf, S. R.; Rogers, W. J.; Mannan, M. S. Using screening test data to recognize reactive chemical hazards. *J. Hazard. Mater.* **2003**, *104*, 255.
- (29) Saraf, S. R.; Rogers, W. J.; Ford, D. M.; Mannan, M. S.; Integrating molecular modeling and process safety research. *Fluid Phase Equilib.* **2004**, *222*, 205.
- (30) Tokmakov, I. V.; Alavi, S.; Thompson, D. L.; Urea and Urea Nitrate Decomposition Pathways: A Quantum Chemistry Study. *J. Phys. Chem. A*, **2006**, *110*, 2759.
- (31) Grewer, T.; Frurip, D. J.; Harrison, B. K. Prediction of thermal hazards of chemical reactions. *J. Loss Prev. Process Ind.* **1999**, *12*, 391.
- (32) Prana, V.; Fayet, G.; Rotureau, P.; Adamo, C. Development of validated QSPR models for impact sensitivity of nitroaliphatic compounds. *J. Hazard. Mater.* **2012**, *235*, 169.
- (33) Di Tommaso, S.; Rotureau, P.; Crescenzi, O.; Adamo, C. Oxidation mechanism of diethyl ether: a complex process for a simple molecule. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14636.
- (34) Joseph, G. Recent reactive incidents and fundamental concepts that can help prevent them. *J. Hazard. Mater.* **2003**, *104*, 65.
- (35) Chang, R.-H.; Shu, C.-M.; Duh, Y.-S.; Jehng, J.-M.; Calorimetric studies on the thermal hazard of methyl ethyl ketone peroxide with incompatible substances. *J. Hazard. Mater.* **2007**, *141*, 762.
- (36) Lu, K.-T.; Chen, T.-C.; Hu, K.-H. Investigation of the decomposition reaction and dust explosion characteristics of crystalline benzoyl peroxides. *J. Hazard. Mater.* **2009**, *161*, 246.

- (37) Dti, Y.; Lee, C.; Hsu, C.; Hwang, D.; Kao, C.; Chemical incompatibility of nitrocompounds. *J. Hazard. Mater.* **1997**, *53*, 183.
- (38) Dechy, N.; Bourdeaux, T.; Ayrault, N.; Kordek, M.-A.; Le Coze, J.-C. First lessons of the Toulouse ammonium nitrate disaster, 21st September 2001, AZF plant, France. *J. Hazard. Mater.* **2004**, *111*, 131.
- (39) Badeen, C. M.; Kwok, Q. S. M.; Vachon, M. C. R.; Turcotte, R.; Jones, D. E. G. Hazard characterization of mixtures of ammonium nitrate with the sodium salt of dichloroisocyanuric acid. *J. Therm. Anal. Cal.* **2005**, *81*, 225.
- (40) Li, X.-R.; Koseki, H. Study on reactivity of ammonium nitrate contaminated by sodium dichloroisocyanurate. *Sci.Tech. Energetic Materials.* **2005**, *66*, 431.
- (41) Guengant, Y.; Della Pietra, P.; Dervaux, M.; Franson, C.; Jacob, G.; Macé, H. *Proceedings of 28th Annual General Meeting of the Federation of European Explosives Manufacturers*, Copenhagen, Denmark, 2004, 218.
- (42) Hecquet, G. Le procès AZF : l'hypothèse chimique. *Actual. Chim.* **2012**, *366*, 3.
- (43) United States Environmental Protection Agency, Occupational Safety and Health Administration, Bureau of Alcohol, Tobacco, Firearms and Explosives, Chemical Advisory: Safe Storage, Handling and Management of Ammonium Nitrate, EPA 550-S-13-001, 08 2013.
- (44) Chaturvedi, S.; Dave, P. N.; Review on Thermal Decomposition of Ammonium Nitrate. *J. Energ. Mater.*, **2013**, *31*, 1.
- (45) Gunawan, R.; Freij, S.; Zhang, D.; Beach, F.; Littlefair, M. A mechanistic study into the reactions of ammonium nitrate with pyrite. *Chem. Eng. Sci.* **2006**, *61*, 5781.
- (46) Oxley, J. C.; Smith, J. L.; Rogers, E.; Yu, M. Ammonium nitrate : thermal stability and explosivity modifiers. *Thermochim. Acta* **2002**, *384*, 23.
- (47) Sinditskii, V. P.; Egorshv, V. Y.; Levshenkov, A. I.; Serushkin, V. V. Ammonium Nitrate : Combustion Mechanism and the Role of Additives. *Propellant, Explos. Pyrotech.* **2005**, *30*, 269.
- (48) Keenan, A. G.; Notz, K.; Franco, N. B. Synergistic Catalysis of Ammonium Nitrate Decomposition. *J. Am. Chem. Soc.* **1968**, *22*, 3168.
- (49) Paul, J.-M.; Hecquet, G.; Mieloszynsky J.-L. Les chloroisocyanuriques : étude de leur aptitude à générer des chloramines par eux-mêmes ou en présence d'espèces azotées. *L'actualité chimique*, **2004**, *274*, 10.
- (50) Rubtsov, Y. I.; Kazakov, A. I.; Nedelko, V.V.; Shastin, Al.V.; Larikova, T.S.; Sorokina, T.V.; Korsounskii, B.L. Thermolysis of ammonium nitrate/potential donor of active chlorine compositions. *J. Therm. Anal. Cal.* **2008**, *93*, 301.
- (51) Cagnina, S.; Rotureau, P.; Fayet, G.; Adamo, C. The ammonium nitrate and its mechanism of decomposition in the gas phase: a theoretical study and a DFT benchmark. *Phys. Chem. Chem. Phys.* **2013**, *15*, 10849.

- (52) Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr.J.A.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N.J.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, Ö.; Foresman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox, D.J.; *Gaussian 09*, rev A.08; Gaussian, Inc.: Wallingford, CT, **2009**.
- (53) Zhao, Y.; Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **2006**, *125*, 194101.
- (54) Krishnan, R.; Binkley, J.S.; Seeger, R.; Pople, J.A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **1980**, *72*, 650.
- (55) McLean, A.D.; Chandler, G.S. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, $Z=11-18$. *J. Chem. Phys.* **1980**, *72*, 5639.
- (56) Gonzalez, C.; Schlegel, H.B. An improved algorithm for reaction path following. *J. Chem. Phys.* **1989**, *90*, 2154.
- (57) Brill T.B., James K.J., Kinetics and mechanisms of thermal decomposition of nitroaromatic explosives, *Chem. Rev.*, **1993**, *3*, 2667.
- (58) Cramer C.J., Bumpus J.A., Lewis A., Stotts C., Characterization of high explosives and other energetic compounds by computational chemistry and molecular modeling, *J. Chem. Educ.*, **2007**, *84*, 329.
- (59) Zhang C., Wang X., Huang H., π -Stacked interactions in explosive crystals : buffers against external mechanical stimuli, *J. Am. Chem. Soc.*, **2008**, *130*, 8359.
- (60) Zhang L., van Duin A.C.T, Zybin S.V., Goddard III W.A., Thermal decomposition of hydrazines from reactive dynamics using the ReaxFF Reactive Force Field, *J. Phys. Chem. B*, **2009**, *113*, 10770.
- (61) Shan T.-R., van Duin A.C.T, Thompson A.P., Development of a ReaxFF Reactive Force Field for ammonium nitrate and application to shock compression and thermal decomposition, *J. Phys. Chem. A*, **2014**, *118*, 1469.
- (62) Information from the accidental data base ARIA, <http://www.aria.developpement-durable.gouv.fr/> (accessed May 25, 2013)
- (63) Seifer, G.B. Cyanuric acid and cyanurates. *Russ. J.Coord. Chem.* **2002**, *28*, 301.

- (64) Mercadier, J.; Pignon, M.; Calabuig, F.; Lédé, J.; Villermaux, J. Kinetics of isocyanuric acid pyrolysis. *J. Anal. Appl. Pyrolysis*. **1994**, *28*, 107.
- (65) Lédé, J.; Mercadier, J. Simulation of the thermal cracking of biomass derived vapours, by the model reaction of decomposition of isocyanuric acid. *J. Anal. Appl. Pyrolysis*, **2003**, *67*, 295.
- (66) Mercadier J. Ph.D. Thesis, INPL-LSGC Nancy, France, **1992**.
- (67) He, Y.; Liu, X.; Lin, M.C.; Melius, C.F. Thermal reaction of HNCO with NO₂ at moderate temperatures. *Int. J. Chem. Kinet.* **1993**, *25*, 845.
- (68) Spiglanin, T.A.; Chandler, D.W. Rotational state distributions of NH(a¹Δ) from HNCO photodissociation. *J. Chem. Phys.* **1987**, *87*, 1577.
- (69) Fang, W.H.; You, X.Z.; Yin, Z. Theoretical studies on photolysis and pyrolysis of isocyanic acid. *Chem. Phys. Lett.* **1995**, *238*, 236.
- (70) Zyrianov, M.; Droz-Georget, Th.; Sanov, A.; Reisler, H.; Competitive photodissociation channels in jetcooled HNCO: thermochemistry and nearthreshold predissociation. *J. Chem. Phys.* **1996**, *105*, 8111.
- (71) Long, L.A. The explosion at concept sciences: hazards of hydroxylamine. *Process Safety Process* **2004**, *23*, 114.
- (72) Wang, Q.; Wei, C.; Pérez, L.M.; Rogers, W.J.; Hall, M.B.; Mannan, M.S. Thermal decomposition pathways of hydroxylamine: theoretical investigation on the initial steps. *J. Phys. Chem. A* **2010**, *114*, 9262.
- (73) Rayson, M.S.; Altarawneh M.; Mackie, J.C.; Kennedy, E.M.; Dlugogorski, B.Z. Theoretical study of the ammonia-hypochlorous Acid reaction mechanism. *J. Phys. Chem. A* **2010**, *114*, 2579.
- (74) Adamo C.; Cossi M.; Barone V.; *J. Comput. Chem.* **1997**, *18*, 1993.
- (75) Di Tommaso S.; David H.; Gomar J.; Leroy F.; Adamo C.; *RSC Adv.* **2014**, *4*, 11029.

Table I. Relative electronic energies (ΔE , without zero point energy corrections), enthalpies (ΔH) and Gibb's energies (ΔG) of the reaction between ammonium nitrate and sodium salt of dichloroisocyanuric acid. All the values are in kcal/mol.

	ΔE	ΔH	ΔG
NH_4NO_3	0.0	0.0	0.0
$\text{NH}_3 + \text{HNO}_3$	15.3	14.0	4.9
TS_{SDIC+NH3}	60.8	60.8	62.9
$\text{NH}_2\text{Cl} + \text{SMIC}$	8.1	7.7	-1.9
<i>Decomposition of SMIC</i>			
TS₁	57.0	57.9	30.2
Intermediate I + NH_2Cl	1.6	2.2	-37.5
TS₂	31.6	31.3	4.8
Intermediate II + NaOH	21.6	22.3	-5.1
Intermediate III	72.9	70.0	30.6
TS₃	102.7	97.9	58.0
Intermediate IV	88.9	85.0	43.1
TS₄	122.4	116.5	73.8
Intermediate V	108.0	101.6	47.7
TS₅	129.6	121.4	67.3
$\text{HNCO} + \text{NCO}\cdot$	120.3	110.9	49.9
<i>Decomposition of NH_2Cl</i>			
<i>Path [A]</i>			
TS1_A	11.6	12.6	12.2
$\text{NH}_2\text{OH} + \text{Cl}\cdot$	1.8	4.6	-3.1
TS2_A	55.4	54.9	47.4
NH_3O	27.0	29.9	22.5
TS3_A	92.0	87.8	80.3
$\text{H}_2 + \text{HNO}$	49.9	44.2	28.3
<i>Path [B]</i>			
TS1_B	28.2	28.6	29.9
$\text{NH}_2\text{NO}_2 + \text{Cl}\cdot$	6.3	8.3	9.1
TS2_B	48.8	47.1	47.7
$\text{HN}=\text{NO}(\text{OH})$	15.7	17.6	18.4
TS3_B	56.8	54.3	54.5
$\text{N}_2\text{O} + \text{H}_2\text{O}$	-27.3	-26.8	-30.9
Cl_2	-54.4	-51.6	-52.5
NH_2Cl	-62.7	-56.5	-56.2
HOCl	-53.9	-49.2	-49.7
<i>Path [C]</i>			
TS1_C	7.0	9.1	19.0
$\text{NHCl}_2 + \text{H}_2\text{O}$	-72.3	-68.0	-68.0
TS2_C	-19.7	-16.9	-6.6
$\text{NCl}_3 + \text{H}_2\text{O}$	-88.2	-85.0	-84.1

Scheme and figure captions.

Scheme 1. Reaction path for the favored reaction of decomposition of sodium salt of dichloroisocyanuric acid (SDIC).

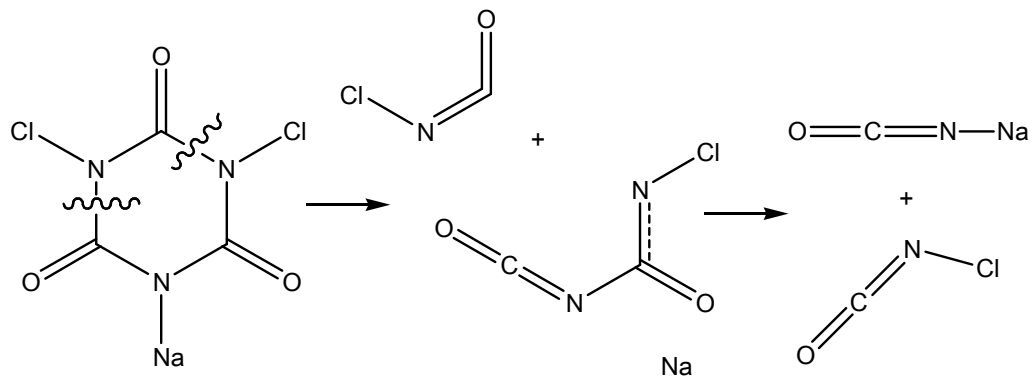
Scheme 2. Reaction path for the decomposition of monochloramine, resulting from the reaction between the ammonia and the dichloroisocyanuric acid.

Figure 1. Chemical representation of the sodium salt of dichloroisocyanuric acid (SDIC) and of the sodium salt of monochloroisocyanuric acid (SMIC) when $R = \text{Cl}$ or H .

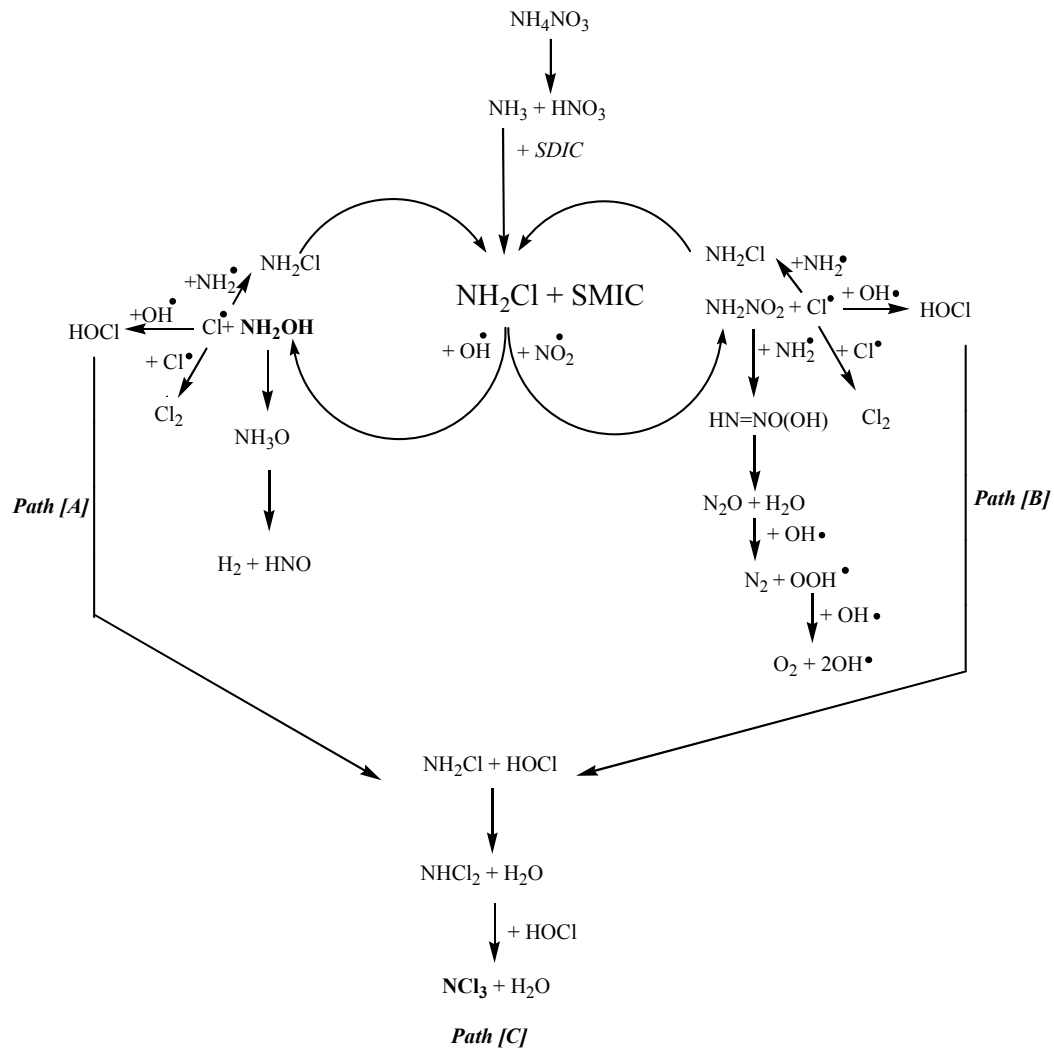
Figure 2. Gibbs free energy profiles for the decomposition of SMIC with the relative geometries of the intermediates involved.

Figure 3. Gibbs free energy profiles for the decomposition of NH_2Cl .

Figure 4. Comparison of Gibbs free energy profiles for the reaction between AN and SDIC in the gas phase and with a water molecule.



Scheme 1.



Scheme 2.

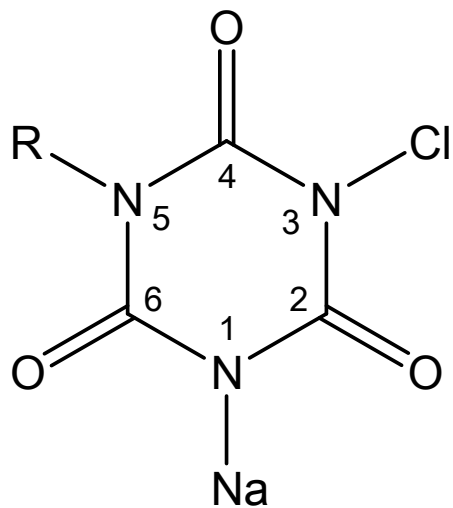


Figure 1.

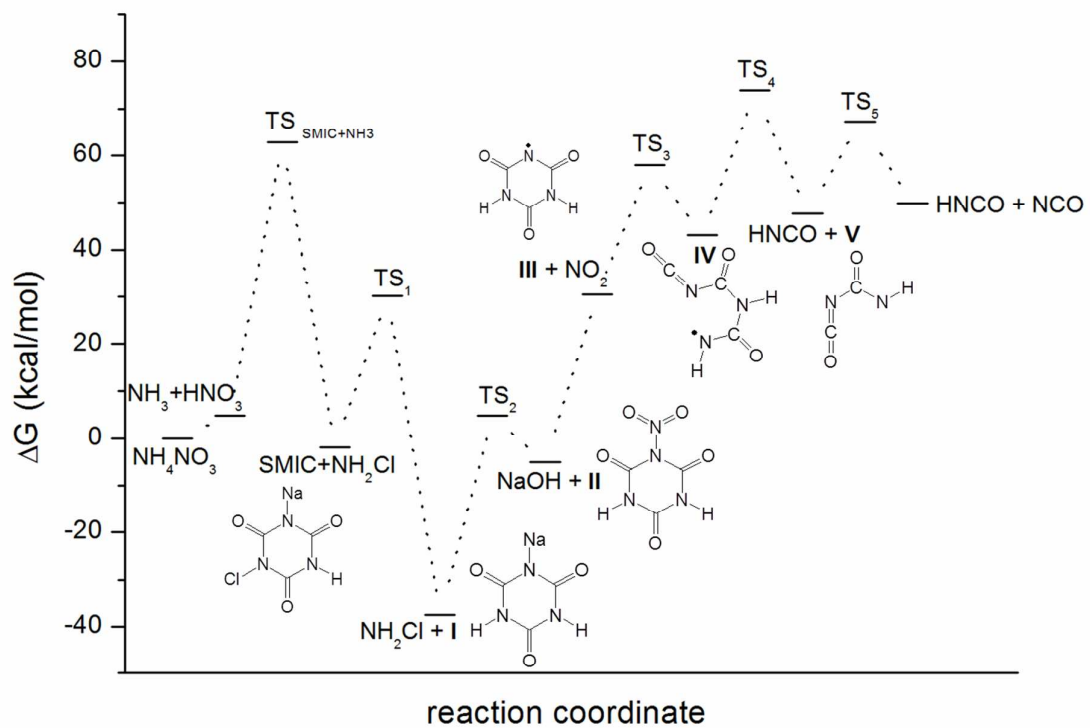


Figure 2.

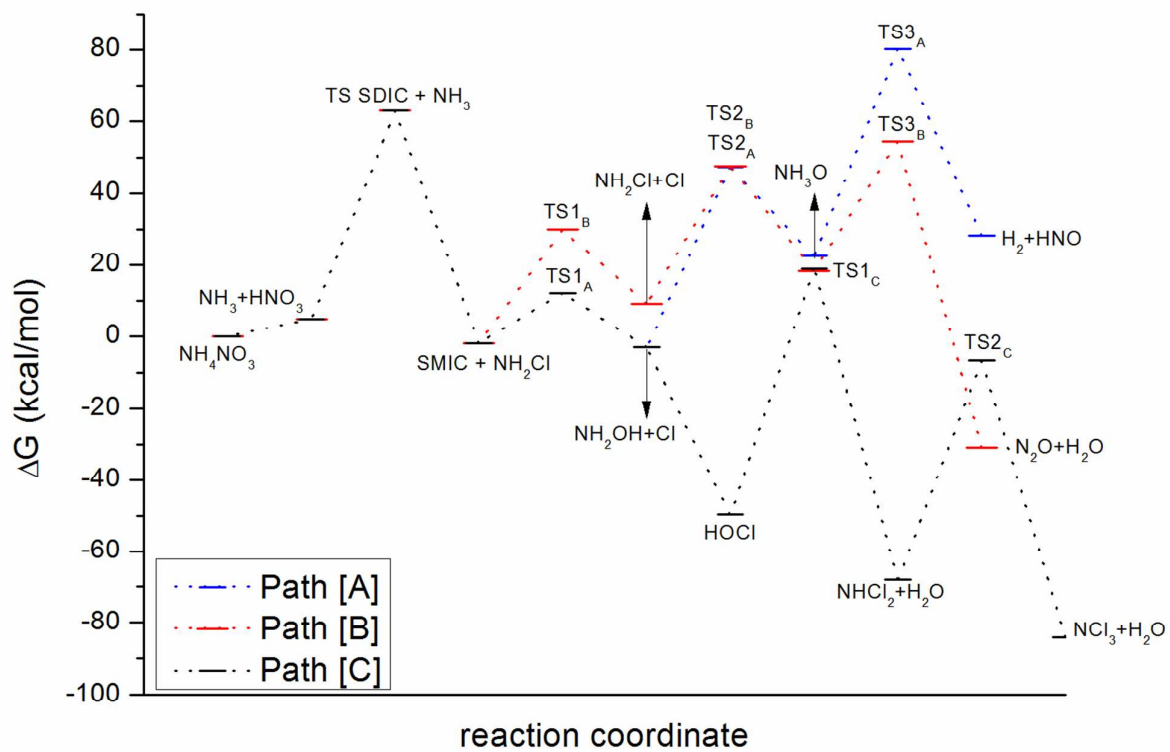


Figure 3.

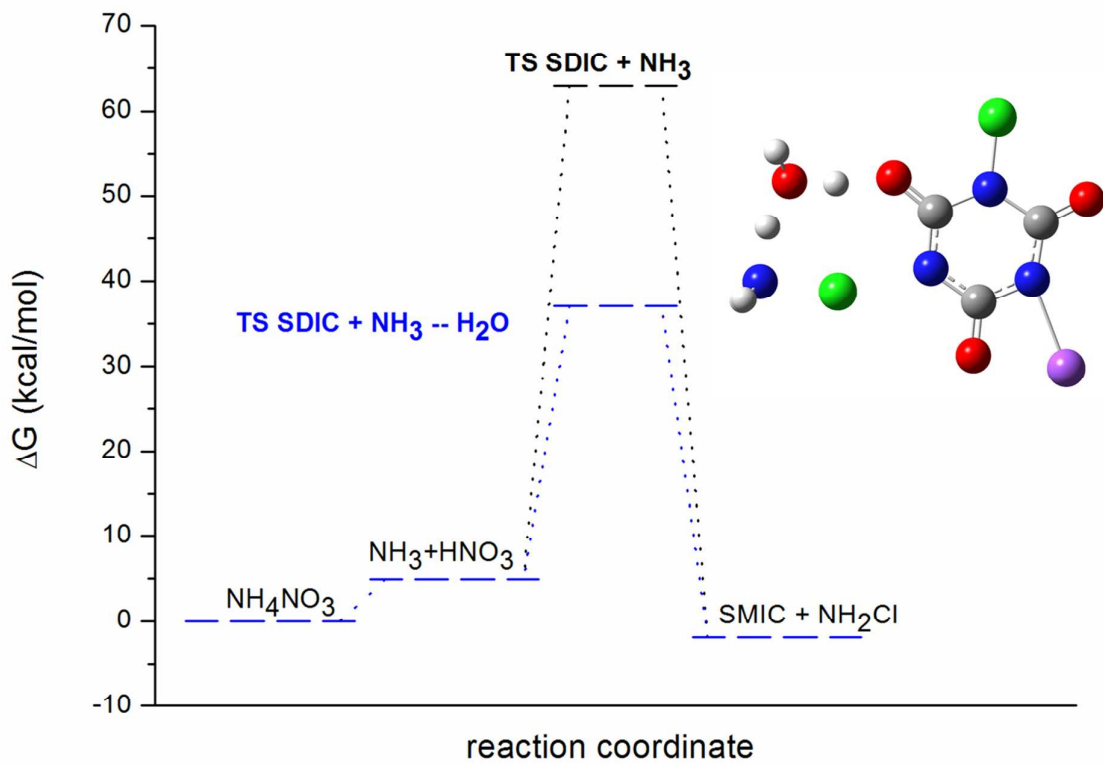


Figure 4.