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

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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.

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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 charts[13-17] 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-Labelling-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 experiments[32] 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 techniques[34-37], 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 Toulouse[38] . This accident, promoted some experimental work to study incompatibility issues between these chemicals[39-41] 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 AN[48-50].

Several experimental studies were carried out on the AN/SDIC mixture. In particular, calorimetric analysis[39,40] revealed that pure AN[40] and pure SDIC[39] 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°C[39]. 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 chemicals[49] 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 functional[53] 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 $\mathbf{S}^2$, 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 study[51] and five main reaction channels, giving the experimentally characterized compounds (N_2, H_2O, O_2, ·OH, HNO, ·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 (ΔG = 4.9 kcal mol^{-1}). The nitric acid then undergoes a homolytic breaking at high energy (ΔG = 40.2 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 ($NH_2^{\bullet}$) 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 $OH^{\bullet}$. The decomposition of H_2NONO leads to the formation of $NO^{\bullet}$ that can, in turn, react with the amidogen radical to produce N_2 + H_2O and N_2H +$OH^{\bullet}$ radicals.

The $OH^{\bullet}$ 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 exits, at the best of our knowledge, in the literature. However, interesting publications[63-65] 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 CO_2, CO, N_2, H_2 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 ($\Delta G^{\neq}$ = 44.1 kcal mol^{-1}) to form a molecule of chlorine isocyanate. The rest of the initial cycle decomposes with a low energetic barrier ($\Delta G^{\#}$ = 12.6 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 (ΔG = 48.0 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, $\Delta G^{\#}$, of 78.4 kcal/mol. Therefore this mechanism is not energetically favored with respect to the decomposition of pure ammonium nitrate ($\Delta G^{\#}$ =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 ($\Delta G^{\#}$ = 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 ($\Delta G^{\#}$) of 58.0 kcal mol^{-1} and leads to the formation of exothermic products (ΔG = -6.8 kcal mol^{-1}). The reaction between nitric acid and SDIC presents a $\Delta G^{\#}$ of 45.9 kcal mol^{-1} and gives endothermic products (ΔG = 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, $TS_{SDIC+NH3}$, 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 $\Delta G^{\#}$ of 32.1 kcal mol^{-1} and leads to the formation of NH_2Cl and **I** that are two exothermic products (ΔG= -35.6 kcal mol^{-1}). The reaction between nitric acid and SMIC presents, instead, a $\Delta G^{\#}$ of 14.4 kcal mol^{-1} and it gives endothermic products (ΔG = 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 kcal mol^{-1}. Then a homolytic rupture of the N-N bond (ΔG =35.7 kcal mol^{-1}) gives the formation of $\cdot NO_2$ radical and intermediate **III**, which decomposes to **IV**, through a transition state, TS_3, of 27.4 kcal/mol. The reaction proceeds with a $\Delta G^{\#}$ 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 $NCO^{\bullet}$ radical are easily formed $\Delta G^{\#}$ =19.6 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 ($OH^{\bullet}$), present in the reactive environment, to form hydroxylamine (NH_2OH) and chlorine radical, passing through the transition state $TS1_A$ at 14.1 kcal mol^{-1}. Hydroxylamine is an 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 ($NH_2^{\bullet}$), 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 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 ($HNO^{\bullet}$). 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 (NH_2NO_2) and chlorine radical, passing by the transition state, $TS1_B$, of 31.8 kcal mol^{-1}. The energy needed to generate the crucial $NO_2^{\bullet}$ radical is released, as above mentioned, along the path [A]. The NH_2NO_2 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 N_2O, N_2 and O_2. 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 ($NHCl_2$) 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 (NCl_3) 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 products[39] (N_2, NO, HCl, NO_2, Cl_2, H_2O, N_2O), 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 NH_3 with SDIC, leading to NH_2Cl 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 environment[44]. The presence of water or moisture in the AZF plant in Toulouse has not been excluded[49] 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 NH_3 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 Toulouse[38].

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.

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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
NH_3+HNO_3	15.3	14.0	4.9
$TS_{SDIC+NH3}$	60.8	60.8	62.9
NH_2Cl+SMIC	8.1	7.7	-1.9
Decomposition of SMIC			
TS_1	57.0	57.9	30.2
Intermediate I + NH_2Cl	1.6	2.2	-37.5
TS_2	31.6	31.3	4.8
Intermediate II + NaOH	21.6	22.3	-5.1
Intermediate III	72.9	70.0	30.6
TS_3	102.7	97.9	58.0
Intermediate IV	88.9	85.0	43.1
TS_4	122.4	116.5	73.8
Intermediate V	108.0	101.6	47.7
TS_5	129.6	121.4	67.3
HNCO + NCO·	120.3	110.9	49.9
Decomposition of NH_2Cl			
Path [A]			
$TS1_A$	11.6	12.6	12.2
NH_2OH+Cl·	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
H_2 + HNO	49.9	44.2	28.3
Path [B]			
$TS1_B$	28.2	28.6	29.9
NH_2NO_2 + Cl·	6.3	8.3	9.1
$TS2_B$	48.8	47.1	47.7
HN=NO(OH)	15.7	17.6	18.4
$TS3_B$	56.8	54.3	54.5
N_2O+H_2O	-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
Path [C]			
$TS1_C$	7.0	9.1	19.0
$NHCl_2$ + H_2O	-72.3	-68.0	-68.0
$TS2_C$	-19.7	-16.9	-6.6
NCl_3 + H_2O	-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).

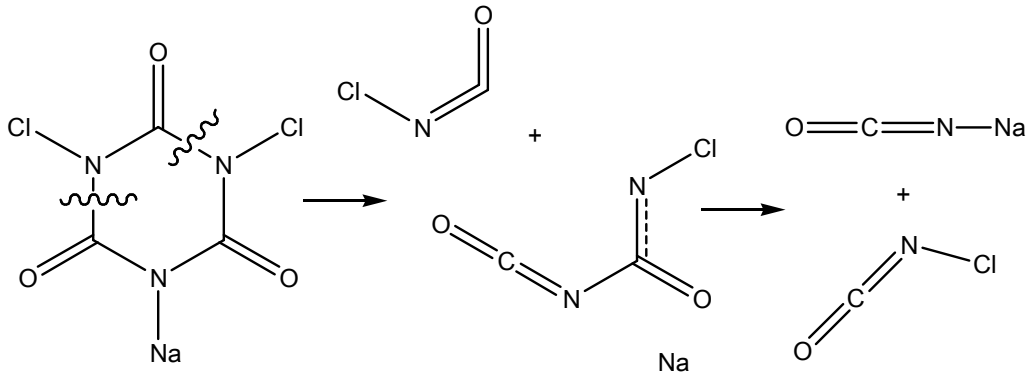
Scheme 2.Reaction path for the decomposition of monochloramine, resulting from the reaction between the ammonia and the dichloroisocyanuric acid.

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

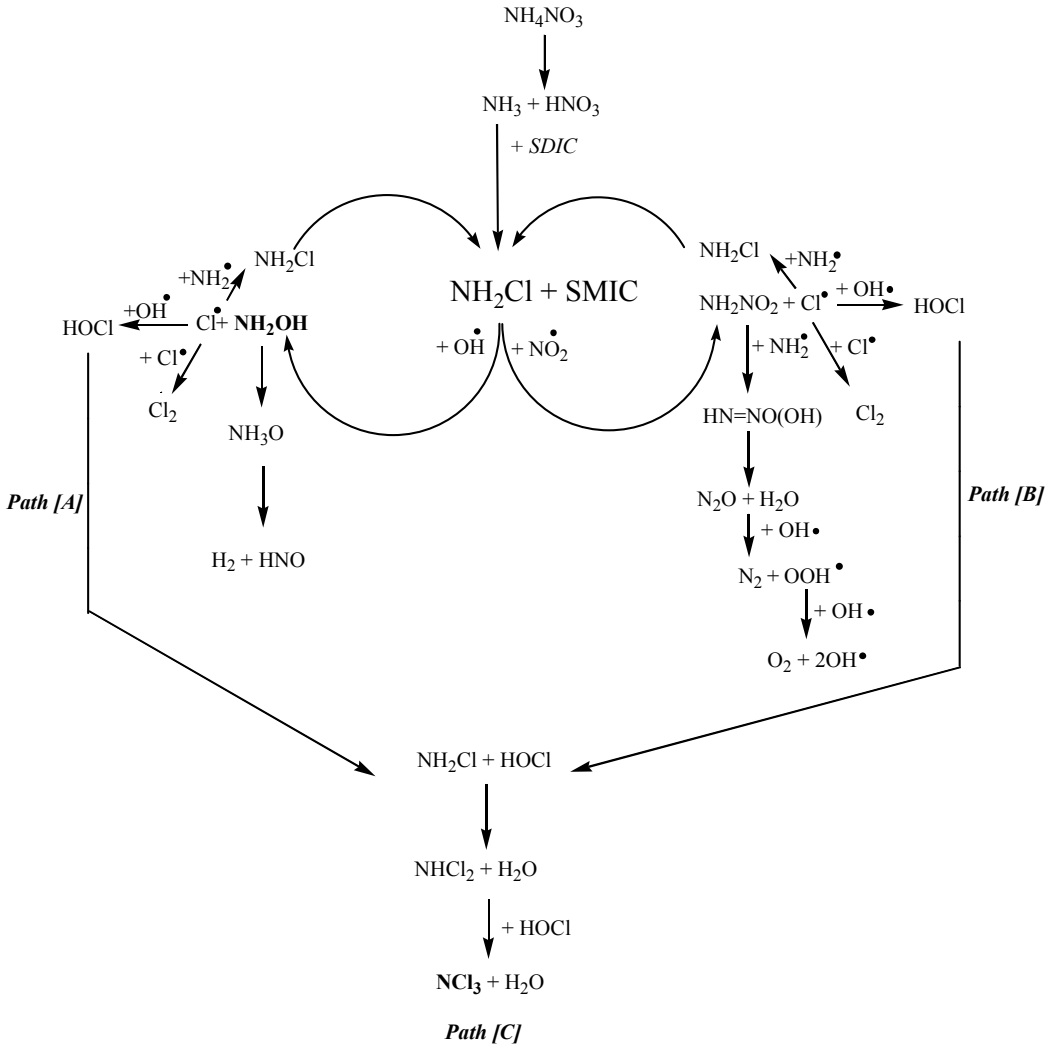
Figure 2. Gibbs free energy profiles for the decomposition of SMIC with the relative geometries of the intermediates involved.

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.


NH4NO3
NH3 + HNO3
+ SDIC
NH2Cl + SMIC
+ OH•
+ NO2•
NH2Cl
+NH2•
Cl• + NH2OH
+OH•
HOCl
+ Cl•
Cl2
NH3O
H2 + HNO
Path [A]
NH2Cl
+NH2•
NH2NO2 + Cl•
+ OH•
HOCl
+ NH2•
+ Cl•
HN=NO(OH)
Cl2
N2O + H2O
+ OH•
N2 + OOH•
+ OH•
O2 + 2OH•
Path [B]
NH2Cl + HOCl
NHCl2 + H2O
+ HOCl
NCl3 + H2O
Path [C]

Scheme 2.

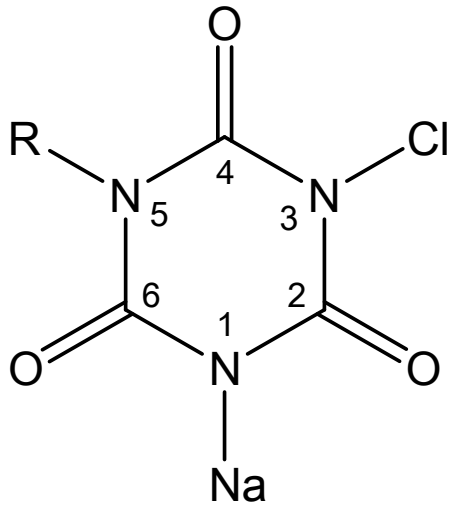


Figure 1.

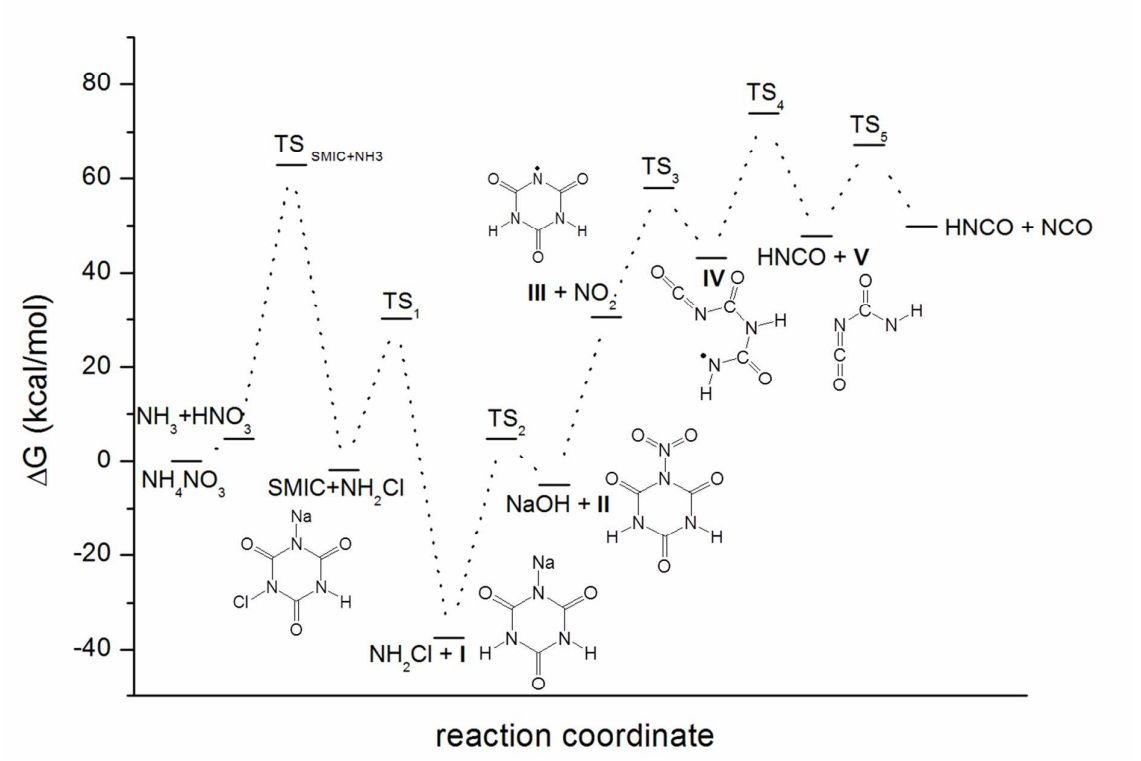

80
60
40
20
0
-20
-40
ΔG (kcal/mol)
reaction coordinate
NH3+HNO3
NH4NO3
TS SMIC+NH3
SMIC+NH2Cl
TS1
NH2Cl + I
TS2
NaOH + II
III + NO2
TS3
IV
TS4
HNCO + V
TS5
HNCO + NCO

Figure 2.

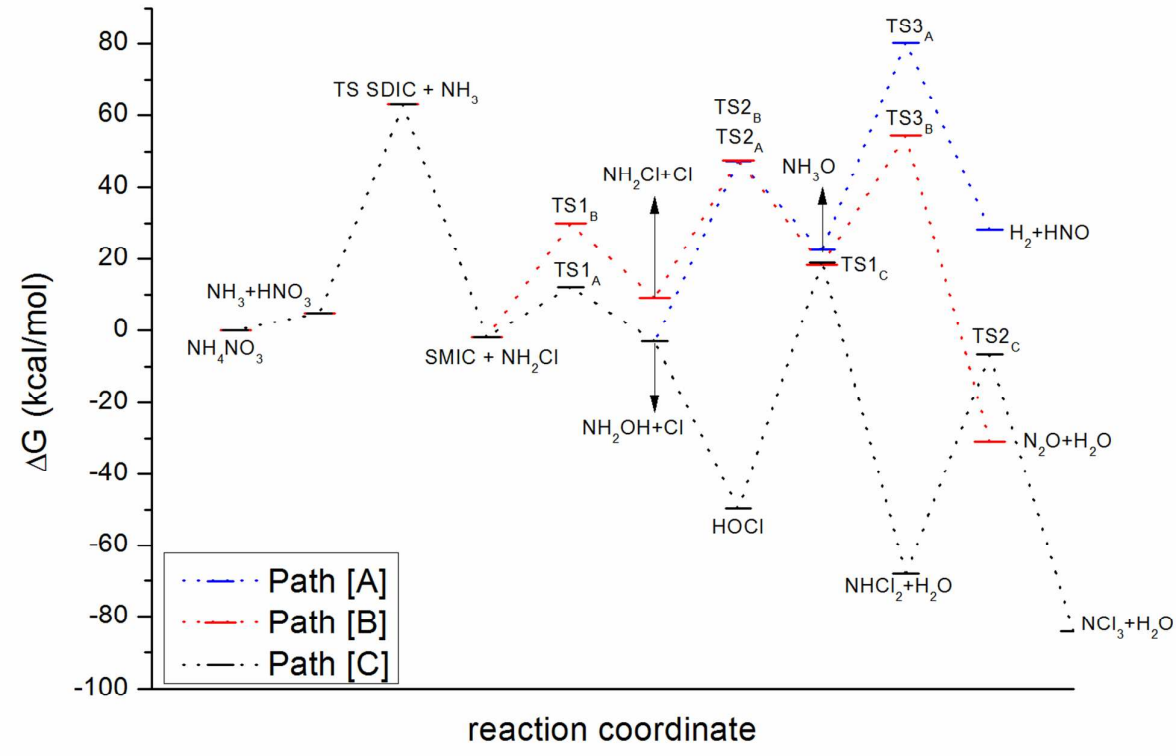

80
60
40
20
0
-20
-40
-60
-80
-100
ΔG (kcal/mol)
reaction coordinate
TS SDIC + NH3
NH3+HNO3
NH4NO3
SMIC + NH2Cl
TS1B
TS1A
NH2Cl+Cl
NH2OH+Cl
TS2B
TS2A
HOCl
NH3O
TS1C
TS3A
TS3B
NHCl2+H2O
H2+HNO
TS2C
N2O+H2O
NCl3+H2O
Path [A]
Path [B]
Path [C]

Figure 3.

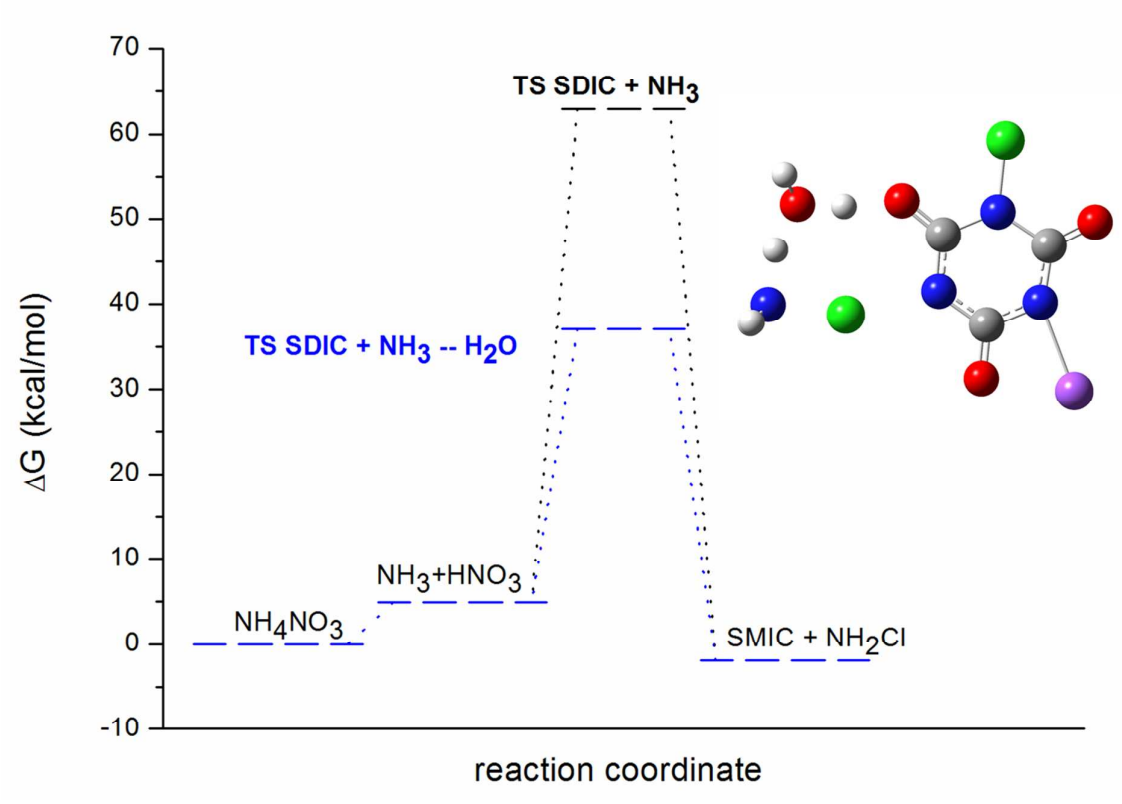

70
60
50
40
30
20
10
0
-10
ΔG (kcal/mol)
TS SDIC + NH3
TS SDIC + NH3 -- H2O
NH3+HNO3
NH4NO3
SMIC + NH2Cl
reaction coordinate

Figure 4.