Unexpected Reactivity of Amidogen Radical in the Gas Phase Degradation of Nitric Acid

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S *Supporting Information*

ABSTRACT: The gas phase reaction between nitric acid and amidogen radical has been investigated employing high level quantun-mechanical electronic structure methods and variational transition state theory kinetic calculations. Our results show that the reaction proceeds through a *proton coupled electron transfer* mechanism with a rate constant of 1.81×10^{-13} cm^3·molecule^{-1}·s^{-1} at 298 K. This value is similar to the rate constants for the reactions of hydroxyl radical with either ammonia or nitric acid. An analysis of these data in the context of the chemistry of the atmosphere suggests that the amidogen radical, formed in the oxidation of ammonia by hydroxyl radical, reacts with nitric acid regenerating ammonia. On the basis of these findings, we propose a potential new catalytic-like cycle which couples the oxidation of ammonia by hydroxyl radical and the reaction of nitric acid with amidogen radical in the Earth's atmosphere.

Nitric acid (HNO$_3$) and ammonia (NH$_3$) are important trace species in the Earth's atmosphere. HNO$_3$ is formed from oxidation of NO$_x$ and is believed to be the final major product in the atmospheric oxidation of gaseous nitrogen compounds. It can be removed by dry deposition, rain out, or reaction with hydroxyl radical (OH) (reaction eq 1), which converts nitric acid into the reactive nitrate radical (NO$_3$).[1,2]

$$HNO_3 + OH \rightarrow NO_3 + H_2O \tag{1}$$
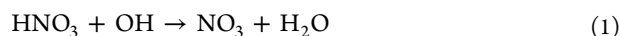
Ammonia is emitted to the atmosphere from biogenic and anthropogenic sources and constitutes the third most abundant gaseous nitrogen compound in the troposphere.[3–6] It is the only alkaline gas in the atmosphere and plays an important role in the atmospheric heterogeneous chemistry and in the formation of aerosols.[7,8] In the gas phase, NH$_3$ is oxidized by OH leading to the formation of amidogen radical (NH$_2$) and water (reaction eq 2). This reaction is also important in the combustion of fossil fuels and in the atmospheric formation and elimination of NO$_x$.[9]

$$NH_3 + OH \rightarrow NH_2 + H_2O \tag{2}$$
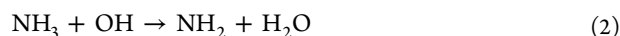
Due to the importance of these reactions, several experimental and theoretical works have been reported in the literature[10–22] aiming to elucidate their reaction mechanism and to determine the rate constants. For the reaction between nitric acid and hydroxyl radical (reaction eq 1), a theoretical estimate of 1.1×10^{-13} cm^3·molecule^{-1}·s^{-1} at 298 K has been reported[17] and experimental values in the range between 1.26×10^{-13} and 1.64×10^{-13} cm^3·molecule^{-1}·s^{-1} have been measured for different pressures at 298 K.[10–13] For the reaction between NH$_3$ and OH (reaction eq 2), a theoretical estimate of 1.4×10^{-13} cm^3·molecule^{-1}·s^{-1} at 300 K has been reported,[21] whereas the most recent experimental rate constants range between 1.47×10^{-13} and 1.60×10^{-13} cm^3·molecule^{-1}·s^{-1} at 298 K.[18,23]

Field observations and laboratory investigations have revealed the existence of interdependence between nitric acid and ammonia concentrations in the atmosphere.[24–28] For atmospheric chemistry purposes, it is convenient to write the reaction rates for eqs 1 and 2 (designated by v$_1$ and v$_2$, respectively) as

$$v_1 = k_1[HNO_3][OH] \tag{3}$$

$$v_2 = k_2[NH_3][OH] \tag{4}$$

where k_1 and k_2 are the rate constants of reactions eqs 1 and 2, respectively.

It is now interesting to write the relative rates between reactions eqs 2 and 1 as

$$\frac{v_2}{v_1} = \frac{k_2[NH_3][OH]}{k_1[HNO_3][OH]]} = \frac{k_2[NH_3]}{k_1[HNO_3]} \tag{5}$$

The rate constants k_1 and k_2 are very similar to each other, so that we can assume that the k_2/k_1 ratio is close to 1. Consequently, we conclude that the ratio v_2/v_1 of the reaction rates for the OH radical oxidations of ammonia and nitric acid depends on the relative concentration of these species.

Field observations have reported atmospheric concentration of nitric acid and ammonia ranging between 1.16×10^{10} and 1.32×10^{12} molecule·cm^{-3},[29,30] and in the range between 1.97×10^{11} and 3.74×10^{12} molecule·cm^{-3}, respectively.[30,31] Moreover, mean simultaneous concentrations measures of ammonia and nitric acid, observed at different rural and urban areas, indicate that the ratio [NH$_3$]/[HNO$_3$] ranges between 17 and 64.[30,32–34] These findings suggest that, in atmospheric situations with large ammonia concentrations, the OH radical

should oxidize NH_3 (reaction eq 2) rather than HNO_3 (reaction eq 1). However, reaction eq 2 produces amidogen radical, which can further react with nitric acid (reaction eq 6), leading to the formation of nitrate radical and regenerating ammonia.

$$HNO_3 + NH_2 \rightarrow NO_3 + NH_3 \qquad (6)$$

In an attempt to assess the potential role of the amidogen radical in the tropospheric degradation of nitric acid, here we report the results of high level quantum-mechanical electronic structure calculations on the ground-state potential energy surface (PES) of reaction eq 6. In addition, an estimate of the rate constants of the elementary reactions considered, based on the variational transition state theory calculations, is provided.

Figure 1 displays a schematic energy profile showing the most relevant structures concerning the lowest-energy pathway
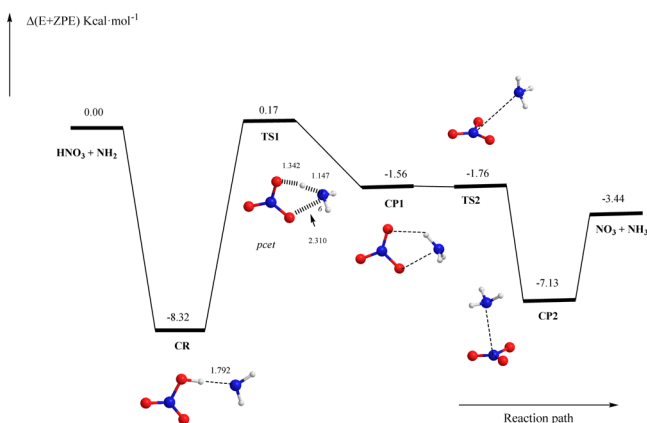

Figure 1. Schematic potential energy surface for the reaction between HNO_3 and NH_2.

on the ground-state PES. First, the reaction begins with a barrierless formation of a pre-reactive complex (**CR**) which has a quite large binding energy (8.32 kcal·mol^{-1} at CCSD(T)/CBS//QCID/6-311+G(2df,2p) level of theory). This result is in line with the study reported recently by Clark et al.,[35] although we predict a larger binding energy by 1.1 kcal·mol^{-1} according to the largest basis set used in this work. Next, the reaction goes on through a transition state (**TS1**), before the formation of two post reactive complexes and the release of the NO_3 and NH_3 products. From the relative energies calculated at the zero-point energy corrected CCSD(T)/CBS//QCID/6-311+G(2df,2p) level of theory, **TS1** is predicted to lie 0.17 kcal·mol^{-1} above the energy of the separate reactants and the reaction energy of reaction eq 6 is computed to be −3.44 kcal·mol^{-1}. It is worth mentioning that the lowest-energy transition state for reaction eq 1 is calculated to lie 2.54 kcal·mol^{-1} above the energy of the separate reactants.[17]

The analysis of the QCISD wave function in terms of the natural orbitals obtained from the first-order density matrix indicates that the reaction between nitric acid and amidogen radical takes place through *a proton coupled electron transfer mechanism* (*pcet*). In this process, the two moieties, HNO_3 and NH_2, approach toward each other in such a way that the nitrogen atom lone pair of the amidogen radical is directed toward the hydrogen of the nitric acid, whereas the unpaired electron of the NH_2 radical interacts with one oxygen atom of the NO_2 group, so that there is a shift of one electron from the oxygen atom to the nitrogen atom of the amidogen moiety and,

simultaneously, the proton of nitric acid is transferred to the NH_2 group. This process is depicted in Scheme 1, which

Scheme 1. Pictorial Representation of the Electronic Features of the Transition State TS1[a]
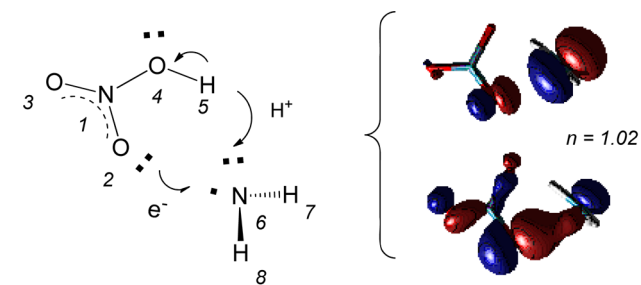
[a] *n* stands for the electron occupation of the natural orbitals of the QCISD wave function.

includes the two center O2−N6 bonding and antibonding natural orbitals (with electron occupations 1.93 and 1.02, respectively) arising from the interaction between the lone pair of the oxygen atom and the unpaired electron of the amidogen radical. At this point it is worth noting that the *pcet* mechanism of reaction eq 6 shows the same electronic features described for the gas phase oxidation of atmospheric acids by hydroxyl radical.[17,36−40]

According to its *pcet* mechanism, the gas phase reaction between nitric acid and amidogen radical is a two-step process as described by eq 7, where the pre-reactive complex **CR** is in equilibrium with the reactants, and the reaction proceeds through the unimolecular decomposition of this complex.

$$HNO_3 + NH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HNO_3 \cdots NH_2 \overset{k_2}{\rightarrow} NO_3 + NH_3 \qquad (7)$$
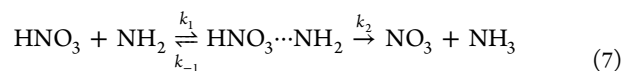
Now, the rate constant can be approximated as

$$k_{TS} = \frac{k_1}{k_{-1}} k_2 = K_{eq} k_2 \qquad (8)$$

where K_{eq} is the equilibrium constant for the formation of the **CR** complex and k_2 is the unimolecular rate constant for its decomposition.

The equilibrium constant has been evaluated from the relative energies obtained at CCSD(T)/CBS level of theory and partition functions computed at QCISD/6-311+G(2df,2p) level of theory, whereas for k_2, we have carried out variational transition state theory calculations (VTST) employing energies obtained at CCSD(T)/CBS level of theory and partition functions computed at BH&HLYP/6-311+G(2df,2p) level of theory. The tunneling factor has been evaluated by using the small curvature approximation.

The results of the kinetic study are collected in Table 1, which shows large values of the equilibrium constants for the formation of the **CR** complex, ranging between 2.05×10^{-18} and 1.99×10^{-19} cm^3·molecule^{-1}, at temperatures within the 270−320 K range. These values are in agreement with the large binding energy predicted for this complex and are about 7.1 and 7.5 times larger than those reported recently by Clark et al.[35]

Our VTST calculations predict a rate constant of 1.81×10^{-13} cm^3·molecule^{-1}·s^{-1} at 298 K. This value remains practically constant in the range of temperatures investigated

Table 1. Calculated Values, at Different Temperatures (in K) of Tunneling Factors, κ, Equilibrium Constants (K_{eq} in cm^3·molecule^{-1}), k_2 (in s^{-1}), and Rate Constants (k_{TS} in cm^3·molecule^{-1}·s^{-1})[a]

T	K_{eq}	κ[b]	k_2[b]	k_{TS}
270	2.05×10^{-18}	2.27	4.11×10^4	1.91×10^{-13}
280	1.20×10^{-18}	2.15	7.36×10^4	1.87×10^{-13}
290	7.27×10^{-19}	2.05	1.23×10^5	1.83×10^{-13}
298	5.00×10^{-19}	1.97	1.84×10^5	1.81×10^{-13}
300	4.57×10^{-19}	1.96	2.02×10^5	1.81×10^{-13}
310	2.97×10^{-19}	1.86	3.22×10^5	1.79×10^{-13}
320	1.99×10^{-19}	1.80	4.96×10^5	1.78×10^{-13}

[a]See Supporting Information for more details of these calculations. [b]The k_2 value of eq 8 corresponds to $\kappa \cdot k_2$ in Table 1.

(between 270 and 320 K). We observe that the value of this rate constant is very similar (though slightly larger) to the rate constants of reactions eqs 1 and 2. These results lead us to conclude that, in those atmospheric conditions where the concentration of ammonia is greater than the concentration of nitric acid and where hydroxyl radical should preferentially oxidize ammonia, *amidogen radical could contribute to the atmospheric degradation of nitric acid through* reaction eq 6. However, the small exothermicity of this reaction suggests the possibility of reaction eq 6 to be reversible. Thus, we have calculated a rate constant of 6.33×10^{-17} cm^3·molecule^{-1}·s^{-1} at 298 K for the reverse reaction of eq 6 (see the Supporting Information), which is roughly 4 orders of magnitude smaller than for the forward reaction. Despite this great difference in the values of the rate constants, under large atmospheric concentrations of NO$_3$ and NH$_3$, the reaction rate of the reverse reaction could be larger than the reaction rate of the forward one. This can occur at night with large concentrations of nitrate radical, but the rapid photolysis of NO$_3$ during the day[9] would prevent this situation.

The findings discussed above lead us to consider possible atmospheric implications of the reaction investigated in this work, so that the reactions of eqs 2 and 6 are coupled to each other forming an atmospheric *catalytic-like cycle* such as displayed in Figure 2. In this catalytic cycle, ammonia is
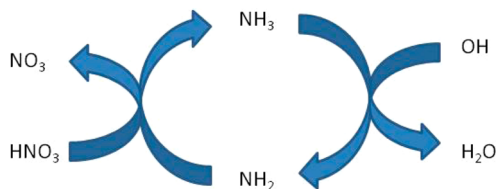

Figure 2. Catalytic cycle involving the oxidation of NH$_3$ by OH radical and the reaction between amidogen radical and nitric acid.

oxidized by OH radical to form NH$_2$ radical and then amidogen radical further reacts with nitric acid yielding nitrate radical and regenerating ammonia so that the catalytic cycle is closed.

The proposed cycle may be less operative or even inoperative depending on the presence and concentration of other atmospheric trace gases that can compete with the reactions considered in the present study, in the same way as occurs in many other atmospheric cycles that cannot be treated independently. In particular, high relative humidity and low temperature favors formation of particulate ammonium nitrate

according to the equilibrium eq 9,[32] and consequently reduces the atmospheric concentration of gas phase nitric acid and ammonia, or the presence of some aldehydes or nitrogen oxides, among others, that can compete with the reactions investigated.

$$HNO_3 + NH_3 \leftrightarrow NH_4NO_3 \qquad (9)$$
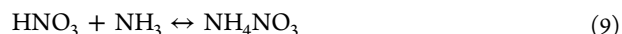
Finally, it is worth pointing out that the reaction investigated in this work may have important implications in combustion and postcombustion environments, where amidogen radical and NO$_x$ compounds play an important role.[41,42] In fact, this is true if one realizes that the reaction mechanism described in this work is not necessarily restricted to the reaction with nitric acid.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Theoretical methods employed in this work, details of the results regarding the potential energy surface and the kinetic study along with the absolute energies and Cartesian coordinates of all stationary point considered; kinetic study of the reverse reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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