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Reaction of a charge-separated ONONO₂ species with water in the formation of HONO: an MP2 Molecular Dynamics study†

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The reaction of (NO⁺)(NO₃[−]) with water is modelled in ONONO₂·(H₂O)₄ clusters. Molecular Dynamics simulations using second-order Møller–Plesset perturbation (MP2) theory support the feasibility of the reaction of a charge-separated species to produce HONO and nitric acid.

It is well known that nitrous acid (HONO) plays a major role in the chemistry of the atmosphere, *e.g.* as a source of hydroxyl (OH) radicals.^{1,2} While heterogeneous reactions of NO₂ with water on tropospheric surfaces are believed to be important in generating HONO, the actual mechanisms involved are not known with certainty. On a chemical basis, the involvement of the NO₂ dimer seems reasonable,³ although other mechanisms have been proposed for production of HONO both in the dark and under irradiation.^{4–11} Initial steps of one proposed mechanism³ include NO₂ dimerization to form N₂O₄ and autoionization of asymmetric N₂O₄, *i.e.* ONONO₂, to form (NO⁺)(NO₃[−]).

Reaction of the (NO⁺)(NO₃[−]) ion pair with water to form HONO and nitric acid (HONO₂) is the final step.

A number of studies have addressed the formation of NO₂ dimers in both the symmetric (with a central NN bond) and asymmetric (ONONO₂) forms, and the interconversion between the two.^{12–18} While the symmetric form of the dimer is favoured, there are pathways that can generate the asymmetric *trans*-ONONO₂ form that is the most likely precursor to the ion pair and subsequently HONO.^{12,13,15,16,18} de Jesus Medeiros and Pimentel, in a study of the dimerization of NO₂ and the symmetric to asymmetric

isomerization of the dimer in water clusters, predicted direct HONO formation from the NO₂·(H₂O)_{*n*} + NO₂ reaction and from the transition state for symmetric to asymmetric isomerization.¹⁵ These modifications of the proposed mechanism described above bypass formation of (NO⁺)(NO₃[−]) through autoionization or, in the case of the NO₂·(H₂O)_{*n*} + NO₂ reaction, formation of the NO₂ dimer. Further exploration of the (NO⁺)(NO₃[−]) path will allow for comparison between potential routes and provide additional insight into the detailed mechanism that converts NO₂ in the presence of water to HONO. This is particularly useful for understanding other important reactions of NO₂ on surfaces in the presence of water, such as the reaction with HCl to form ClNO, since such chemistry likely shares common intermediates with NO₂ hydrolysis.^{19–21}

In *ab initio* Molecular Dynamics [AIMD], the reaction trajectory is propagated classically on the *ab initio* potential surface providing a means for studying reactive processes and the influence of the immediate environment.²² The system wave function or electron density is calculated at each time step, *i.e.* on-the-fly, for determination of the energy, the interatomic forces and other properties. Partial charges are an obvious metric to investigate charge separation in the reaction of an ion pair as charge characteristics can indicate a shift in the nature of the interaction that would be less obvious from a slight change in structural parameters. Following the changes in partial charges with time, or the charge trajectory, is a very useful tool for understanding the mechanism of the reaction studied here.

A computational study of the minimum energy path for HONO formation by Luo and Chen used a *trans*-ONONO₂·(H₂O)₂ reactant cluster and accounted for additional solvation through use of an empirical force field.²³ In the present study of the ion pair reaction, a *trans*-ONONO₂·(H₂O)₄ cluster was chosen as the model system to examine the influence, and participation, of the surrounding water. The *ab initio* treatment of additional water molecules allows for greater flexibility in the reaction dynamics explored in these simulations. Both experimental and theoretical studies confirm that while certain water configurations promote the formation of HONO in the (NO⁺)(H₂O)₄ cluster, the reaction does not proceed

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† Electronic supplementary information (ESI) available: Additional relative energies at various levels of theory, a brief discussion of the *cis*-ONONO₂ isomer and figures including the additional trajectories are available. See DOI: 10.1039/c3cp55024a

in $(\text{NO}^+)(\text{H}_2\text{O})_n$ clusters for $n \leq 3$.^{24–26} This previous work on HONO formation in absence of the NO_3^- anion motivated the choice of water cluster size and configuration in the present study. In previous work by Miller and Gerber, a similar cluster model was employed in studies of N_2O_4 autoionization as well as proton recombination with the NO_3^- anion.^{27,28}

In choosing a method for calculation of the energy and interatomic forces for an AIMD study, or any computational study, computational cost and chemical accuracy must be weighed. Treatment using density functional theory^{15,21} or a small basis set²⁷ may be necessary in a dynamics study where thousands of gradient calculations are required for each picosecond (ps) simulated. However, in a study of the N_2O_4 potential surface, the B3LYP density functional was found to overestimate the stability of $(\text{NO}^+)(\text{NO}_3^-)$ predicting a stable ion pair, while the more accurate *ab initio* methods found this structure to be a transition state.¹⁸ Additionally, the sensitivity of the interaction between the NO^+ cation and water to the level of correlation, *i.e.* MP2 *vs.* CCSD, has been noted previously.^{26,29} We found that the description of the relevant portions of the $\text{ONONO}_2(\text{H}_2\text{O})_4$ potential surface is qualitatively incorrect when B3LYP, an insufficient basis set or MP2 without spin-component scaling are employed (see ESI†). We have selected the MP2 method with scaling of opposite spin and a basis set with diffuse functions to efficiently and accurately describe the region of the $\text{ONONO}_2(\text{H}_2\text{O})_4$ potential surface of interest.

A *trans*- $\text{ONONO}_2(\text{H}_2\text{O})_4$ cluster with a branched water configuration similar to that of the reactive $(\text{NO}^+)(\text{H}_2\text{O})_4$ cluster²⁶ was identified, as well as a lower energy isomer with a square water configuration. In Fig. 1, the *trans*- $\text{ONONO}_2(\text{H}_2\text{O})_4$ clusters with (a) a square water configuration and (b) branched configuration are presented along with transition state [TS] structures from the branched configuration for proton transfer to (c) the NO_3^- anion and (d) H_2O . The product of proton transfer to the NO_3^- anion, (e) the *cis*-HONO-HONO₂·(H_2O)₃ cluster, and the product of proton transfer to H_2O , (f) the *trans*-HONO·(NO_3^-)·(H_3O^+)·(H_2O)₂ cluster, are also included in Fig. 1. The relative energies of these clusters are presented in Table 1. While the branched configuration, Fig. 1(b), is approximately 3 kcal mol^{−1} above the *trans*- ONONO_2 minimum with a square water configuration, the branched configuration promotes reactivity of ONONO_2 as seen in the lengthening of the distance between the NO and NO_3 fragments. The ON-ONO₂ distance extends from 1.76 Å in the cluster with a square water configuration, Fig. 1(a), to 1.84 Å in the cluster with a branched water configuration, Fig. 1(b), prior to insertion of the reacting water between the NO and NO_3 fragments, Fig. 1(c) and (d). In the minimum energy cluster, the partial charge on the NO and NO_3 fragments are $\delta(\text{NO}) = 0.46$ and $\delta(\text{NO}_3) = -0.45$ for a charge separation, $\delta(\text{NO}) - \delta(\text{NO}_3)$, of 0.9. In the cluster with a branched water configuration, the charge separation increases to 1.1 with a partial charge of 0.55 on the NO fragment and -0.54 on the NO_3 fragment. Below, the charge separation will be used to describe the nature of the reactant and as one of the metrics indicating product formation.

These simulations explore the ion pair reaction given that the system has sufficient energy to reach one of two proton transfer transition states. Thus it is important to accurately

Fig. 1 Structures of (a) *trans*- $\text{ONONO}_2(\text{H}_2\text{O})_4$ minimum [ON-ONO₂ distance = 1.76 Å], (b) *trans*- $\text{ONONO}_2(\text{H}_2\text{O})_4$ branched isomer [ON-ONO₂ distance = 1.84 Å], (c) TS for proton transfer to NO_3^- , (d) TS for proton transfer to H_2O , (e) *cis*-HONO-HONO₂·(H_2O)₃ product cluster and (f) *trans*-HONO·(NO_3^-)·(H_3O^+)·(H_2O)₂ product cluster. The NO_3 fragment is red, NO fragment is magenta, H_2O is blue with the reacting H_2O molecule a lighter blue.

determine the energy barrier relative to the *trans*- $\text{ONONO}_2(\text{H}_2\text{O})_4$ configurations. The SOS-RIMP2^{30,31} method and the SVP^{32,33} basis set with added diffuse functions^{34,35} [aSV] were chosen for a sufficient qualitative description of the relative energies along the reaction path. For a more accurate determination of the energies, the structures were optimized at the SOS-RIMP2 level of theory with a larger basis set, the Dunning aug-cc-pVTZ^{34–36} [aTZ] basis set, followed by single point calculation at the CCSD³⁷ level. Following optimizations at the SOS-RIMP2 level with the aug-cc-pVDZ basis set, the CCSD(T)³⁸ energy was calculated. The CCSD/aTZ//SOS-RIMP2/aTZ and the CCSD(T)/aDZ//SOS-RIMP2/aDZ energies are included in Table 1 alongside the SOS-RIMP2/aSV energies. The energetic ordering of the isomers is correctly predicted at the lower level of theory with the exception of the products. The energy of the products relative to the $\text{ONONO}_2(\text{H}_2\text{O})_4$ minimum is more sensitive to the basis size and method (see ESI†). However, the SOS-RIMP2/aSV approach gives a qualitatively correct description of the reactant and TS energetics and the formation of the products from the transition states is sufficiently exothermic to prevent the reverse reaction in the short simulations presented here. The branched reactive cluster is predicted to be approximately 3 kcal mol^{−1} above the minimum energy *trans*- $\text{ONONO}_2(\text{H}_2\text{O})_4$ cluster and the transition states roughly an additional 2 to 3 kcal mol^{−1} higher at the higher levels of theory.

Table 1 Relative energies of reactant, TS and product clusters, as well as the total energies at which low and high energy simulations were run

Cluster	SOS-RIMP2/aSVP (kcal mol ⁻¹)	CCSD/aTZ ^a (kcal mol ⁻¹)	CCSD(T)/aDZ ^b (kcal mol ⁻¹)
(a) ONONO ₂ ·(H ₂ O) ₄ minimum	0.0	0.0	0.0
(b) ONONO ₂ ·(H ₂ O) ₄ branched	2.8	3.3	3.4
(c) TS: proton transfer to NO ₃ ⁻	7.3	5.8	6.3
(d) TS: proton transfer to H ₂ O	7.2	5.7	5.2
(e) HONO·HONO ₂ ·(H ₂ O) ₃	0.3	-4.9	-0.1
(f) HONO·(NO ₃ ⁻)·(H ₃ O ⁺)·(H ₂ O) ₂	2.8	-3.2	0.2
Low energy (50 K) simulations	9.5–9.7 ^c		
High energy (300 K) simulations	21.4–21.6 ^c		

^a At the SOS-RIMP2/aTZ geometry. ^b At the SOS-RIMP2/aDZ geometry. ^c Total energy varies with the energy of the TS used as a starting structure.

To study the charge characteristics of the clusters during the evolution of this reaction, the charge separation, determined through Natural Population Analysis,³⁹ was monitored in AIMD simulations⁴⁰ in addition to bond distances. Beginning from the proton transfer transition states, trajectories were propagated forward and reversed to connect the reactants and products. Results of a simulation beginning from the transition state for proton transfer to the nitrate anion (Fig. 1c) are presented in Fig. 2. The charge separation of the NO and NO₃ fragments, $\delta(\text{NO}) - \delta(\text{NO}_3)$, is plotted in the upper panel (a) and in the lower panel (b) the central NO distance of HONO is plotted showing bond formation. In Fig. 2a, the charge separation of the reactant (Fig. 1b) and product (Fig. 1e) clusters are given for reference as red and blue dashed lines respectively. In Fig. 2b, the HO–NO distance in the product cluster is given for reference as a blue dashed line.

As the trajectory is propagated forward in time from 0 ps, the charge separation quickly drops from approximately 1.1 to oscillate about the value determined for the *cis*-HONO product cluster, just less than 0.7. The change in the plotted distance showing formation of the central

HO–NO bond also indicates quick association to form HONO and oscillation about the value of the *cis*-HONO cluster (1.4 Å). When the initial velocities are reversed and propagated from the transition state, the plotted NO distance, which on the reactant side is the distance between the NO fragment and the reacting water, gradually increases as the reacting water migrates away.

On the reactant side, 0 ps to -3 ps, the charge separation increases to a maximum greater than 1.5 before decreasing to eventually oscillate near the value determined for the branched reactant cluster, approximately 1.1. This charge trajectory indicates a passage through a more charge-separated form of ONONO₂ between reactant cluster and transition state. While the charge trajectory does demonstrate the role of a charge-separated species, formation of a true (NO⁺)(NO₃⁻) ion pair with $\delta(\text{NO}^+) - \delta(\text{NO}_3^-)$ of 2 does not occur here. Charge separation of approximately 1.5 corresponds that of a local minimum with an ON–ONO₂ distance of 2.4 Å and an H₂O–NO distance of 1.9 Å. This structure is 1.8 kcal mol⁻¹ at the SOS-RIMP2/aSVP level (1.5 kcal mol⁻¹ at the CCSD/aTZ level) above the branched reactant cluster (Fig. 1b), which has an ON–ONO₂ distance of 1.8 Å and an H₂O–NO distance of 2.5 Å. While harmonic frequency analysis confirms that this is a local minimum (zero imaginary frequencies), it may not be considered a true intermediate as there is not a significant barrier between this (NO^{δ+})(NO₃^{δ-})·(H₂O)₄ cluster and the branched water configuration of *trans*-ONONO₂·(H₂O)₄. The charge separation for the minimum energy *trans*-ONONO₂·(H₂O)₄ cluster with a square water configuration is just under 0.9. In these short simulations, the cluster did not isomerize to the lower energy configuration and the charge separation only briefly dropped below 1.0 on the reactant side at approximately -2.7 ps. The branched water configuration promotes a greater (NO^{δ+})(NO₃^{δ-}) charge separation and places a water molecule in closer proximity to the NO fragment for reaction.

Six additional trajectories from the same starting geometry with the same total energy and alternate random initial velocities were propagated to -1 and 1 ps. Five of the six additional trajectories showed similar behaviour. In the sixth additional trajectory, products rapidly formed as the velocities were reversed as well as for the forward trajectory. While seven trajectories are not sufficient to obtain quantitative rates, the consistent result for several trajectories supports a qualitative description of the mechanism and timescale of this reaction (see ESI† for additional trajectories).

Fig. 2 Plots of (a) the difference in the partial charges on the NO and NO₃ fragments, $\delta(\text{NO}) - \delta(\text{NO}_3)$, and (b) the HO–NO distance versus time for a low energy simulation demonstrating the formation of *cis*-HONO and HONO₂ from *trans*-ONONO₂ and H₂O. Reference values are indicated by dashed horizontal lines for the *trans*-ONONO₂·(H₂O)₄ branched reactant cluster (red) and *cis*-HONO·HONO₂·(H₂O)₃ product cluster (blue).

Fig. 3 Plots of (a) the difference in the partial charges on the NO and NO_3 fragments, $\delta(\text{NO}) - \delta(\text{NO}_3)$, and (b) the HO–NO distance versus time for a low energy simulation demonstrating the formation of *trans*-HONO, NO_3^- and H_3O^+ from *trans*-ONONO₂ and H_2O (black) and high energy simulation leading to production of HONO₂ (grey). Reference values are indicated by dashed horizontal lines for the *trans*-ONONO₂·(H_2O)₄ branched reactant cluster (red) and the *trans*-HONO·(NO_3^-)·(H_3O^+)·(H_2O)₂ product cluster (blue).

Results from a simulation begun at the transition state for proton transfer to the nearby water (Fig. 1d) are presented in Fig. 3. The results are quite similar to those in Fig. 2 with the largest difference being the charge separation (Fig. 3a) on the product side. The partial charge on the NO fragment drops to 0.16 upon formation of HONO, but the partial charge for the NO_3 anion is -0.86 in the *trans*-HONO·(NO_3^-)·(H_3O^+)·(H_2O)₂ product cluster. The charge separation, $\delta(\text{NO}) - \delta(\text{NO}_3) = 1.0$, for this product is similar to the reactant value, approximately 1.1. This is greater than the value for the *cis*-HONO·HONO₂·(H_2O)₃ cluster, 0.7, due to the difference in the partial charge on the NO_3 fragment, which is approximately -0.6 when protonated to form nitric acid. A maximum in the charge separation of similar magnitude again separates the reactant from the transition state and product. The central NO distance of HONO plotted in Fig. 3b again shows rapid formation of HONO. Five of six additional trajectories (see ESI†) showed similar behaviour.

A trajectory from a similar simulation, with the same starting structure but greater total energy, is also included in Fig. 3. On the reactant side of Fig. 3a, the time spent in the configuration of greater charge separation is significantly shorter than in the lower energy simulations and oscillations in charge separation have much greater amplitude. However, it is the product cluster on which the greater energy has a more significant effect. Just after 1 ps, the charge separation decreases to below the value determined for the *trans*-HONO·(NO_3^-)·(H_3O^+)·(H_2O)₂ product cluster (1.0) and remains at a value similar to that of the *cis*-HONO·HONO₂·(H_2O)₃ product cluster (less than 0.7). This indicates that further proton transfer occurred along a “water wire”^{41,42} to form *trans*-HONO·HONO₂·(H_2O)₃. With one bridging water between the H_3O^+ and NO_3^- ions, concerted

transfer of two protons occurs to form nitric acid. For this higher energy simulation, three of the six additional trajectories (See ESI†) reproduced the initial result seen here.

This work demonstrates the feasibility of the ion pair reaction with water in the formation of HONO following autoionization of *trans*-ONONO₂. This reaction could proceed through diffusive separation of the ions followed by reaction of NO^+ with water in absence of the counter ion. However, in the current simulations the water configuration that promotes charge separation and the reaction with water also leads to the nearly immediate formation of HONO making diffusive separation unlikely. The many studies indicating a preference for the molecular form of nitric acid at a water surface rather than the deprotonated NO_3^- anion offer an additional driving force for reaction immediately following autoionization.^{6,43–47}

Based on gas phase calculations, Liu and Goddard suggest that NO_2 hydrolysis likely occurs through direct formation of the *cis* asymmetric dimer followed by isomerization to the *trans* isomer circumventing the high symmetric to asymmetric barrier.¹⁸ They found no barrier for formation of the *cis* isomer and the barrier for the *cis*–*trans* isomerization was predicted to be 3 kcal mol^{−1} above the *cis* minimum. Direct formation of the asymmetric isomer in the gas phase and deposition on a water surface could proceed to HONO formation through the transition states presented here.

Conclusions

In the current work the reaction of an $(\text{NO}^+)(\text{NO}_3^-)$ ion pair with water was studied using a cluster model, the opposite-spin scaled variant of MP2 and a suitable basis set. The simulations presented here predict essentially simultaneous production of HONO and HONO₂ and support the feasibility of the ion pair reaction, or rather, passage through a significantly charge-separated species, as a major step in the hydrolysis of NO_2 through the asymmetric dimer ONONO₂. There is considerable evidence for the accuracy of MP2 in describing water clusters in many cases. The merits of MP2 were enhanced here by using scaling of opposite-spin components and an adequate basis set. As the calculations are not too demanding computationally, we suggest the use of SOS-RIMP2 for MD simulations of other reactions in water clusters.

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