Title
Mechanisms and competition of halide substitution and hydrolysis in reactions of N2O5 with seawater.

Permalink
https://escholarship.org/uc/item/9hh5d7mr

Journal
Science advances, 5(6)

ISSN
2375-2548

Authors
McCaslin, Laura M
Johnson, Mark A
Gerber, R Benny

Publication Date
2019-06-05

DOI
10.1126/sciadv.aav6503

License
https://creativecommons.org/licenses/by/4.0/ 4.0

Peer reviewed
Mechanisms and competition of halide substitution and hydrolysis in reactions of N₂O₅ with seawater

Laura M. McCaslin¹, Mark A. Johnson², R. Benny Gerber¹,³*

Sₐ₂-type halide substitution and hydrolysis are two of the most ubiquitous reactions in chemistry. The interplay between these processes is fundamental in atmospheric chemistry through reactions of N₂O₅ and seawater. N₂O₅ plays a major role in regulating levels of O₃, OH, NO₃, and CH₄. While the reactions of N₂O₅ and seawater are of central importance, little is known about their mechanisms. Of interest is the activation of Cl in seawater by the formation of gaseous ClNO₂, which occurs despite the fact that hydrolysis (to HNO₃) is energetically more favorable. We determine key features of the reaction landscape that account for this behavior in a theoretical study of the cluster N₂O₅/Cl⁻/H₂O. This was carried out using ab initio molecular dynamics to determine reaction pathways, structures, and time scales. While hydrolysis of N₂O₅ occurs in the absence of Cl⁻, results here reveal that a low-lying pathway featuring halide substitution intermediates enhances hydrolysis.

INTRODUCTION

Hydrolysis and Sₐ₂-type halide substitution reactions are two ubiquitous families of reactions that are important throughout many disciplines of chemistry. One area in which the interplay of these key processes has major implications in heterogeneous atmospheric chemistry is the reactions of N₂O₅ with seawater and halide-containing sea spray aerosols. The reactive uptake of N₂O₅ on sea spray aerosols is widely believed to be the most influential set of reactions in heterogeneous atmospheric chemistry (1–7). Model studies indicate that changes in the probability of the reactive uptake of N₂O₅ on aerosols change atmospheric levels of NO₅, O₃, and OH by up to 25, 12, and 15%, respectively (2). N₂O₅ is formed from NO₂ and NO₃ during the night, as NO₃ is photolyzed by sunlight. HNO₃, the hydrolysis product of N₂O₅ reactions with seawater, serves as a major sink for NO₃ species in the atmosphere, which has been validated by a variety of modeling and field studies (1, 2, 7–11). NO₅ species are widely known to affect levels of O₃, OH, and CH₄, thus motivating the need to study their formation and depletion pathways (12). Studies have also shown formation of ClNO₂ from N₂O₅ interacting with chloride-containing liquids, aerosols, and small water clusters (7, 13–16) in a wide range of chloride concentrations. These ClNO₂ compounds can photolyze to form NO₂ and chlorine radicals, which is a major source of activated Cl in the atmosphere (17, 18). The competition between formation of ClNO₂ from halide substitution reactions and HNO₃ from hydrolysis reactions of N₂O₅ and seawater thus has major consequences for the fate of NO₅ species, CH₄, and O₃, which are known to greatly affect Earth’s radiative forcing and thus global climate (19).

Recently, experiments on both liquid surfaces and aerosols have been performed to unravel the competition between numerous reaction pathways when N₂O₅ interacts with seawater and sea spray aerosols (20–23). Limits on the total reactive uptake of N₂O₅ on both pure and salty water have been determined to be between 0.01 and 0.03. However, due to the complexity of chemical environments of sea spray aerosols, studies of the relative yields of ClNO₂ and HNO₃ are still under way (15, 24, 25). While some theoretical studies have explored hydrolysis and halide substitution of N₂O₅ interacting with small water clusters, mechanisms of the competition between these reactions have yet to be established (16, 26–33).

Faced with the need to understand these complex reactions and their mutual influence on each other, it is necessary to design model systems that help to develop intuition from first-principles studies. In this work, we seek to reveal intrinsic features of the reaction between N₂O₅ and aqueous Cl⁻ that control the competition between hydrolysis and halide substitution reactions. We specifically address how water competes with Cl⁻ for reaction with N₂O₅ in a theoretical study of the ternary ionic cluster with composition N₂O₅/Cl⁻/H₂O. Scrutiny of this microscopic regime is also warranted by the results of a recent mass spectrometric experimental study of N₂O₅ interactions with small halide-water clusters [X⁻(H₂O)n = 1–5]. (16). Intermediates were isolated and characterized with infrared spectroscopy to reveal formation of XNO₂/NO₃⁻ species with composition X⁻(N₂O₅). In the present work, we address the features in the reaction dynamics that control the competition between halide substitution and hydrolysis in a sufficiently small system that it can be studied using very accurate ab initio methods. In studying the reaction pathways and time scales of these processes, insights will be gained into the microscopic details of unresolved questions in heterogeneous atmospheric chemistry. Our method integrates the calculations of transition states (TSs), intrinsic reaction coordinates (IRCs), and ab initio molecular dynamics (AIMD). An additional strength of this small model is its ability to evaluate how mechanistic details for the reactions of N₂O₅ with aqueous chloride will evolve in larger systems. We take the perspective that even in bulk environments, the chemistry of halide substitution and hydrolysis of N₂O₅ is likely a local phenomenon. Thus, even as the addition of water molecules to the system will inevitably change the rates of the processes because of a decrease in accessibility of the TS, the configurations and relative energies of the TS will be preserved and continue to provide a microscopic paradigm for the overall kinetics.

¹Institute of Chemistry and the Fritz Haber Center for Molecular Dynamics, The Hebrew University, Jerusalem 9190401, Israel. ²Department of Chemistry, Yale University, New Haven, CT 06525, USA. ³Department of Chemistry, University of California, Irvine, Irvine, CA 92697, USA.
*Corresponding author. Email: benny@fh.huji.ac.il
RESULTS AND DISCUSSION

Figure 1 represents the reaction pathway for N2O3 interacting with H2O and Cl−. Solid lines connecting the various structures indicate an IRC, the steepest gradient pathway from a TS to nearest local minimum (34). Here, two TSs and thus two IRCs are indicated. First, the left IRC corresponds to the pathway from Cl−/H2O interacting with intact N2O3 through an extremely small barrier (0.6 kcal/mol) into the formation of substitution products: ClNO2, NO3−, and H2O. This small barrier to substitution and small distance in configuration space between the reactant and TS1 structures implies a very fast process. Within the substitution product region (i.e., configurations of ClNO2/NO3−/H2O), there is a rich array of configurations accessible to the system at ambient temperatures due to the electrostatically bound nature of the ternary cluster. Besides the local minima associated with IRCs, an additional minimum is indicated: a planar conformation of ClNO2/NO3−/H2O. The planar ClNO2/NO3− substructure has the same orientation as the reaction intermediate recently detected by Kelleher et al. (16). As Kelleher et al. found, this structure with a relative energy of 15.6 kcal/mol has the lowest energy of the substitution products. The third substitution structure shown in Fig. 1 (differing in orientation and number of hydrogen bonds) has a relative energy of 21.1 kcal/mol and connects to the second IRC shown in Fig. 1, linking substitution and hydrolysis reactions (i.e., configurations of HNO2/NO3−/HCl or 2HNO3/Cl−). The TS with relative energy of 35.5 kcal/mol connecting the substitution and hydrolysis product regions (TS2) exhibits the interesting structural feature that the charge-separated NO2− and NO3− moieties accommodate Cl− and H2O on opposite sides of the NO2− constituent such that both nucleophiles are positioned to attack the nitrogen atom. This configuration illustrates the mutual influence of the halide substitution and hydrolysis reactions of N2O5, indicating that the conditions for one reaction necessarily affect the other. On the right side of the second IRC, a structure corresponding to a hydrolysis reaction sits at 0.0 kcal/mol, the lowest-lying structure found. This HCl/NO3−/HNO3 structure is 15.6 kcal/mol and 30.4 kcal/mol more stable than the lowest-lying substitution and intact N2O3 configurations, respectively. Both O−H bonds of the water have broken, and the protons have formed new bonds to make HCl and HNO3. Last, another low-lying minimum structure of 2HNO3/Cl− is shown to the far right at 0.4 kcal/mol.

Thermodynamically, the trends in the potential energy surface are clear: Hydrolysis products are by far the most stable species, although substitution products are more stable than intact N2O3/Cl−/H2O by 9.3 to 14.8 kcal/mol. The stability of the hydrolysis products fits the current model of HNO3 as a sink for NOx species (2, 35, 36). We note that ClNO2 production is found to exceed that of HNO3 in most media, although the relative yields of these species need further investigation (20, 22, 37). Analogous studies of the hydrolysis reaction of N2O5 with two water molecules (where a second H2O replaces Cl− in our system) determine the barrier to reaction from the associated N2O5/2H2O cluster to be ~20 kcal/mol (24). Here, the difference between the low-lying isomer of N2O5 at 30.4 kcal/mol (Fig. 1) and the TS to hydrolysis (TS2) at 41.3 kcal/mol (Fig. 1) is a mere 5.1 kcal/mol. Despite this ~15 kcal/mol lowering of the barrier to N2O5 hydrolysis in the presence of Cl−, the addition of a third body adds entropic complexity. The presence of Cl−, as opposed to another water molecule, near NO2− stabilizes the hydrolysis process by removing a proton from the water, lowering the barrier to hydrolysis. While the hydrolysis process is thermodynamically favored, the substitution process occurs much more quickly because of its low barrier. The heights of the barriers are correlated with the configurational distance between reactants and products. Because the TS of the halide substitution process (TS1) is very close in configuration to the intact N2O3/Cl−/H2O minimum, the barrier is quite small (0.6 kcal/mol). Despite the close proximity of the attacking water to NO2− in TS2, the system must undergo a much greater change in geometry between the adjacent ClNO2/H2O/NO3− minimum and charge-separated TS structure, resulting in a much higher barrier (14.4 kcal/mol).

Because of the rich array of pathways through the substitution product region, a simple calculation of rates using, for example, transition state theory, is not sufficient for determining the time scales of these reactions. For such a system, exploration via AIMD is likely to yield greater insight into the conformationally complex pathways connecting the two IRCs shown in Fig. 1 due to the propensity for these systems to explore portions of the potential energy landscape away from the IRC.

It is not computationally feasible to run trajectories from initial reagents to the final products since the total simulation time required is prohibitively long. AIMD simulations were therefore performed such that the initial geometry was one of the two TS structures shown in Fig. 1. Thus, an understanding of the time scales involved in this process is formed from “stitching” together the process from multiple post-TS calculations. Initial velocities were sampled from a Boltzmann distribution at 300 K and run for a maximum of 10 ps. These initial conditions allow large regions of the potential energy surface to be efficiently sampled and thus provide new insights into reaction probabilities, time scales, and dissociation products.

Figure 2 illustrates a computed sequence of events, hence a reaction mechanism, for the halide substitution and hydrolysis reactions of N2O3 interacting with Cl− and H2O. As expected from the small barrier and proximity of the TS and minimum, halide substitution is a fast process, with an average time of 188 fs between minima, as shown in Fig. 2 (A to C). While there is no substantial geometrical difference between intact N2O3/Cl−/H2O and the TS structure (shown in Fig. 2, A and B), the O−N bond in N2O3 adjacent to the Cl− is stretched to 1.80 Å at TS1 and relaxed to 1.62 Å at the minimum. The relaxation of this bond takes an average of 94 fs. Subsequent formation of the Cl−N bond in Fig. 2C also requires, on average, 94 fs. The mean time scales between local structures on the IRC is of the same order of magnitude as the Cl−N vibrational period of ClNO2, which is ~90 fs (38). Thus, the reactive events are neither ballistic nor slow with respect to intra-molecular vibrations.

---

McCaslin et al., Sci. Adv. 2019; 5 : eaav6503 5 June 2019
CONCLUSIONS

This theoretical study has identified mechanisms and time scales for the competing halide substitution and hydrolysis reactions of N2O5/H2O/Cl−, thus providing the first microscopic understanding of the key features underlying the reaction kinetics and pathways available for reactive uptake of N2O5 in the presence of aqueous Cl−. Although the presence of Cl− lowers the barrier to hydrolysis relative to the three-body N2O5/(H2O)2 reaction by ~15 kcal/mol, the third body adds significant entropic complexity. The predominance of halide substitution over hydrolysis is enabled by the proximity of the halide to N2O5 in the ternary cluster. In systems with larger water content, halide substitution is therefore expected to become less probable relative to hydrolysis. Qualitative insights into the behavior of these processes in more complicated systems such as larger clusters and macroscopic aerosols should nonetheless benefit from analysis of the local structures of the reagent molecules.

MATERIALS AND METHODS

Analysis

In analysis of bond formation and breaking in the molecular dynamics trajectories, various bond lengths were used as cutoffs. For formation of the Cl–N bond, a cutoff of 1.93 Å was used, which corresponds to the longest Cl–N bond length seen in the computed minima. The O–N bond distance cutoff in the hydrolysis reaction was set at 1.34 Å, the longer length observed in the hydrolysis products.

Theoretical calculations

All stationary geometries on the potential energy surface were optimized with the long-range corrected hybrid density functional ωB97X-D and basis set aug-cc-pVDZ (39–41). The diffuse functions included in the aug-cc-pVDZ basis set were needed to describe the diffuse nature of the negatively charged system. Zero-point energy corrections were made to the stationary point energies, computed using the harmonic approximation. IRCs were computed as described by Fukui (34).

To improve calculations of the relative energies of the structures in Fig. 1, single-point energy calculations were performed on top of the ωB97X-D–optimized geometries using coupled cluster theory with single, double, and perturbative triple excitations [CCSD(T)] paired with the aug-cc-pVQZ basis set (40–43).

AIMD calculations were performed at the ωB97X-D/aug-cc-pVQZ level of theory, as used for geometry optimizations and harmonic calculations. All calculations were initialized from each of the two TS structures shown in Fig. 1 (25 trajectories initialized from each geometry). Each trajectory was run with a time step of 0.2 fs for 10 ps or until the cluster dissociated. The relatively small time step was chosen to accurately describe hydrogen motion. All initial velocities were sampled from a Boltzmann distribution at 300 K. Fock extrapolation was performed with polynomial order 6 over 12 points (44, 45). All calculations reported here were performed using Q-Chem (46) except for the CCSD(T)/aug-cc-pVQZ single-point energy calculations, which were performed in Cfour (47).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/6/eaav6503/DC1

Table S1. Geometries optimized at the B97X-D/aug-cc-pVDZ level of theory, corresponding to those shown in Fig. 1 from left to right.

Table S2. Absolute and relative energies of eight structures shown in Fig. 1 calculated with ωB97X-D/aug-cc-pVQZ and CCSD(T)/aug-cc-pVQZ.

REFERENCES AND NOTES

1. X. Tie, G. Brasseur, L. Emmons, L. Horowitz, D. Kinnison, Effects of aerosols on tropospheric oxidants: A global model study. J. Geophys. Res. Atmos. 106, 22931–22964 (2001).
2. H. L. MacIntyre, M. J. Evans, Sensitivity of a global model to the uptake of N2O5 by tropospheric aerosol. Atmos. Chem. Phys. 10, 7409–7414 (2010).
3. W. L. Chang, P. V. Bhave, S. S. Brown, N. Riemer, J. Stutz, D. Dabdub, Heterogeneous atmospheric chemistry, ambient measurements, and model calculations of N2O5: A review. Aerosol Sci. Tech. 45, 655–695 (2011).
4. S. S. Brown, J. Stutz, Nighttime radical observations and chemistry. Chem. Soc. Rev. 41, 6405–6447 (2012).
5. J. P. D. Abbatt, A. K. Y. Lee, J. A. Thornton, Quantifying trace gas uptake to tropospheric aerosol: Recent advances and remaining challenges. Chem. Soc. Rev. 41, 6555–6581 (2012).
6. R. B. Gerber, M. E. Varner, A. D. Hammerich, S. Rilkonen, G. Murdachaew, D. Shemesh, B. J. Finlayson-Pitts, Computational studies of atmospherically-relevant chemical reactions in water clusters and on liquid water and ice surfaces. Acc. Chem. Res. 48, 399–406 (2015).
C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see www.cfour.de.

**Acknowledgments**

**Funding:** This work was supported by the U.S. National Science Foundation Center for Aerosol Impacts on Chemistry of the Environment (NSF-CAICE), CHE-1801971, XSEDE allocation TG-CHE17006, and Zuckerman STEM Leadership Program. **Author contributions:** L.M.M. performed the calculations and analysis and wrote the majority of the manuscript. M.A.J. provided insights into the connection to cluster studies. R.B.G. proposed the model system and contributed to the analysis. All authors contributed to the interpretation of the results.

**Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** Data needed to evaluate the conclusions in the paper can be accessed from the NSF-CAICE Data Repository (doi:10.6075/J0S75DPT). All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

**Citation:** L. M. McCaslin, M. A. Johnson, R. B. Gerber, Mechanisms and competition of halide substitution and hydrolysis in reactions of N_2O_5 with seawater. *Sci. Adv.*, 5, eaav6503 (2019).