

UC Irvine

UC Irvine Previously Published Works

Title

Reactions between Criegee Intermediates and the Inorganic Acids HCl and HNO₃: Kinetics and Atmospheric Implications

Permalink

<https://escholarship.org/uc/item/0r5253wx>

Journal

Angewandte Chemie International Edition, 55(35)

ISSN

1433-7851

Authors

Foreman, Elizabeth S
Kapnas, Kara M
Murray, Craig

Publication Date

2016-08-22

DOI

10.1002/anie.201604662

Peer reviewed

Kinetics and Atmospheric Implications of the Reactions between Criegee Intermediates and the Inorganic Acids HCl and HNO₃

Elizabeth S. Foreman, Kara M. Kapnas, and Craig Murray*

Department of Chemistry, University of California, Irvine, Irvine CA 92697, USA

* Email: craig.murray@uci.edu; Telephone: +1-949-824-4218

Abstract

Criegee intermediates (CIs) are a class of reactive radicals that are thought to play a key role in atmospheric chemistry through reactions with trace species that can lead to aerosol particle formation. Recent work has suggested that water vapor is likely the dominant sink for some CIs, although reactions with trace species that are sufficiently rapid can be locally competitive. In this work, we use broadband transient absorption spectroscopy to measure rate constants for the reactions of the simplest CI, CH_2OO , with two inorganic acids, HCl and HNO_3 , both of which are present in polluted urban atmospheres. Both reactions are fast: at 295 K, reactions of CH_2OO with HCl and HNO_3 have rate constants of $4.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $5.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, respectively. Complementary quantum chemistry calculations show that these reactions form substituted hydroperoxides with no energy barrier. These reaction products are implicated in pulmonary inflammation resulting from production of reactive oxygen species in lung tissue. The results suggest that reactions of CIs with HNO_3 in particular are likely to be competitive with water vapor in polluted urban areas under conditions of modest relative humidity.

Carbonyl oxides (R_1R_2COO), known as Criegee intermediates (CIs), are formed in the atmosphere by alkene ozonolysis.^[1,2] They are thought to have a significant influence on the oxidative capacity of the atmosphere and, through reaction with trace species, to contribute to new particle formation.^[3-9] Unimolecular dissociation of vibrationally hot nascent CIs is a major source of night-time OH in the troposphere.^[3,10] Stabilized CIs react quickly ($\sim 10^{-12}$ – 10^{-10} $\text{cm}^3 \text{ s}^{-1}$) with many trace atmospheric gases.^[8,11-14] Under humid conditions, reaction with SO_2 leads to H_2SO_4 which catalyzes growth of atmospheric aerosol particles.^[4,15-18]

The steady state concentrations of CIs in the atmosphere are limited by reactions with scavengers, the most important of which is water vapor. While reported rate constants for reaction of the simplest CI, CH_2OO , with H_2O are small ($k_{\text{water}} \approx 10^{-17}$ – 10^{-15} $\text{cm}^3 \text{ s}^{-1}$),^[11,19-21] the reaction with $(\text{H}_2\text{O})_2$ is significantly faster ($k_{\text{dimer}} \approx 10^{-11}$ $\text{cm}^3 \text{ s}^{-1}$)^[20-23] and shows a strong negative temperature dependence.^[22] CI loss rates resulting from reaction with water vapor are sensitive to both relative humidity (RH) and temperature and are expected to show significant regional and seasonal variation.^[22,24]

The importance of CI reactions with trace species in the atmosphere requires that they be competitive with water vapor, or more specifically, $(\text{H}_2\text{O})_2$. CI reactivity is dependent on structure. CH_3CHOO can exist as *syn* and *anti* conformers and conformer-specific reactivity has been demonstrated towards SO_2 and H_2O .^[25,26] $(\text{CH}_3)_2\text{COO}$ is likely to survive longer in humid environments than CH_2OO and play a greater role in H_2SO_4 production, as it is comparatively unreactive to H_2O and $(\text{H}_2\text{O})_2$, but more reactive to SO_2 .^[24] Alternatively, reactions with trace species may be locally important if they are sufficiently fast. For example, the reactions of organic acids with CH_2OO and CH_3CHOO are collision-limited ($k_{\text{R(O)OH}} > 10^{-10}$ $\text{cm}^3 \text{ s}^{-1}$), and are likely to make a significant contribution to acid removal in equatorial regions and high northern latitudes.^[13]

While a great deal of attention has been focused on reactions of CI with SO₂, NO₂, and organic acids, other atmospheric trace gases such as inorganic acids have been neglected. Recent chamber studies of *trans*-3-hexene ozonolysis have demonstrated that trace concentrations of HCl can suppress formation of low-volatility oligomers, the first step to new particle formation, suggesting that it may also be an effective scavenger of CIs.^[27] The inorganic acids HCl and HNO₃ have both biogenic and anthropogenic sources (see Supporting Information) and are present in the troposphere at mixing ratios similar to organic acids and SO₂ (ppbv to pptv), with peak concentrations found in coastal and polluted urban areas.^[28–30]

Here, we report direct measurements of rate constants for the reactions of the simplest CI with HCl and HNO₃:



The experimental kinetics measurements are supported by quantum chemical calculations that elucidate reaction mechanisms and identify the products as substituted hydroperoxides. Reaction R2 in particular is found to be sufficiently fast that it is expected to be locally competitive with water vapor under conditions of modest RH.

Experiments were performed in a transient absorption flow cell apparatus that has been described previously.^[31] Pulsed laser photolysis of CH₂I₂ at 355 nm generated CH₂I radicals, which reacted rapidly with O₂ to produce CH₂OO in high yield.^[32–36] Transient absorption spectroscopy using broadband pulsed LEDs was used to measure the time-dependent concentration of CH₂OO in the absence and presence of a controlled concentration of acid. The LED output spanned the wavelength range 365–388 nm, capturing several characteristic vibronic bands of the CH₂OO \tilde{B} –

\tilde{X} transition.^[31,37,38] Selectivity is important because secondary chemistry results in formation of IO,^[35,39] which absorbs in the same spectral window. Typical transient spectra obtained at several time delays in the absence of acid are shown in Figure 1. The absorbance transients are fit to linear combinations of reference spectra,^[31,40]

$$A(\lambda)/l = n_{\text{CH}_2\text{OO}}\sigma_{\text{CH}_2\text{OO}}(\lambda) + n_{\text{IO}}\sigma_{\text{IO}}(\lambda) + C \quad (\text{E1})$$

which return absolute concentrations of CH₂OO and IO at each photolysis-probe time delay. The vibrational progression is washed out at longer delays as CH₂OO is consumed and the absorption due to IO, which is formed and removed far more slowly, grows in.

Kinetics measurements were made at total cell pressures of 27–35 Torr (~1% CH₂I₂, ~15% O₂, and N₂ balance). Maximum CH₂OO concentrations were reached promptly (<10 μs) after photolysis and kinetics data are obtained from analysis of only loss, which is generally slower than formation. In the absence of acid, CH₂OO is consumed by self-reaction, reaction with other radical species (I and CH₂IOO), or by reaction with the CH₂I₂ precursor, which was present in excess. The observed loss of CH₂OO showed single exponential behavior, allowing the assumption of pseudo-first-order conditions,

$$n_{\text{CH}_2\text{OO}}(t) \approx n_{\text{CH}_2\text{OO}}(0) \exp(-k'_0 t) \quad (\text{E3})$$

where k'_0 represents the background, acid-free loss rate that can be attributed largely to reaction with the CH₂I₂ precursor (see Supporting Information). The observed loss rates, k' , increased rapidly with increasing acid concentration and remained mono-exponential. The increase in the CH₂OO loss rate over the acid-free loss rate is attributed to reaction with the acid i.e. $k'_{\text{acid}} = k' - k'_0$ where $k'_{\text{acid}} = k_{\text{acid}}n_{\text{acid}}$.

Figure 2 shows pseudo-first-order plots of k'_{acid} as a function of the acid concentration, n_{acid} . Linear fits to the data shown in Figure 2 yield bimolecular rate constants of $k_{\text{HCl}} = (4.6 \pm 1) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $k_{\text{HNO}_3} = (5.4 \pm 1) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, where the uncertainties (1σ) in the measured rate constants are dominated by the uncertainties in the acid concentrations. The reaction between CH_2OO and HNO_3 is fast and is greater than the estimated hard sphere collision rate; it is likely that long-range attractive interactions are important. Thermally-averaged capture cross sections are dominated by dipole-dipole interactions, but are similar for the reactions with H_2O , HCl and HNO_3 and are not rate-limiting. The trend in the rate constants follows the gas phase acidities, a correlation first noted in an indirect investigation of rates of reactions between the C13 Criegee intermediate and acidic organic compounds.^[41] The suggestion that the transition states (TSs) are highly polar is supported by quantum chemistry calculations, described below.

Quantum chemistry calculations using coupled-cluster theory were performed to characterize stationary points on the potential energy surfaces for the reactions of CH_2OO with H_2O , $(\text{H}_2\text{O})_2$, HCl and HNO_3 . The calculated reaction profiles are shown in Figure 3. All four reactions are exothermic by $\sim 40 \text{ kcal mol}^{-1}$ and form substituted hydroperoxides. The barrier for reaction with H_2O is $2.4 \text{ kcal mol}^{-1}$ above the reactant asymptote, and this tight TS is the rate-limiting bottleneck. For the reaction with $(\text{H}_2\text{O})_2$, there is a submerged barrier of $5.2 \text{ kcal mol}^{-1}$ relative to the $\text{Cl}-(\text{H}_2\text{O})_2$ complex in good agreement with previous theoretical investigations.^[23] In contrast, the acid reactions have submerged classical barriers that are only slightly higher in energy than the reactant complexes and are washed out completely upon inclusion of zero-point energy corrections. The H_2O and HCl reactions proceed via an insertion mechanism, forming hydroxymethyl hydroperoxide (HMHP) and chloromethyl hydroperoxide (CMHP), respectively. A previous study of the ozonolysis of asymmetric alkenes in the presence of HCl identified CMHP as the

product of R1 in the solution phase.^[42] While HMHP is also the product of the $\text{CI} + (\text{H}_2\text{O})_2$ reaction, the apparent mechanism involves two concerted H-atom transfers; that is, the hydroxyl group and the hydroperoxy H-atom originate in different water molecules. The $\text{CI} + \text{HNO}_3$ reaction forms the analogous nitrooxymethyl hydroperoxide (NMHP), although the mechanism is not insertion, since the O–C bond is formed with the nitro– group, rather than the –OH group (see Figure S4). The order of magnitude smaller rate constant measured for HCl relative to HNO_3 may be a consequence of the significantly smaller density of states in the TS region, since the latter lies lower in energy and has more low frequency modes.

The atmospheric importance of reactions R1 and R2 depends upon their capacity to compete with consumption of CH_2OO by water vapor, which depends on temperature and RH. There are several conflicting factors at play; higher temperatures increase the saturation vapor pressure of H_2O , but decreases the equilibrium constant, disfavoring dimer formation.^[43] The rate constant for the dimer reaction also decreases at higher temperatures.^[22] The temperature dependence of the rate constant for the H_2O reaction is unknown, although Arrhenius-like behavior is expected. The temperature dependences of k_{HCl} and k_{HNO_3} are not presently known and are assumed to be constant. Figure 4 shows estimated CH_2OO loss rates due to reaction with H_2O , $(\text{H}_2\text{O})_2$, HCl, and HNO_3 at 275–315 K, over a RH range spanning 10–90% using average concentrations of 8 ppbv and 20 ppbv for HCl and HNO_3 , respectively, which are representative of Southern California.^[30] We estimate reactions with HCl and HNO_3 contribute to atmospheric loss rates for CH_2OO of 9.2 s^{-1} and 270 s^{-1} . Under all conditions of temperature and RH, HCl makes a minor contribution to the CH_2OO loss rate. Reaction with HNO_3 , however, becomes increasingly competitive with $(\text{H}_2\text{O})_2$ as the RH decreases, and dominates under dry conditions ($\text{RH} < 30\%$). The importance of HNO_3 as a reactive sink for CH_2OO is accentuated further at lower temperatures and would be even more significant

if, as seems likely, the rate constant for R2 were to exhibit negative temperature dependence. HNO_3 concentration is expected to be significant, although lower than Southern California, in other heavily polluted environments such as Beijing^[44] or Mexico City.^[45] The role of the substituted inorganic hydroperoxides $[\text{R}(\text{X})\text{OOH}$ ($\text{X} = \text{Cl}, \text{ONO}_2$) produced from R1 and R2 in the atmosphere is uncertain although they may be important species in their own right. For example, exposure to H_2O_2 has been shown to produce elevated levels of reactive oxygen species in alveolar macrophages, which can exacerbate the effects of fine particulate matter inhalation.^[46] In the atmosphere, the fate of CMHP and NMHP is likely dominated by photolysis, as for other peroxides. HMHP absorption extends into the actinic region and photolysis to form $\text{OH} + \text{R}(\text{X})\text{O}$ is assumed to occur with unit quantum yield.^[47] Peroxides are also key oxidants of sulfur species in clouds/fogs and facilitators of rainwater acidification rain and particle growth.^[48] Reaction with OH to form $\text{R}(\text{X})\text{O}_2$ radicals and H_2O is also possible.^[49]

In conclusion, the reaction between CIs and HNO_3 in particular is likely to be an important sink in polluted urban areas under relatively dry conditions. Although the studies reported here focused on CH_2OO , reactions with inorganic acids may be even more significant for substituted CIs, which show reduced reactivity relative to CH_2OO towards H_2O and $(\text{H}_2\text{O})_2$.^[24] Quantum chemistry calculations (see Supporting Information) suggest that the reactions of HNO_3 with CH_3CHOO and $(\text{CH}_3)_2\text{COO}$ can also proceed to form nitrooxy-substituted hydroperoxides without barriers. Assuming similar rate constants, reaction with HNO_3 is likely to be a competitive loss process even for $(\text{CH}_3)_2\text{COO}$, where thermal unimolecular dissociation is rapid, and particularly so at lower temperatures.^[50] Measurement of the temperature dependence as well as rate constants for reactions between inorganic acids and substituted CIs that are resistant to scavenging by water vapor will be important future work. A more complete assessment of the impact on new particle

formation and air quality will require inclusion of these reactions in regional atmospheric chemical models.

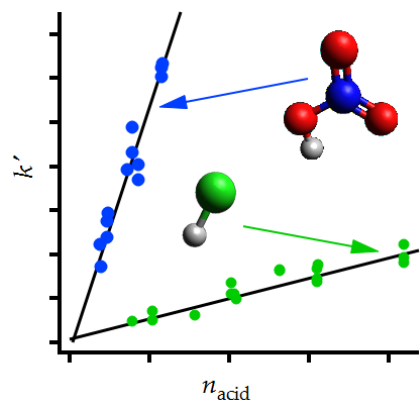
Acknowledgements

We are grateful to Barbara Finlayson-Pitts for helpful discussions and AirUCI for support.

References

- [1] R. Criegee, *Angew. Chem. Int. Ed.* **1975**, *14*, 745–752.
- [2] D. Johnson, G. Marston, *Chem. Soc. Rev.* **2008**, *37*, 699–716.
- [3] S. E. Paulson, J. J. Orlando, *Geophys. Res. Lett.* **1996**, *23*, 3727–3730.
- [4] S. Hatakeyama, H. Akimoto, *Res. Chem. Intermediat.* **1994**, *20*, 503–524.
- [5] A. Sadezky, R. Winterhalter, B. Kanawati, A. Römpp, B. Spengler, A. Mellouki, G. Le Bras, P. Chaimbault, G. K. Moortgat, *Atmos. Chem. Phys.* **2008**, *8*, 2667–2699.
- [6] M. Hallquist, J. C. Wenger, U. Baltensperger, Y. Rudich, D. Simpson, M. Claeys, J. Dommen, N. M. Donahue, C. George, A. H. Goldstein, et al., *Atmos. Chem. Phys.* **2009**, *9*, 5155–5236.
- [7] Y. Sakamoto, S. Inomata, J. Hirokawa, *J. Phys. Chem. A* **2013**, *117*, 12912–12921.
- [8] C. A. Taatjes, D. E. Shallcross, C. J. Percival, *Phys. Chem. Chem. Phys.* **2014**, *16*, 1704–1718.
- [9] E. Miliordos, S. S. Xantheas, *Angew. Chem. Int. Ed.* **2016**, *55*, 1015–1019.
- [10] B. J. Finlayson, J. N. Pitts, H. Akimoto, *Chem. Phys. Lett.* **1972**, *12*, 495–498.
- [11] O. Welz, J. D. Savee, D. L. Osborn, S. S. Vasu, C. J. Percival, D. E. Shallcross, C. A. Taatjes, *Science* **2012**, *335*, 204–207.
- [12] C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, D. L. Osborn, E. P. F. Lee, J. M. Dyke, D. W. K. Mok, D. E. Shallcross, C. J. Percival, *Phys. Chem. Chem. Phys.* **2012**, *14*, 10391.
- [13] O. Welz, A. J. Eskola, L. Sheps, B. Rotavera, J. D. Savee, A. M. Scheer, D. L. Osborn, D. Lowe, A. Murray Booth, P. Xiao, et al., *Angew. Chem. Int. Ed.* **2014**, *126*, 4635–4638.
- [14] D. L. Osborn, C. A. Taatjes, *Int. Rev. Phys. Chem.* **2015**, *34*, 309–360.
- [15] M. Jang, *Science* **2002**, *298*, 814–817.
- [16] R. A. Cox, S. A. Penkett, *Nature* **1971**, *230*, 321–322.
- [17] R. L. Mauldin III, T. Berndt, M. Sipilä, P. Paasonen, T. Petäjä, S. Kim, T. Kurtén, F. Stratmann, V.-M. Kerminen, M. Kulmala, *Nature* **2012**, *488*, 193–196.
- [18] M. Boy, D. Mogensen, S. Smolander, L. Zhou, T. Nieminen, P. Paasonen, C. Plass-Dülmer, M. Sipilä, T. Petäjä, L. Mauldin, et al., *Atmos. Chem. Phys.* **2013**, *13*, 3865–3879.
- [19] D. Stone, M. Blitz, L. Daubney, N. U. M. Howes, P. Seakins, *Phys. Chem. Chem. Phys.* **2013**, *16*, 1139–1149.
- [20] W. Chao, J.-T. Hsieh, C.-H. Chang, J. J.-M. Lin, *Science* **2015**, *347*, 751–754.
- [21] T. R. Lewis, M. A. Blitz, D. E. Heard, P. W. Seakins, *Phys. Chem. Chem. Phys.* **2015**, *17*, 4859–4863.
- [22] M. C. Smith, C.-H. Chang, W. Chao, L.-C. Lin, K. Takahashi, K. A. Boering, J. J.-M. Lin, *J. Phys. Chem. Lett.* **2015**, *6*, 2708–2713.
- [23] A. B. Ryzhkov, P. A. Ariya, *Physical Chemistry Chemical Physics* **2004**, *6*, 5042.
- [24] H.-L. Huang, W. Chao, J. J.-M. Lin, *Proc. Nat. Acad. Sci.* **2015**, *112*, 10857–10862.

- [25] C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke, D. K. W. Mok, et al., *Science* **2013**, *340*, 177–180.
- [26] L. Sheps, A. M. Scully, K. Au, *Phys. Chem. Chem. Phys.* **2014**, *16*, 26701–26706.
- [27] Y. Zhao, L. M. Wingen, V. Perraud, J. Greaves, B. J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.* **2015**, *17*, 12500–12514.
- [28] E. Sanhueza, *Tellus B* **2001**, *53*, 122–132.
- [29] I. Bey, D. J. Jacob, R. M. Yantosca, J. A. Logan, B. D. Field, A. M. Fiore, Q. Li, H. Y. Liu, L. J. Mickley, M. G. Schultz, *J. Geophys. Res.* **2001**, *106*, 23073–23095.
- [30] T. A. Crisp, B. M. Lerner, E. J. Williams, P. K. Quinn, T. S. Bates, T. H. Bertram, *J. Geophys. Res.* **2014**, *119*, 6897–6915.
- [31] E. S. Foreman, K. M. Kapnas, Y. Jou, J. Kalinowski, D. Feng, R. B. Gerber, C. Murray, *Phys. Chem. Chem. Phys.* **2015**, *17*, 32539–32546.
- [32] A. J. Eskola, D. Wojcik-Pastuszka, E. Ratajczak, R. S. Timonen, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1416.
- [33] H. Huang, A. J. Eskola, C. A. Taatjes, *J. Phys. Chem. Lett.* **2012**, *3*, 3399–3403.
- [34] H. Huang, B. Rotavera, A. J. Eskola, C. A. Taatjes, *J. Phys. Chem. Lett.* **2013**, *4*, 3824–3824.
- [35] W.-L. Ting, C.-H. Chang, Y.-F. Lee, H. Matsui, Y.-P. Lee, J. J.-M. Lin, *J. Chem. Phys.* **2014**, *141*, 104308.
- [36] Y.-H. Huang, L.-W. Chen, Y.-P. Lee, *J. Phys. Chem. Lett.* **2015**, *6*, 4610–4615.
- [37] L. Sheps, *J. Phys. Chem. Lett.* **2013**, *4*, 4201–4205.
- [38] W.-L. Ting, Y.-H. Chen, W. Chao, M. C. Smith, J. J.-M. Lin, *Phys. Chem. Chem. Phys.* **2014**, *16*, 10438–10443.
- [39] E. S. Foreman, C. Murray, *J. Phys. Chem. A* **2015**, *119*, 8981–8990.
- [40] P. Spietz, J. C. Gómez Martín, J. P. Burrows, *J. Photochem. Photobio. A* **2005**, *176*, 50–67.
- [41] H. J. Tobias, P. J. Ziemann, *J. Phys. Chem. A* **2001**, *105*, 6129–6135.
- [42] W. V. Turner, S. Gäb, *J. Org. Chem.* **1992**, *57*, 1610–1613.
- [43] B. Ruscic, *J. Phys. Chem. A* **2013**, *117*, 11940–11953.
- [44] A. Ianniello, F. Spataro, G. Esposito, I. Allegrini, M. Hu, T. Zhu, *Atmos. Chem. Phys.* **2011**, *11*, 10803–10822.
- [45] L. T. Molina, S. Madronich, J. S. Gaffney, E. Apel, B. de Foy, J. Fast, R. Ferrare, S. Herndon, J. L. Jimenez, B. Lamb, et al., *Atmos. Chem. Phys.* **2010**, *10*, 8697–8760.
- [46] L. A. Morio, K. A. Hooper, J. Brittingham, T.-H. Li, R. E. Gordon, B. J. Turpin, D. L. Laskin, *Toxicol. Appl. Pharm.* **2001**, *177*, 188–199.
- [47] J. B. Burkholder, S. P. Sander, J. Abbatt, J. R. Barker, R. E. Huie, C. E. Kolb, M. J. Kurylo, V. L. Orkin, D. M. Wilmoth, and P. H. Wine “Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18,” JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, 2015 [Http://jpldataeval.jpl.nasa.gov](http://jpldataeval.jpl.nasa.gov)
- [48] A. V. Jackson, C. N. Hewitt, *Crit. Rev. Env. Sci. Tech.* **1999**, *29*, 175–228.
- [49] M. Baasandorj, D. K. Papanastasiou, R. K. Talukdar, A. S. Hasson, J. B. Burkholder, *Physical Chemistry Chemical Physics* **2010**, *12*, 12101.
- [50] M. C. Smith, W. Chao, K. Takahashi, K. A. Boering, J. J.-M. Lin, *J. Phys. Chem. A* **2016**, DOI 10.1021/acs.jpca.5b12124.



Novel sink for Criegee Intermediates: Rate constants for the reaction of the simplest Criegee Intermediate CH_2OO with HCl and HNO_3 were directly measured using broadband transient absorption spectroscopy. Both reactions occur at or near the collision limit.

Keywords: kinetics, UV/Vis spectroscopy, atmospheric chemistry, gas-phase reactions, ab initio calculations

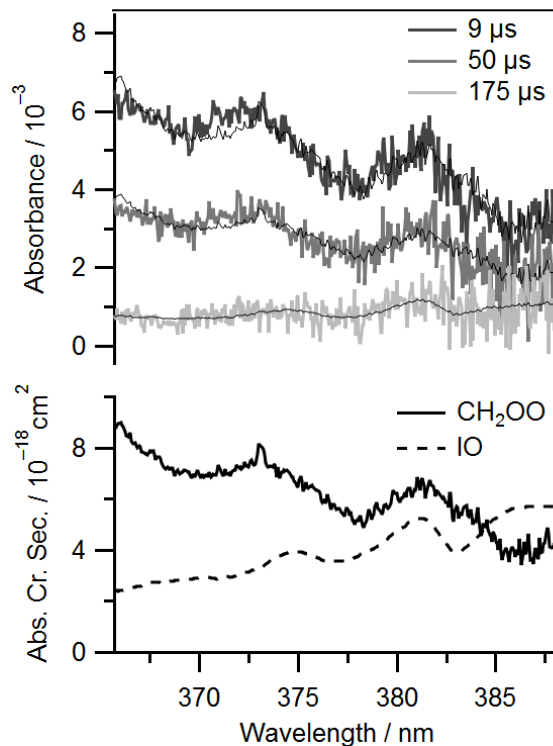


Figure 1: Top: Absorbance transients at several time delays in the absence of acid. The experimental absorbance at each time delay is shown in gray. Fits used to extract the CH_2OO and IO concentrations are overlaid in black. Bottom: Absorption cross sections for CH_2OO (solid) and IO (dashed).

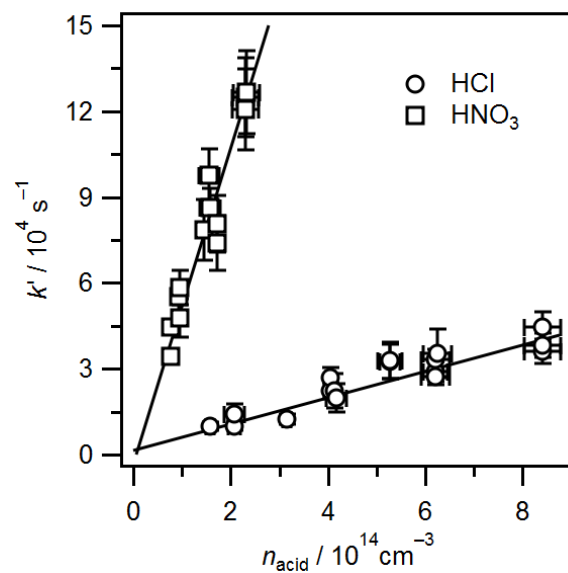


Figure 2: Pseudo-first order plot of the of CH_2OO loss rates as a function of HCl (circles) and HNO_3 (squares) concentrations.

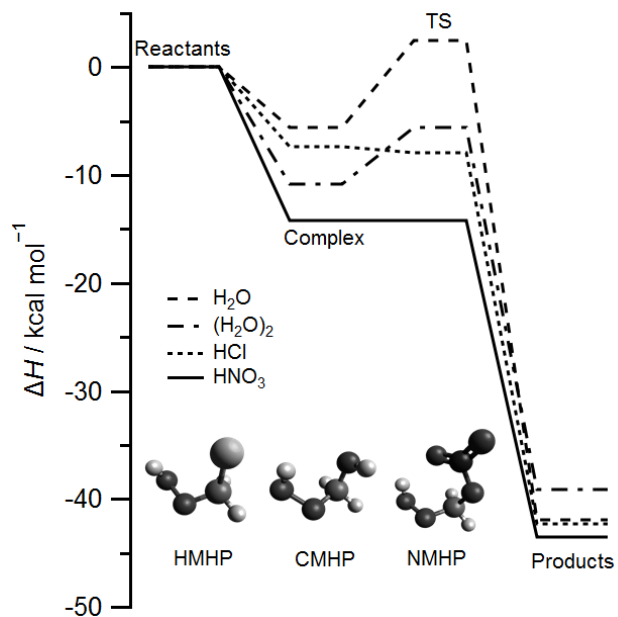


Figure 3: Enthalpy changes (at 0 K) for the reactions of CH_2OO with H_2O (dash), $(\text{H}_2\text{O})_2$ (dot-dash), HCl (dots), and HNO_3 (solid) to form HMHP (left), HMHP + H_2O , CMHP (center), and NMHP (right).

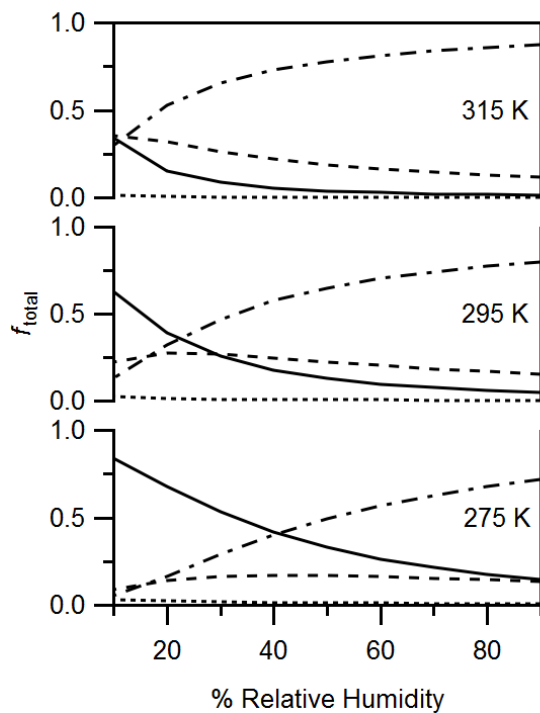


Figure 4: Fractional contribution of each species to the total loss rate of CH_2OO loss rates due to reaction with HNO_3 (solid), $(\text{H}_2\text{O})_2$ (dot-dash), HCl (dots), and H_2O (dash), as a function of relative humidity and temperature.