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Permalink
https://escholarship.org/uc/item/93b1q53c

Journal
Angewandte Chemie, 128(35)

ISSN
0044-8249

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Publication Date
2016-08-22

DOI
10.1002/ange.201604662

Peer reviewed
Kinetics and Atmospheric Implications of the Reactions between Criegee Intermediates and the Inorganic Acids HCl and HNO$_3$

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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, CH₂OO, with two inorganic acids, HCl and HNO₃, both of which are present in polluted urban atmospheres. Both reactions are fast: at 295 K, reactions of CH₂OO with HCl and HNO₃ have rate constants of 4.6×10⁻¹¹ cm³ s⁻¹ and 5.4×10⁻¹⁰ cm³ 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 HNO₃ in particular are likely to be competitive with water vapor in polluted urban areas under conditions of modest relative humidity.
Carbonyl oxides (R₁R₂COO), known as Criegee intermediates (CIs), are formed in the atmosphere by alkene ozonolysis.\textsuperscript{[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.\textsuperscript{[3–9]} Unimolecular dissociation of vibrationally hot nascent CIs is a major source of night-time OH in the troposphere.\textsuperscript{[3,10]} Stabilized CIs react quickly (\(\sim 10^{-12}–10^{-10} \text{ cm}^3 \text{ s}^{-1}\)) with many trace atmospheric gases.\textsuperscript{[8,11–14]} Under humid conditions, reaction with SO₂ leads to H₂SO₄ which catalyzes growth of atmospheric aerosol particles.\textsuperscript{[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, CH₂OO, with H₂O are small (\(k_{\text{water}} \approx 10^{-17}–10^{-15} \text{ cm}^3 \text{ s}^{-1}\)),\textsuperscript{[11,19–21]} the reaction with (H₂O)₂ is significantly faster (\(k_{\text{dimer}} \approx 10^{-11} \text{ cm}^3 \text{ s}^{-1}\))\textsuperscript{[20–23]} and shows a strong negative temperature dependence.\textsuperscript{[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.\textsuperscript{[22,24]}

The importance of CI reactions with trace species in the atmosphere requires that they be competitive with water vapor, or more specifically, (H₂O)₂. CI reactivity is dependent on structure. CH₃CHO can exist as syn and anti conformers and conformer-specific reactivity has been demonstrated towards SO₂ and H₂O.\textsuperscript{[25,26]} (CH₃)₂COO is likely to survive longer in humid environments than CH₂OO and play a greater role in H₂SO₄ production, as it is comparatively unreactive to H₂O and (H₂O)₂, but more reactive to SO₂.\textsuperscript{[24]} Alternatively, reactions with trace species may be locally important if they are sufficiently fast. For example, the reactions of organic acids with CH₂OO and CH₃CHO can be 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.\textsuperscript{[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. 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.

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

\[ \text{CH}_2\text{OO} + \text{HCl} \rightarrow \text{products} \]  
\[ \text{R1} \]

\[ \text{CH}_2\text{OO} + \text{HNO}_3 \rightarrow \text{products} \]  
\[ \text{R2} \]

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. Pulsed laser photolysis of CH₂I₂ at 355 nm generated CH₂I radicals, which reacted rapidly with O₂ to produce CH₂OO in high yield. 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 Ŵ–
Selectivity is important because secondary chemistry results in formation of IO, 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,

\[ A(\lambda)/l = n_{\text{CH}_2\text{OO}} \sigma_{\text{CH}_2\text{OO}}(\lambda) + n_{\text{IO}} \sigma_{\text{IO}}(\lambda) + C \]  

(E1)

which return absolute concentrations of \text{CH}_2\text{OO} and IO at each photolysis-probe time delay. The vibrational progression is washed out at longer delays as \text{CH}_2\text{OO} 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% \text{CH}_2\text{I}_2, ~15% \text{O}_2, and \text{N}_2 balance). Maximum \text{CH}_2\text{OO} 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, \text{CH}_2\text{OO} is consumed by self-reaction, reaction with other radical species (I and \text{CH}_2\text{IOO}), or by reaction with the \text{CH}_2\text{I}_2 precursor, which was present in excess. The observed loss of \text{CH}_2\text{OO} showed single exponential behavior, allowing the assumption of pseudo-first-order conditions,

\[ n_{\text{CH}_2\text{OO}}(t) \approx n_{\text{CH}_2\text{OO}}(0) \exp(-k'_0 t) \]  

(E3)

where \( k'_0 \) represents the background, acid-free loss rate that can be attributed largely to reaction with the \text{CH}_2\text{I}_2 precursor (see Supporting Information). The observed loss rates, \( k' \), increased rapidly with increasing acid concentration and remained mono-exponential. The increase in the \text{CH}_2\text{OO} 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 $k'_{\text{acid}}$ as a function of the acid concentration, $n_{\text{acid}}$. Linear fits to the data shown in Figure 2 yield bimolecular rate constants of $k_{\text{HCl}} = (4.6 \pm 1) \times 10^{-11}$ cm$^3$ s$^{-1}$ and $k_{\text{HNO}_3} = (5.4 \pm 1) \times 10^{-10}$ cm$^3$ s$^{-1}$, where the uncertainties (1σ) in the measured rate constants are dominated by the uncertainties in the acid concentrations. The reaction between CH$_2$OO 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$_2$O, 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$_2$OO with H$_2$O, (H$_2$O)$_2$, HCl and HNO$_3$. The calculated reaction profiles are shown in Figure 3. All four reactions are exothermic by $\sim$40 kcal mol$^{-1}$ and form substituted hydroperoxides. The barrier for reaction with H$_2$O is 2.4 kcal mol$^{-1}$ above the reactant asymptote, and this tight TS is the rate-limiting bottleneck. For the reaction with (H$_2$O)$_2$, there is a submerged barrier of 5.2 kcal mol$^{-1}$ relative to the Cl–(H$_2$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$_2$O 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 CI + (H₂O)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 CI + HNO₃ 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 HNO₃ 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 CH₂OO by water vapor, which depends on temperature and RH. There are several conflicting factors at play; higher temperatures increase the saturation vapor pressure of H₂O, 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 H₂O reaction is unknown, although Arrhenius-like behavior is expected. The temperature dependences of $k_{\text{HCl}}$ and $k_{\text{HNO}_3}$ are not presently known and are assumed to be constant. Figure 4 shows estimated CH₂OO loss rates due to reaction with H₂O, (H₂O)₂, HCl, and HNO₃ at 275–315 K, over a RH range spanning 10–90% using average concentrations of 8 ppbv and 20 ppbv for HCl and HNO₃, respectively, which are representative of Southern California.[30] We estimate reactions with HCl and HNO₃ contribute to atmospheric loss rates for CH₂OO of 9.2 s⁻¹ and 270 s⁻¹. Under all conditions of temperature and RH, HCl makes a minor contribution to the CH₂OO loss rate. Reaction with HNO₃, however, becomes increasingly competitive with (H₂O)₂ as the RH decreases, and dominates under dry conditions (RH < 30%). The importance of HNO₃ as a reactive sink for CH₂OO 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 [R(X)OOH (X = Cl, 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$_2$O$_2$ 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 OH + R(X)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 R(X)O$_2$ radicals and H$_2$O 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$_2$OO, reactions with inorganic acids may be even more significant for substituted CIs, which show reduced reactivity relative to CH$_2$OO towards H$_2$O and (H$_2$O)$_2$.$^{[24]}$ Quantum chemistry calculations (see Supporting Information) suggest that the reactions of HNO$_3$ with CH$_3$CHOO and (CH$_3$)$_2$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 (CH$_3$)$_2$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

**Novel sink for Criegee Intermediates:** Rate constants for the reaction of the simplest Criegee Intermediate CH₂OO with HCl and HNO₃ 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$_2$OO and IO concentrations are overlaid in black. Bottom: Absorption cross sections for CH$_2$OO (solid) and IO (dashed).
Figure 2: Pseudo-first order plot of the of CH$_2$OO 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$_2$OO with H$_2$O (dash), (H$_2$O)$_2$(dot-dash), HCl (dots), and HNO$_3$(solid) to form HMHP(left), HMHP + H$_2$O, CMHP (center), and NMHP (right).
Figure 4: Fractional contribution of each species to the total loss rate of CH$_2$OO loss rates due to reaction with HNO$_3$ (solid), (H$_2$O)$_2$ (dot-dash), HCl (dots), and H$_2$O (dash), as a function of relative humidity and temperature.