Gas-Phase Reactions **Hot Paper**

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Reactions between Criegee Intermediates and the Inorganic Acids HCl and HNO_3: Kinetics and Atmospheric Implications

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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 to be the dominant sink for some CIs, although reactions with trace species that are sufficiently rapid can be locally competitive. Herein, 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, the reactions of CH_2OO with HCl and HNO_3 have rate constants of 4.6×10^{-11} $cm^3 s^{-1}$ and 5.4×10^{-10} $cm^3 s^{-1}$, respectively. Complementary quantum-chemical calculations show that these reactions form substituted hydroperoxides with no energy barrier. The results suggest that reactions of CIs with HNO_3 in particular are likely to be competitive with those 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 the formation of new particles.[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 (ca. 10^{-12}–10^{-10} $cm^3 s^{-1}$) with many trace atmospheric gases.[8,11–14] Under humid conditions, reaction with SO_2 leads to H_2SO_4, which catalyzes the 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 the reported rate constants for the reaction of the simplest CI, CH_2OO, with H_2O are small ($k_{water}\approx10^{-17}$–10^{-15} $cm^3 s^{-1}$),[11,19–21] the reaction with $(H_2O)_2$ is significantly faster ($k_{dimer}\approx10^{-11}$ $cm^3 s^{-1}$)[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, $(H_2O)_2$. 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] $(CH_3)_2COO$ 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 towards H_2O and $(H_2O)_2$, but more reactive towards 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 ($k_{R(O)OH} > 10^{-10}$ $cm^3 s^{-1}$), and are likely to make a significant contribution to acid removal in equatorial regions and high northern latitudes.[13]

Whereas a great deal of attention has been focused on reactions of CIs with SO_2, NO_2, 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 the 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 HNO_3 have both biogenic and anthropogenic sources (see the Supporting Information) and are present in the troposphere at mixing ratios similar to those of organic acids and SO_2 (parts per billion by volume (ppbv) to parts per trillion by volume (pptv)), with peak concentrations found in coastal and polluted urban areas.[28–30]

Herein, we report direct measurements of the rate constants for the reactions of the simplest CI with HCl and HNO_3:

$$CH_2OO + HCl \rightarrow \text{products} \qquad (R1)$$

$$CH_2OO + HNO_3 \rightarrow \text{products} \qquad (R2)$$

The experimental kinetic measurements were supported by quantum-chemical calculations that elucidated the reaction mechanisms and identified the products as substituted hydroperoxides. Reaction R2, in particular, was found to be sufficiently fast to be locally competitive with the reaction 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 CH_2I_2 at 355 nm generated CH_2I radicals, which reacted rapidly with O_2 to produce CH_2OO in high yield.[32–36] Transient absorption spectroscopy using

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broadband pulsed LEDs was used to measure the time-dependent concentration of CH_2OO 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 CH_2OO $\tilde{B}$–$\tilde{X}$ transition.[31,37,38] Selectivity is important because secondary chemistry results in the 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 were fit to linear combinations of reference spectra,[31,40]

$$A(\lambda)/l = n_{CH_2OO}\sigma_{CH_2OO}(\lambda) + n_{IO}\sigma_{IO}(\lambda) + C \tag{E1}$$

which return absolute concentrations of CH_2OO and IO at each photolysis-probe time delay. The vibrational progression is washed out at longer delays as CH_2OO is consumed and the absorption that is due to IO, which is formed and removed far more slowly, grows in intensity.

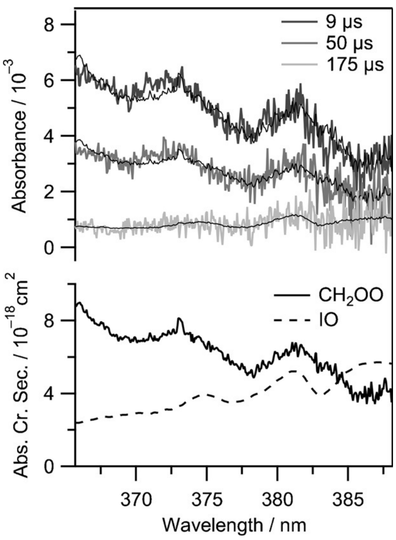

Figure 1. Top: Absorbance transients at several time delays in the absence of acid. The experimental absorbance at each time delay is shown in gray. Fits used to extract the CH_2OO and IO concentrations are overlaid in black. Bottom: Absorption cross-sections for CH_2OO (——) and IO (-----).

Kinetic measurements were made at total cell pressures of 27–35 torr (ca. 1% CH_2I_2, ca. 15% O_2, and N_2 balance). Maximum CH_2OO concentrations were reached promptly (< 10 μs) after photolysis, and the kinetic data were obtained from analysis of loss only, which is generally slower than formation. In the absence of acid, CH_2OO is consumed through self-reaction, reactions with other radical species (I and CH_2IOO), or by reaction with the CH_2I_2 precursor, which was present in excess. The observed loss of CH_2OO showed single-exponential behavior, allowing the assumption of pseudo-first-order conditions,

$$n_{CH_2OO}(t) \approx n_{CH_2OO}(0)\exp(-k_0' t) \tag{E2}$$

where k_0' represents the background, acid-free loss rate that can be attributed largely to reactions with the CH_2I_2 precursor (see the Supporting Information). The observed loss rate, k', increased rapidly with increasing acid concentration and remained mono-exponential. The increase in the CH_2OO loss rate over the acid-free loss rate is attributed to reaction with the acid, that is, $k_{acid}' = k' - k_0'$ where $k_{acid}' = k_{acid}n_{acid}$.

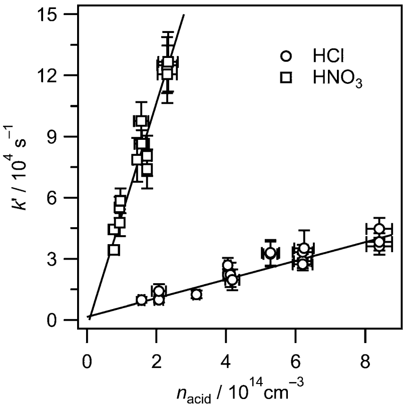

Figure 2. Pseudo-first-order plot of the CH_2OO loss rates as a function of HCl (○) and HNO_3 (□) concentration.

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 $k_{HCl} = (4.6\pm1)\times10^{-11}\,cm^3\,s^{-1}$ and $k_{HNO_3} = (5.4\pm1)\times10^{-10}\,cm^3\,s^{-1}$, where the uncertainties (1σ) in the measured rate constants are dominated by the uncertainties in the acid concentrations. The reaction between CH_2OO and HNO_3 is fast, and its rate 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 the rates of reactions between the C13 Criegee intermediate and acidic organic compounds.[41] The suggestion that the transition states (TSs) are highly polar was supported by quantum-chemical calculations, as described below.

Quantum-chemical 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, $(H_2O)_2$, HCl, and HNO_3. The calculated reaction profiles are shown in Figure 3. All four reactions are exothermic by about 40 kcal mol^{-1} and form substituted hydroperoxides. The barrier for reaction with H_2O is 2.4 kcal mol^{-1} above the reactant asymptote, and this tight TS is the rate-limiting bottleneck. For the reaction with $(H_2O)_2$, there is a submerged barrier of 5.2 kcal mol^{-1} relative to the CI–$(H_2O)_2$ complex, which is 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

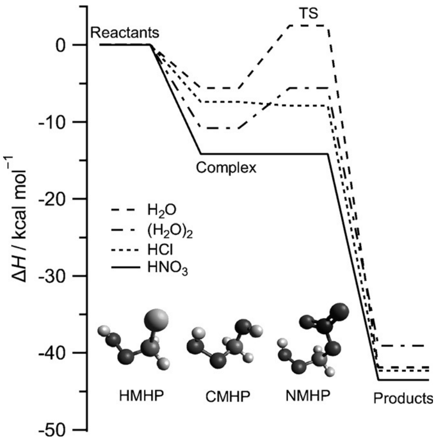

Figure 3. Enthalpy changes (at 0 K) for the reactions of CH_2OO with H_2O (-----), $(H_2O)_2$ (–•–•), HCl (•••••), and HNO_3 (——) to form HMHP (left), HMHP and H_2O, CMHP (center), and NMHP (right).

completely upon inclusion of zero-point energy corrections. The H_2O and HCl reactions proceed through 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+$(H_2O)_2$ reaction, the apparent mechanism involves two concerted hydrogen atom transfers; that is, the hydroxy group and the hydroperoxy hydrogen atom end up in different water molecules. The CI+HNO_3 reaction forms the analogous nitrooxymethyl hydroperoxide (NMHP), although the mechanism is not insertion, as 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 as that of the latter reaction 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 the 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 decrease 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 insignificant. Figure 4 shows the estimated CH_2OO loss rates that are due to reaction with H_2O, $(H_2O)_2$, HCl, and HNO_3 at 275–315 K over a RH range of 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 estimated that 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 $(H_2O)_2$ as the RH decreases, and dominates under dry conditions (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. The HNO_3 concentration is expected to be significant, although lower than in 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_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 OH+R(X)O is assumed to occur with unity quantum yield.[47] Peroxides are also key oxidants of sulfur species in clouds/fogs and facilitators of rainwater acidification and particle growth.[48] Reactions with OH to form $R(X)O_2$ radicals and H_2O are also possible.[49]

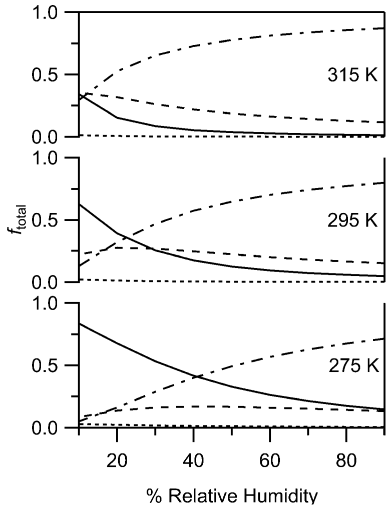

Figure 4. Fractional contribution of each species to the total CH_2OO loss rate by reaction with HNO_3 (——), $(H_2O)_2$ (–•–•), HCl (•••••), and H_2O (-----), as a function of relative humidity and temperature.

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 towards H_2O and $(H_2O)_2$ relative to CH_2OO.[24] Quantum-chemical calculations (see the Supporting Information) suggest that the reactions of HNO_3 with CH_3CHOO and $(CH_3)_2COO$ 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 $(CH_3)_2COO$, where thermal unimolecular dissociation is rapid, and particularly so at lower temperatures.[50] Measuring the temperature dependence as well as the 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.

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