

import warmer water, decrease the supply of nutrients, or decrease the volume of zooplankton carried by the California Current.

The future consequences of the observed decline in zooplankton volume are closely tied to the question of causality. If the decline is part of a natural cycle that reverses in coming years, then any impact may be similarly transient. On the other hand, if the zooplankton decline is anthropogenic or is a natural trend of longer duration, then the large magnitude of the response is of great concern for the coastal ecosystem. The suppression of nutrient supply by enhanced stratification is not a mechanism confined to coastal oceans. If there is a global temperature rise of 1° to 2°C in the next 40 years and stratification increases globally, the biological impacts could be devastating. Our study also demonstrates that climate studies dominated by short-term process-oriented experiments cannot

simply be extrapolated to decadal time scales, where the balance of terms is different from monthly or seasonal balances.

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2. From 1949 until 1978, zooplankton were measured by oblique net tows with the use of a ring net (mouth diameter 1 m) and a towing bridle [P. Smith, *CalCOFI Atlas No. 20* (State of California, 1974)]. Target depths were 140 m from 1949 to 1969 and 210 m from 1969 to the present. Because zooplankton abundance decreases with depth, this change could have biased our post-1969 averages downward. The systematic effect of this change is not known, but it would be less than a 33% decrease in the post-1969 estimates even under the extreme assumption of no zooplankton below 140 m. After 1978, a "bongo" net was introduced that had been shown to collect more plankton per unit volume of water filtered, hence any systematic effect of this change would be an increase rather than the observed decrease in zooplankton abundance [J. A. McGowan and D. Brown, *Scripps Inst. Ref.* 66-23 (1966); E. Brinton and A. W. Townsend, *CalCOFI Rep. vol. XXII* (1981)].
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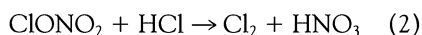
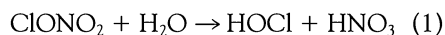
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The Reaction of ClONO₂ with Submicrometer Sulfuric Acid Aerosol

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The measured reaction probability, γ , for the reaction of chlorine nitrate (ClONO₂) with 60 percent (by weight) sulfuric acid aerosol increases monotonically with particle size at 250 kelvin. The reacto-diffusive length (ℓ , the effective liquid depth over which reaction occurs) derived from these experiments is 0.037 ± 0.007 micrometer (95 percent confidence level for precision). The reaction probability for the reaction of ClONO₂ with 60 percent sulfuric acid aerosol doped with $\sim 7 \times 10^{-4}$ M hydrochloric acid at 250 kelvin is larger by about a factor of 4 than in the absence of hydrochloric acid and varies less with particle size ($\ell = 0.009 \pm 0.005$ micrometer). These results provide a test of the theory for gas-particle reactions and further insight into the reactivity of atmospheric aerosol.

Both ClONO₂ and HCl are relatively stable, gas-phase reservoirs of Cl in the stratosphere. Mechanisms that release Cl from these reservoirs enhance O₃ destruction by accelerating the Cl catalytic destruction cycles for O₃. The following heterogeneous reactions are important mechanisms for converting reservoir species into products that are readily photolyzed and that release Cl atoms:



These reactions contribute to the winter-spring polar O₃ loss (1) and to the global destruction of O₃ during volcanic aerosol loadings (2, 3).

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Although the uptake of ClONO₂ by bulk liquid H₂SO₄ solutions has been studied extensively (4–6), the reaction probability of ClONO₂ with submicrometer H₂SO₄ aerosol is unknown, and the parameters necessary to extrapolate the bulk results to the small aerosol that is characteristic of the stratosphere are uncertain. In this report, we describe measurements of the variation of the ClONO₂ reaction probability with particle size for submicrometer-sized H₂SO₄ aerosol, with and without HCl. These results provide an unprecedented test for the theory of the kinetics of gas-particle reactions and a basis for understanding the reactivity of atmospheric aerosol.

The rate of processing of a gas-phase reactant (x) by monodisperse aerosol is given by

$$\frac{d[x]}{dt} = -\gamma c \pi r^2 [P][x] \quad (3)$$

where γ is the reaction probability, c is the mean molecular speed of x in the gas phase,

r is the particle radius, $[P]$ is the particle concentration, and $[x]$ is the concentration of x in the gas phase. For clarity, we do not discuss the small corrections for the diffusion of the gas-phase reactant to the particle (7). The reaction probability (γ) is given by

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{c}{4HRT\sqrt{k'D_\ell} \left[\coth\left(\frac{r}{\ell}\right) - \frac{\ell}{r} \right]} \quad (4)$$

where α is the accommodation coefficient (the fraction of collisions that lead to accommodation by the liquid surface), H is the effective Henry's law coefficient (ratio of the liquid-phase concentration to the gas-phase concentration at equilibrium), R is Boltzmann's constant, T is the absolute temperature, k^1 is the first-order rate coefficient for loss of x in the liquid phase, D_ℓ is the diffusion coefficient of species x in the liquid, and ℓ is the reacto-diffusive length defined as $\ell = \sqrt{D_\ell/k^1}$ (3, 8, 9). The reacto-diffusive length ℓ is the effective depth of liquid in which reaction occurs. Equation 4 demonstrates that the resistance to loss of the gas-phase species ($1/\gamma$) is the sum of the interfacial resistance ($1/\alpha$) and the reactive resistance (second term on the right side of Eq. 4). For small reaction probabilities ($\gamma \ll \alpha$), the reaction probability is given to a good approximation by

$$\gamma \approx \frac{4HRT\sqrt{k'D_\ell} \left[\coth\left(\frac{r}{\ell}\right) - \frac{\ell}{r} \right]}{c} = \gamma_0 \left[\coth\left(\frac{r}{\ell}\right) - \frac{\ell}{r} \right] \quad (5)$$

where γ_0 is the bulk reaction probability.

When ℓ is small relative to the size of the particle ($\ell \ll r$), the reactant is consumed

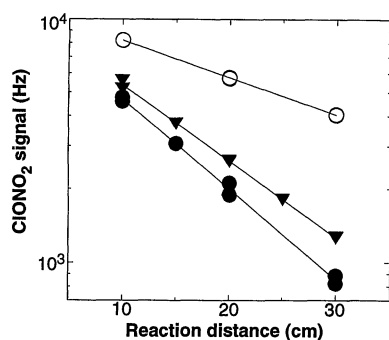


Fig. 1. Plot of ClONO_2 signal as a function of reaction distance. Loss due to reaction on the wall (open circles) and two different aerosol samples (filled circles and inverted triangles) are shown: 5.0×10^5 particles per cubic centimeter (log-normal radius distribution parameters [see (11)]: $r_{\text{pk}} = 0.26 \mu\text{m}$ and $\log s = 0.08$) and 6.7×10^5 particles per cubic centimeter ($r_{\text{pk}} = 0.28 \mu\text{m}$ and $\log s = 0.09$). Reaction conditions: $p = 630$ torr N_2 , $T = 250$ K, and average flow velocity $= 1.3 \text{ cm s}^{-1}$.

very close to the liquid surface and the size-dependent term $[\coth(r/\ell) - (\ell/r)]$ approaches unity. In this case, γ is independent of the particle radius, and the rate of processing of the gas-phase reactant is proportional to the aerosol surface area. When ℓ is larger than the size of the particle ($\ell \gg r$), the reactant is consumed throughout the volume of the particle, and the size-dependent term approaches $r/(3\ell)$. In this case, γ is proportional to the radius of the aerosol and the rate of processing is proportional to the aerosol volume.

For measurements on bulk substrates, the reaction is usually not volume-limited (liquid depth $\gg \ell$), and measurement of γ yields the product $H\sqrt{k^1 D_\ell}$ (Eq. 5). In general, the individual parameters, H , k^1 , and D_ℓ are not known and are difficult to measure independently. Therefore, it is usually not possible to determine ℓ (which is needed to calculate the processing rate by small particles) from the bulk reaction probability.

Measurements on bulk H_2SO_4 solutions (4–6) show that the reactive uptake of ClONO_2 increases strongly as the amount of water in solution increases. Hanson and Ravishankara (6) have modeled the variation of the ClONO_2 reaction probability as a function of $[\text{HCl}]$ in H_2SO_4 - H_2O solutions and extracted the ratio of the rate coefficients for the solution-phase reactions of ClONO_2 with H_2O and HCl . They estimated the first-order rate coefficient for the hydrolysis reaction ($k^1 \approx 100 \text{ s}^{-1}$, 60% H_2SO_4 , 202 K) by assuming that the HCl reaction ($\text{ClONO}_2 + \text{Cl}^-$) occurs at the diffusion-limited rate. This result, combined with an estimate for the liquid-phase diffusion coefficient, gave a rough estimate for ℓ of

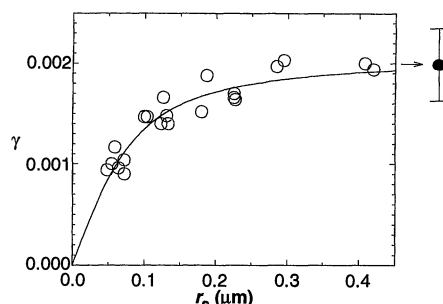


Fig. 2. Reaction probability (γ) for $\text{ClONO}_2 + 60\%$ H_2SO_4 aerosol at 250 K as a function of surface area-weighted particle radius, r_s ($r_s = r_{\text{pk}} \exp [2.5 (\ln s)^2]$ for a log-normal distribution). Each point is the average of two to four measurements for a range of particle number densities. The precision of the measurements of γ is about $\pm 15\%$ at the 95% confidence level. The line is a fit of Eq. 5 to the data, giving $\gamma_0 = 0.0021 \pm 0.0002$ and $\ell = 0.037 \pm 0.007 \mu\text{m}$. The quoted errors are the 95% confidence intervals for precision. The filled circle is the reaction probability measured on a bulk 60% H_2SO_4 sample at 250 K ($\gamma = 0.002 \pm 0.0004$) with the use of the wetted-wall experimental procedure (5).

$\sim 0.05 \mu\text{m}$ for ClONO_2 hydrolysis in 60% (by weight) H_2SO_4 at 202 K (6).

We measured reaction probabilities of ClONO_2 with H_2SO_4 aerosol by monitoring the concentration of ClONO_2 at the exit of a cylindrical, laminar-flow reactor as a function of the contact distance with the aerosol. The experimental apparatus and procedures used in this work are similar to those used to measure the reactive uptake of N_2O_5 by H_2SO_4 aerosol (10). Additional experimental details specific to the present study are given in (11).

The ClONO_2 signal (the count rate of the NO_3^- ion produced in the reaction of I^- with ClONO_2 in the chemical ionization mass spectrometer) decreased exponentially as a function of reaction distance (Fig. 1) in accord with a simple first-order loss process. We calculated the first-order rate coefficients for loss on the aerosol from the observed decays by solving the continuity equation for the reactor dynamics (12), and γ was calculated from the measured rate coefficients and the particle surface-area concentrations. The reaction probabilities for $\text{ClONO}_2 + 60\%$ H_2SO_4 at 250 K increase as the size of the particles increases (Fig. 2). A fit of the size dependence to Eq. 5 gives an ℓ value of $0.037 \pm 0.007 \mu\text{m}$. The reaction probability measured on bulk liquid with the same composition is in excellent agreement with the reaction probability for large particles ($r > 0.3 \mu\text{m}$).

The reaction probabilities for $\text{ClONO}_2 + 60\%$ H_2SO_4 doped with HCl (the contribution due to $\text{ClONO}_2 + \text{H}_2\text{O}$ is $< 10\%$) do not vary significantly with par-

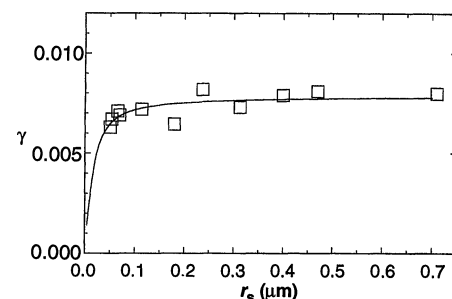


Fig. 3. Reaction probability (γ) for $\text{ClONO}_2 + 60\%$ H_2SO_4 aerosol doped with HCl ($\approx 7 \times 10^{-4} \text{ M}$) at 250 K as a function of surface area-weighted particle radius, r_s . The line is a fit of Eq. 5 to the data, giving $\gamma_0 = 0.0079 \pm 0.0008$ and $\ell = 0.009 \pm 0.005 \mu\text{m}$.

ticle size down to about $0.05 \mu\text{m}$ (Fig. 3), giving a smaller ℓ value of $0.009 \pm 0.005 \mu\text{m}$. The value of γ for these conditions (0.0079 ± 0.0008 with $[\text{HCl}] \sim 6.6 \times 10^{-4} \text{ M}$) (13) is about four times the value measured without HCl present. The addition of HCl increased k^1 without significantly changing the solubility (H) or D_ℓ of ClONO_2 . According to the theory for gas-particle reactions (Eq. 5), ℓ should have varied inversely with the change in the bulk reaction probability [$\gamma \propto (k^1)^{1/2}$ and $\ell \propto (k^1)^{-1/2}$]. The fourfold increase in γ upon HCl addition was associated with a fourfold decrease in ℓ , as predicted by theory. The fourfold increase in γ also suggests that the value of k^1 for the reaction of ClONO_2 and 60% H_2SO_4 with $\sim 7 \times 10^{-4} \text{ M}$ HCl is about 16 times the value of k^1 due to hydrolysis [$\gamma \propto (k^1)^{1/2}$, Eq. 5] (14).

Because of experimental difficulties at low temperatures, we measured reaction probabilities at 250 K, which is about 50 K warmer than the stratospherically relevant temperature for 60% H_2SO_4 (15). However, we believe that the value of ℓ for the $\text{ClONO}_2 + \text{H}_2\text{O}$ reaction is not a strong function of temperature at these temperatures (16).

Typical background stratospheric aerosol has a surface area-weighted mean radius of about $0.2 \mu\text{m}$ (17) and a composition ranging from 40 to 80% H_2SO_4 (18). Volcanic aerosol has an even larger mean radius (2). Because the value of ℓ for ClONO_2 uptake by 60% H_2SO_4 is less than one-quarter of the mean aerosol size, the ClONO_2 processing rate scales approximately with the aerosol surface area, and the γ is given to a good approximation by γ_0 . For a typical concentration of HCl in the stratosphere ($\sim 2 \times 10^9$ molecules per cubic centimeter), a 60% H_2SO_4 particle will contain about 10^{-5} M HCl (3). The first-order loss rate coefficients for ClONO_2 hydrolysis and HCl reaction are nearly comparable for these conditions and the

HCl reaction decreases the ClONO_2 reaction depth slightly. The contribution of the HCl reaction increases in more dilute stratospheric aerosol because of the strong increase in the HCl solubility (19).

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11. Typical carrier gas (N_2 or $\text{N}_2\text{-O}_2$) flow velocities in the reactor were 1 to 1.5 cm s^{-1} (pressure = 620 torr) and $[\text{ClONO}_2]_0$ ranged from 10^{12} to 10^{13} molecules per cubic centimeter. We determined the aerosol size distribution and the surface-area concentration by measuring the aerosol number density and the extinction of ultraviolet light (200 to 400 nm) by the aerosol. The aerosol is characterized by a log-normal radius distribution (10) given by

$$dN = \frac{N}{\sqrt{2\pi} \log s} \exp \left\{ \frac{[-\log(r_{pk}/r)]^2}{2(\log s)^2} \right\} d \log r$$
 where N is the number of particles, r_{pk} is the peak radius, and s is the geometric standard deviation. The H_2SO_4 aerosol was generated by passing a portion of the carrier gas over hot concentrated H_2SO_4 and then into a cool region. The aerosol size was varied by changing the gas flow rate and the temperature of the liquid H_2SO_4 . We adjusted the composition of the aerosol by passing the aerosol through a conditioner containing a 59.9% H_2SO_4 solution (by weight) held at the same temperature as the flow tube reactor. The conditioner was either a 35-cm-long cylindrical tube with an inside diameter of 3 cm half filled with the solution or a coiled (~ 0.5 cm inside diameter by 100 cm long) glass tube coated with the solution. On the basis of model calculations of the liquid-to-aerosol vapor transfer rate within the conditioners, the composition of the aerosol exiting the conditioners was within 1% (by weight) of the conditioner liquid composition. For the experiments with HCl, the carrier gas was bubbled through a 59.9% H_2SO_4 solution (by weight) doped with 7.8×10^{-4} M HCl, before mixing with the aerosol. The aerosol stream was then passed through the coiled conditioner, which was charged with the same solution as the bubbler. The conditioner and bubbler transferred both H_2O and HCl vapor to the aerosol and were maintained at the same temperature (± 1 K) as the reactor by circulating chilled methanol through their jackets.
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14. In our experiments, $[\text{HCl}]$ was $\approx 6.6 \times 10^{-4}$ M and the activity of H_2O was ≈ 0.12 (that is, $[\text{H}_2\text{O}] \sim 6.4$ M). Therefore, the ratio of the second-order rate coefficient for $\text{ClONO}_2 + \text{HCl}$ to that of $\text{ClONO}_2 + \text{H}_2\text{O}$ is approximately 1.5×10^5 , which is comparable to the ratio extracted from measurements at 202 K ($\sim 1 \times 10^5$) (6). We did not account for a possible surface reaction between HCl-Cl^- and ClONO_2 (6). It is expected that the surface reaction will contribute $<15\%$ to the reactivity in these experiments. By using the measured ℓ value and an estimate of 1×10^{-6} $\text{cm}^2 \text{s}^{-1}$ for the ClONO_2 diffusion constant, we derive estimates for the hydrolysis and HCl rate coefficients of 1×10^4 and $1.5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$, respectively, for 60% H_2SO_4 at 250 K. The HCl rate coefficient is in the diffusion-limited regime.
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16. The results from the present study suggest that the HCl reaction is diffusion-limited at 250 K in 60% H_2SO_4 solution [see (14)]. In this case, the rate coefficient is proportional to the product of the capture radius and the diffusion constant. If we assume that the capture radius for the $\text{Cl}^- + \text{ClONO}_2$ reaction is independent of temperature, we calculate that ℓ is 0.03 μm for ClONO_2 hydrolysis in 60% H_2SO_4 at 202 K.
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20. This work was supported by the National Oceanic and Atmospheric Administration Global and Climate Change Program.

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Rapid Deformation of the South Flank of Kilauea Volcano, Hawaii

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The south flank of Kilauea volcano has experienced two large [magnitude (M) 7.2 and M 6.1] earthquakes in the past two decades. Global Positioning System measurements conducted between 1990 and 1993 reveal seaward displacements of Kilauea's central south flank at rates of up to about 10 centimeters per year. In contrast, the northern side of the volcano and the distal ends of the south flank did not displace significantly. The observations can be explained by slip on a low-angle fault beneath the south flank combined with dilation deep within Kilauea's rift system, both at rates of at least 15 centimeters per year.

Kilauea volcano, on the island of Hawaii, presents a major seismic as well as volcanic hazard (1). A M 8 earthquake shook the region in 1868 (2). A M 7.2 earthquake in 1975 (3) and a M 6.1 quake in 1989 (4, 5) were caused by seaward motion on a subhorizontal fault that may coincide with the base of the volcanic edifice (6). Swarms of shallow earthquakes accompany intrusions of magma into either of Kilauea's two rift zones (Fig. 1), but these earthquakes are typically small ($M \leq 4$) and nondestructive (7). Earthquakes south of the rift zones have focal depths of 5 to 13 km (7), leading some to suggest that slip occurs on multiple parallel faults (5). However, precise relative relocations place many of the earthquakes on a well-defined northward dipping fault (8). This result, combined with the fact that the larger events occur within a narrow depth range, suggests that there is a single low-

angle fault zone 7 to 9 km beneath Kilauea's south flank.

The structure of the rift system at depths of more than a few kilometers is uncertain because few earthquakes occur below 5 km. This lack of seismicity might indicate that deformation is concentrated in the shallow rift system, or simply that elevated temperatures at depth inhibit brittle failure. Delaney and colleagues (9) suggested that subsidence observed on leveling lines across the rift zones was caused by steady dilation at depths of ~ 4 to 9 km. Dvorak and colleagues (10) argued that deep dilation is not required and that the data can be explained by episodic shallow intrusions in combination with slip on a low-angle fault at 6 km. Horizontal deformation measurements on the north flank could distinguish between competing models of south-flank and rift zone kinematics. Electronic distance measurements (EDM) required line-of-sight visibility, so that it was previously not possible to measure baselines on the heavily forested north flank of Kilauea (11, 12). Furthermore, it was not possible to determine displacements relative to sites removed from active volcanism and seismicity. EDM data for the period 1983 to 1991 have been interpreted to show seaward motion of the

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