splitting could be caused by a ~0.5 Å decrease in the 7.0 Å separation of Mg atoms in the special pair (*1*) (prediction of the simple exciton model with the dipole-dipole approximation). The calculations of Thompson and Fajer (*36*), which take into account the charge-resonance states of P, indicate that the observed blue and red shifts (150 cm^{-1}) of P_+ and P_- are not simply a result of the reduction of the average macrocycle separation distance. Higher level calculations, which take into account, for example, the ruffling of the macrocycles and the orientation of the ring I acetyl group (*37*), may provide plausible structures for the "new special pair."

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Evidence for Photochemical Formation of H_2O_2 and Oxidation of SO_2 in Authentic Fog Water

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When samples of rain and fog water were exposed to ultraviolet and visible light, reactive transients such as hydrogen peroxide were formed and dissolved organic matter and sulfur dioxide were depleted. These results, in conjunction with those from previous studies, imply that dissolved organic compounds and transition metals such as iron ions are involved in the photochemical formation of hydrogen peroxide and other photooxidants in atmospheric waters.

Hydrogen peroxide (H_2O_2) is a key component in the conversion of dissolved sulfur dioxide (SO_2) to sulfuric acid (H_2SO_4), which is a main contributor to acid precipitation (*1–5*). Therefore, there is a great deal of interest in understanding the mechanisms responsible for the formation and degradation of H_2O_2 in the atmospheric liquids. We present evidence for the efficient iron-catalyzed photochemical generation of H_2O_2, the oxidation of dissolved SO_2, and the depletion of oxalic acid and other organic pollutants in fog water.

The occurrence of H_2O_2 in atmospheric water droplets is currently thought to be attributable to the dissolution of gaseous H_2O_2 and disproportionation of HO_2 radicals, which are also scavenged from the gas phase (*6–9*). Recently, however, it has been reported that H_2O_2 is formed by the photolysis of complexes of Fe(III) with oxalic, glyoxalic, and pyruvic acids under the conditions typical of acidified atmospheric waters (*10–13*). The mechanism of the photochemical formation of H_2O_2 is

$$\mathrm{Fe(III)\text{-}L} \xrightarrow{h\nu} \mathrm{Fe(II)} + \mathrm{L}^{\cdot} \qquad (1)$$

$$\mathrm{L}^{\cdot} + \mathrm{O_2} \rightarrow \mathrm{O_2}^{\cdot -} + \text{oxidized L} \qquad (2)$$

$$2\mathrm{O_2}^{\cdot -} + 2\mathrm{H}^+ \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \qquad (3)$$

where $h\nu$ is the energy of a photon, L stands for organic ligands, and $L^{\cdot}$ for an organic radical.

The absorption of a photon by an Fe(III)-organo complex [Fe(III)-L] results in electron transfer from an organic ligand to the ferric ion, producing a ferrous ion and an organic radical. In the presence of O_2, the organic radical can reduce O_2 to form a superoxide ion ($O_2^{\cdot -}$). The $O_2^{\cdot -}$ and its conjugate acid, the hydroperoxyl radical ($HO_2^{\cdot}$), readily undergo a disproportionation reaction to yield H_2O_2 and O_2 in aqueous solutions (*14*).

Dissolved iron species and organic ligands, such as oxalic, pyruvic, and glyoxalic acids, are common constituents of cloud, rain, and fog droplets (*12, 15–22*). Speciation calculations (*10–13*) have shown that the Fe(III) exists predominantly in complexed forms with organic ligands. Therefore, it is reasonable to postulate that $HO_2^{\cdot}/O_2^{\cdot -}$ and its reaction product, H_2O_2, may also be photochemically formed in atmospheric waters by the above mechanism.

To test this postulation, we collected rain, snow, and fog waters in Dübendorf, Switzerland, and stored them at 4°C until used. The samples were filtered (0.45 μm) and analyzed immediately before irradiation. We observed the photochemical gen-

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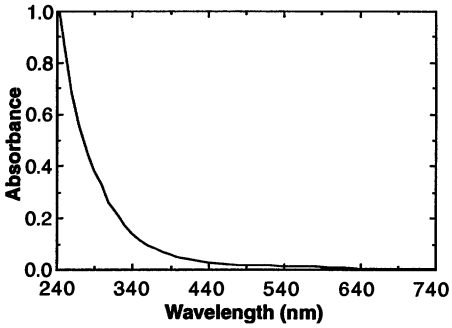

Fig. 1. Absorbance spectrum (path length of 10 cm) of filtered fog water used for irradiation. The absorption spectrum has the characteristic profile of dissolved organic carbon (DOC) or Fe(III)-oxalato complexes in waters (*10, 29*). Analytic data have indicated that carboxylic acids and aldehydes with low molecular weights, such as formic, acetic, oxalic, and pyruvic acids; formaldehyde; and acetaldehyde, are predominant constituents of the measured DOC (*12, 30*). The absorption is likely to be caused by organic chromophores and transition-metal complexes. There is essentially no absorption above 600 nm.

Table 1. Concentrations of the relevant constituents in fog water. Sampling performed with screen collector (*32, 33*) on 28 October 1989 (temperature = 5°C). Sample at pH = 3.7 with a liquid water content of 2.6 × 10^{-4} liter m^{-3}.

Constituent	Concentration (μM)
Fe(III)	1.7
Fe(II)	14
H_2O_2	1.2
DOC	12*
Oxalate	4.8
Sulfite	79
Sulfate	86
Formaldehyde	59

*This measurement is in milligrams per liter.

eration of H_2O_2 in samples of these atmospheric waters. Most experiments were performed with fog waters because they were more active than the rain or snow samples. Typical concentrations of the relevant constituents are given in Table 1 and the absorption spectrum of the fog water is in Fig. 1.

Irradiations were carried out in a water-cooled merry-go-round reactor (MGRR). Samples of fog water (20 ml) saturated with air in separate quartz tubes were exposed to the 313-nm radiation of a 500-W Hg lamp (*10–12*). Although this monochromatic light source does not simulate the solar spectrum, the ratio of the initial rate of H_2O_2 formation in the MGRR to that in September sunlight at a light exposure of 0.3 E m^{-2} (400 to 700 nm) was 1/(5.5 ± 1.3) for solutions containing Fe(III)-oxalato, glyoxalato, and pyruvato complexes.

The depletion of oxalic acid and the simultaneous net accumulation of H_2O_2 with irradiation time is shown in Fig. 2A. The fog water sample contained sulfite (Table 1), which is oxidized in the presence of H_2O_2 (Fig. 2B). The initial rate of SO_2 oxidation is 6 μM $hour^{-1}$ in the MGRR.

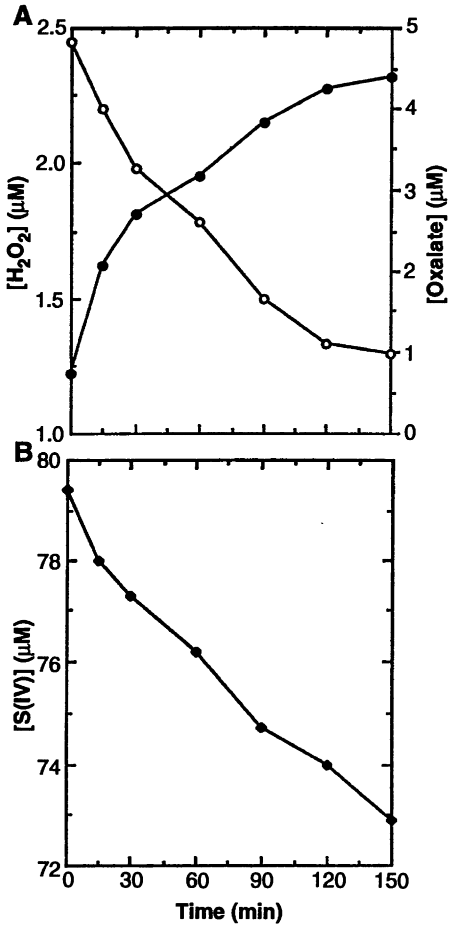

Fig. 2. (**A**) Photochemical formation of H_2O_2 and decomposition of oxalic acid in fog water. Closed circles, H_2O_2; open circles, oxalate. (**B**) Photooxidation of dissolved SO_2 in fog water. Irradiation performed with 313-nm light in MGRR (volume-averaged incident light intensity = 1.2 μE $liter^{-1}$ s^{-1}, valerophenone actinometer). Analysis of H_2O_2 performed immediately after irradiation with the horseradish peroxidase (POD)-*N*,*N*-diethyl-*p*-phenylenediamine (DPD) method (*31*), which is also somewhat sensitive to organic peroxides. The latter can be distinguished from H_2O_2 by examination of the reaction kinetics of the color development or by the use of catalase. Application of these techniques during our experiments indicated that no detectable organic peroxides were present in the irradiated samples. Interference of free Fe^{2+} is inhibited by DOC present in fog water. Oxalate and dissolved sulfite were analyzed by ion chromatography (*10*).

Experimental and theoretical evidence currently indicates that several oxidants are important in the conversion of dissolved SO_2 to H_2SO_4 in the atmospheric aqueous phase. If the pH of water is greater than 5, ozone (O_3) is probably the major oxidant. However, if the pH is lower, H_2O_2 is most likely the dominant oxidant (*1–3*). Computer simulations suggest that, at pH 3, H_2O_2 pathways account for more than 99% of the oxidation of S(IV) to S(VI) (*23*). The pH of the fog water sample used in this experiment was 3.7, and the sample was not exposed to O_3. Furthermore, in the dark (thermal control) experiments, no measurable oxidation of dissolved SO_2 was observed. We can assume that all the SO_2 converted into sulfate was oxidized by H_2O_2 and other reactive transients, such as OH radicals. From this work, we cannot distinguish the contribution of H_2O_2 and other reactive transients to the oxidation of SO_2. The total amount of the reactive transients formed must correspond to the sum of the net accumulated concentration of H_2O_2 formed and the concentration of dissolved SO_2 oxidized to sulfate (Fig. 3).

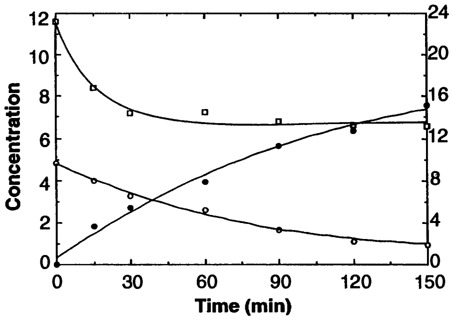

Fig. 3. Total concentration of reactive transients formed (right axis) and degradation of DOC and oxalic acid (left axis). Closed circles, total reactive transients (microequivalents) (the sum of H_2O_2 formed and bisulfite depleted); open circles, oxalic acid (micromolar); open squares, DOC (milligrams per liter). The DOC was measured with wet chemistry and an ultraviolet oxidation technique on a Dohrman (Santa Clara, California) DC-80 carbon analyzer.

After correction for the amount of H_2O_2 consumed, the initial rate of the formation of total reactive transients with 313-nm irradiation is 14 μeq $hour^{-1}$. This value corresponds to a rate of reactive transients formation of 80 ± 20 μeq $hour^{-1}$ in autumnal solar-noon sunlight, which is greater than that expected from gas-to-droplet transfer (*9, 24*). This rate of formation is also greater by a factor of 3 than that from the irradiation of a model solution containing 1.7 μM Fe(III) and 5 μM oxalic acid at pH 3.7. The rest may be contributed by other organic ligands, such as pyruvic and glyoxalic acids, as well as by the catalytic reaction of Fe(II) (*10–13*). The accumulation rate of H_2O_2 increases with the concentration of oxalic acid and with other types of dissolved organic carbon (DOC) because a number of dissolved atmospheric organic compounds can form inner or outer coordination complexes with Fe(III) and some of them absorb sunlight themselves (*10–13, 25, 26*). In other fog waters, higher or lower oxalate and DOC concentrations can occur, and the photochemical formation rate of H_2O_2 varies correspondingly.

A significant amount of H_2O_2 is photochemically formed, and dissolved SO_2 is oxidized in real fog water. With consideration of previous studies, one may suggest that the photochemical cycling of Fe(III)-Fe(II) complexes is involved in this process. The Fe(II) that is formed simultaneously with H_2O_2 can further produce OH radicals by a photo-Fenton reaction (*10–12, 27, 28*).

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Aqueous-Phase Photochemical Formation of Peroxides in Authentic Cloud and Fog Waters

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Gas-to-drop partitioning of hydrogen peroxide and its precursor, the hydroperoxyl radical ($HO_2^{\cdot}$), has been considered the predominant or sole source of hydrogen peroxide in atmospheric water drops. However, atmospheric water can absorb solar ultraviolet radiation, which initiates the photoformation of peroxides (primarily hydrogen peroxide). Measurements of peroxide photoformation rates in authentic atmospheric water samples demonstrate that aqueous-phase photochemical reactions are a significant, and in some cases dominant, source of hydrogen peroxide to cloud and fog drops. This additional source could significantly change the current understanding, and hence, the models, of sulfuric acid deposition because hydrogen peroxide is the limiting reagent in the dominant pathway for the oxidation of sulfur dioxide to sulfuric acid in the troposphere over eastern North America.

Interest in the sources and reactions of peroxides and other oxidants in atmospheric water drops has been motivated by questions that are related to chemical transformations in the troposphere (*1–4*), such as the (i) formation of sulfuric acid, (ii) destruction of ozone, (iii) redox cycling of iron, and (iv) oxidation of organic compounds. The two main sources of hydrogen peroxide (H_2O_2) to cloud and fog drops are aqueous-phase photoformation, which has received little attention, and gas-to-drop partitioning of gas-phase H_2O_2 and its precursor, $HO_2^{\cdot}$, which has been extensively studied. This report focuses on aqueous-phase photochemical sources.

Cloud and fog water samples were obtained from researchers at different sites in the United States and from aircraft flights over Ontario, Canada. Samples were stored in the dark at 2° to 10°C and were untreated except for filtration (0.5-μm Teflon) immediately upon receipt. Peroxides were quantified by the methods of Kok and coworkers (*5*).

Atmospheric waters contain constituents that absorb solar ultraviolet light (*6, 7*). This absorption initiates aqueous-phase photochemical reactions that form peroxides. The peroxide photoformation, and its approach to a photostationary state, that was typically observed is shown in Fig. 1. Speciation studies of the peroxides that were formed showed that in all of the eight cloud and fog waters studied, at least 97% of the detectable peroxides were H_2O_2.

Typical equinox-normalized photoformation rates of H_2O_2 in 44 cloud and fog water samples from six different locations in North America ranged from 0.4 to 3.5 μM hour^{-1}, with rates as high as 5.8 μM hour^{-1} (Table 1) (*8*). By comparison, field studies of clouds over the eastern United States and Canada have shown that all (~100%) winter cloud water samples, most (58 to 100%) spring and fall samples, and few (3 to 7%) summer samples had H_2O_2 concentrations <5 μM (*9, 10*). Moreover, H_2O_2 concentrations in all of the winter cloud water samples were <1 μM (*9*). Thus, the photoformation rates reported in Table 1 demonstrate that the aqueous-phase photochemical formation of H_2O_2 is a significant, and in some cases dominant, source of H_2O_2 to atmospheric water drops. Quantum yields for H_2O_2 formation on exposure to 313-nm light were typically 6 × 10^{-4} to 5 × 10^{-3} (Table 1) (*8*).

The aqueous-phase H_2O_2 photoformation rate was linearly dependent on the irradiance of the simulated sunlight for all seven of the atmospheric waters samples that were studied (Fig. 2). This is consistent with our theoretical predictions that the rate of aqueous-phase H_2O_2 photoformation from reactions of $HO_2^{\cdot}$ or $O_2^{\cdot -}$ with itself or with reductants [such as Fe(II) and

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