Sulfur dioxide as a source of condensation nuclei in the upper troposphere of the Pacific Ocean

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Abstract. The NASA Pacific Exploratory Mission-West A (PEM-West A) experiment in 1991 covered large portions of the northwestern Pacific Ocean troposphere and a transect of the subtropical troposphere of the North Pacific Ocean. Sulfur dioxide consistently increased with altitude from the surface to 11 km except for a few cases of anthropogenic inputs confined to the planetary boundary layer. Using the PEM West A data set for SO2, sulfate, and calculated OH over the central Pacific Ocean, we have estimated the impacts of the SO2 on the formation of condensation nuclei and the lifetimes of SO2 and sulfate for this region.

Introduction

Sulfur dioxide (SO2) in the atmosphere has been studied extensively for its transformation into sulfuric acid (H2SO4) which has a significant role in aerosol formation. The acidic sulfate aerosol, in turn, affects the radiation balance of the earth [Ramanathan et al., 1989], acidic precipitation, and acts as a reaction medium for stratospheric chemistry affecting ozone destruction. Extensive SO2 measurements have been made at the surface and aloft over the continents and nearby offshore marine regions in relation to the acidic precipitation problem. Relatively little effort has been devoted to SO2 measurements in remote marine areas, except near the ocean surface in conjunction with measurements of dimethyl sulfide (DMS) used to test Charlson et al.'s [1987] hypothesis regarding DMS as a possible source of aerosol that could modify climate.

During the Global Atmospheric Measurements of Environmental Trace Aerosols and Gases (GAMETAG) project in 1978, Maroulis et al. [1980] found that SO2 over the central Pacific Ocean was higher in the free troposphere than in the marine boundary layer. More recently, Thornton et al. [1993] found a similar pattern in SO2 but with slightly lower concentrations. Chatfield and Crutzen [1984] used a cloud pumping model to explain the higher concentrations of SO2 in the mid-free troposphere in conjunction with the theory that DMS was the predominant source for SO2 in the remote marine atmosphere. However, typical DMS concentrations observed in the mid-free troposphere were less than 3 parts per trillion by volume (pptv) except in convective clouds [Andreae et al., 1985; Thornton et al., 1993]. Since the maximum contribution of DMS to SO2 occurs at photochemical equilibrium, the maximum contribution to SO2 from DMS is 18 pptv. This assumes that the conversion of DMS to SO2 is 100% efficient. If the efficiency is substantially less than 100% as suggested by Bandy et al. [1992a], the importance of DMS as a precursor of SO2 in the mid and upper troposphere could be much less than the steady-state upper limit.

An alternative explanation to the greater SO2 levels in the remote free troposphere than in the boundary layer relies on long-range transport of SO2 from continental regions and entrainment of SO2 into the boundary layer [Maroulis et al., 1980; Andreae et al., 1988; Thornton and Bandy, 1993; Thornton et al., 1993]. In the boundary layer, SO2 can be lost by dry deposition to the ocean and to the surfaces of atmospheric aerosols. It also can be removed by its reaction with OH radical which has significantly higher levels in the boundary layer than in the free troposphere. While significant long-range transport of aerosols from Asia to the central Pacific have been demonstrated during the spring season [Prospero et al., 1985], there have been few simultaneous measurements of SO2 and aerosols in the free troposphere.

Volcanoes are a natural source of SO2 associated with continents, but they are primarily located near the Pacific Ocean rim and are concentrated in the tropical zone. Some of these volcanoes extend above the boundary layer although most of them in the tropical and subtropical regions have tops in the upper portions of the mixed layer. During 1991 the cataclysmic eruptions of Mount Pinatubo had a major impact on the stratosphere with an estimated 20 Mt of sulfur injected. Little is known about the effect of direct emissions of SO2 to the troposphere and the mixing of stratospheric air containing SO2 from Pinatubo into the upper troposphere.

The Pacific Exploratory Mission-West A (PEM-West A) experiment surveyed the western and central Pacific Ocean troposphere during September-October 1991 [Hoell et al., this issue; Bachmeier et al., this issue]. This experiment's first
phase was to observe the condition of the western Pacific troposphere during a period when it was not impacted by continental outflows from Asia. However, this period also coincided with substantial convective activity associated with typhoons. During PEM-West A we measured SO₂ along with DMS, carbonyl sulfide (OCS), and carbon disulfide (CS₂) aboard the NASA Ames Research Center DC-8 aircraft. On this platform we were able to sample at altitudes up to 12 km compared to 7 km for measurements made on the NCAR Electra [Maroulis et al., 1980; Thornton et al., 1993].

The most significant feature of the SO₂ vertical distribution during PEM-West A was the increase of SO₂ with altitude above the mixed layer for both continental and central Pacific regions and for equatorial and high-latitude regions. The SO₂ distribution apparently was influenced by long-range transport from convective activity over and near continents, by injections of stratospheric air into the troposphere, and possibly by tropospheric emissions from Pinatubo. The elevated SO₂ levels at higher altitudes result in a reservoir of oxidized sulfur in the upper troposphere that can be the precursor of a significant number of condensation nuclei (CN) and cloud condensation nuclei (CCN). These CN and CCN could have a wide spread effect on cloud formation over the Pacific Ocean.

**Experiment**

The SO₂ measurements were made by isotopic dilution gas chromatography/mass spectrometry with cryogenic sample collection and immediate analysis in flight. The details of the gas chromatography-mass spectrometry system with addition of an internal standard of isotopically labeled variants of the sulfur compounds being determined, have been described by Bandy et al. [1992b, 1993]. In short, the technique involves adding an isotopically labeled sulfur gas (e.g., $^{34}$SO₂) to the air sampling inlet as the air is drawn into the aircraft. During PEM-West A, three samples were obtained simultaneously from the same inlet manifold for the determination of SO₂, CS₂, DMS, and OCS. The sampling time was 3-4 min with a turnaround time of 6-7 min. Each of these three samples was enriched cryogenically with liquid argon and then injected onto its own column. The effluents of the columns were then switched to the mass spectrometer in a timed sequence to obtain a determination of each ambient sulfur analyte along with the corresponding enriched isotopomer.

The concentration of SO₂ in the ambient air was determined relative to the internal standard after correcting for the isotopic distribution of the ambient isotopomers. The cylinder containing the isotopically labeled SO₂ was prepared by Scott-Marr Incorporated (Riverside, California) from SO₂ containing 99.99 mol % $^{34}$S supplied by Icon Services (Summit, New Jersey). The working calibration cylinder had a concentration of 188 parts per billion by volume (ppbv), determined by comparison to a permeation tube maintained in our laboratory. Because the standard cylinder contained no detectable $^{33}$SO₂, we could easily check for contamination of the sampling manifold by adding zero air and $^{34}$SO₂ to the inlet, so that ambient air was excluded [Bandy et al., 1993].

The complete set of chemical and physical measurements made aboard the DC-8 is given in the overview paper describing the PEM-West A program [Hoell et al., this issue]. The data archive of the PEM-West A project was used to develop the correlations and supporting information given below. Sulfate measurements were made by Talbot et al. [1992] using large air volume samples with Teflon filter collection of the aerosols with postflight analysis by ion chromatography.

**Results and Discussion**

The major objective of this paper is to evaluate the impact of SO₂ in the middle and upper troposphere in terms of sulfate aerosol production. This evaluation treated a subset of the data for the subtropical and tropical regions which were expected to be relatively less impacted by anthropogenic point sources. To put these impacts into perspective, the general features of the SO₂ distribution found during PEM-West A are described below with some assessments of the possible sources of the SO₂.

The vertical distribution of SO₂ over the North Pacific Ocean during PEM-West A, had a gradient in which SO₂ increased with altitude at all latitudes (Figure 1). The gradient was greatest at high latitudes (Figure 1a, Amas to Alaska to Tokyo), but it was also evident in the tropics and subtropics (Figure 1a, flights from Guam and Wake). For the two missions near Taiwan and one over the Celebes Sea, the gradient with altitude was disrupted by local anthropogenic sources which increased SO₂ concentrations in the mixed layer (Figure 1b). Above the polluted mixed layer the increase in SO₂ with altitude is easily seen.

The two transit flights which passed over the Gulf of Alaska and west of the Aleutian archipelago intercepted stratospheric air [Browell et al., this issue]. During a penetration of a tropopause fold on the mission from Amas to Anchorage, SO₂ reached 630 ppbv and ozone exceeded 240 ppbv at 11 km. On the following day the aircraft flew through another stratospheric intrusion where SO₂ and O₃ reached 300 ppbv. Other chemical markers of the troposphere (e.g., CO, OCS, methane) decreased in the stratospheric air. Although only a small portion of the high-altitude flight leg between the Aleutians and Tokyo was clearly in stratospheric air, the effect of stratospheric air mixed with upper tropospheric air extended over a large portion of the flight track. For example, SO₂ and O₃ steadily decreased and OCS monotonically increased with distance from the stratospheric intrusion. A third case of stratospheric air mixed into the upper troposphere occurred on the transit flight from Hawaii to Amas. On that flight, both SO₂ and O₃ were less strongly enhanced than for the flights farther north. However, above 9.5 km, SO₂ and O₃ levels were approximately 130 ppbv and 70 ppbv and were highly correlated. These levels of SO₂ and O₃ were respectively twice the concentrations found outside this stratospherically influenced air.

In the tropical and subtropical regions over the North Pacific Ocean, no direct evidence of stratospheric air was observed. The height of the tropopause was more than 4 km above the highest aircraft altitudes, and there were no instances of elevated ozone [Browell et al., this issue]. However, SO₂ above 8 km ranged from 60 ppbv near the equator to over 400 ppbv between Guam and Wake (Figure 1a). Closer to the Asian continent, SO₂ concentrations exceeding 100 ppbv above 8 km did not appear to be directly related to the polluted air masses in the mixed layer below (Figure 1b). However, long-range transport from continental sources at altitudes over 8 km was indicated by the hydrocarbon and halocarbon data [Blake et al., this issue; Talbot et al., this issue].

To evaluate the impact of this vertical distribution of SO₂ on the central Pacific Ocean troposphere, we have taken a data...
subset for examining the oxidized sulfur cycle in a region that should be most representative of the remote Pacific troposphere. For this purpose we chose four missions: Guam to the equator near 160°E, Guam to the Celebes Sea, Guam to Wake Island, and Wake Island to Hawaii. The isentropic back trajectories for these missions indicated the air masses had been over the ocean for 10 days and no significant sinking motions were indicated except for one boundary layer point between Wake and Hawaii [Merrill, this issue]. For these four missions the data were categorized into four altitude bands, which were chosen based on the meteorological conditions and the altitudes of the level flight tracks: the mixed layer between 300 and 1000 m (> 850 hPa), the lower portion of the intermediate layer between 1 and 2.5 km (850 - 750 hPa), the upper portion of the intermediate layer between 2.5 and 5.5 km (750 - 550 hPa) and the transit legs in the mid-free troposphere at altitudes between 5.5 and 8.5 km (500 - 350 hPa), as well as between 8.5 and 11 km (330 - 225 hPa).

Even though the region east of Guam is far removed from the Asian continent, there was evidence of long-range transport of SO2 and other anthropogenic compounds for portions of the flight legs at 10-11 km east of Guam and east of Wake Island. Although the 10-day back trajectories did not indicate a recent passage over a continental region, sulfur dioxide levels ranged 400 pptv down to 150 pptv at >10 km, while sulfate aerosol loadings were 15-35 pptv (Figure 2). Nitric oxide levels were near 50 pptv and acetylene levels were near 100 pptv for the periods of elevated SO2.

Smyth et al. [this issue] have shown that the age of an air mass with respect to atmospheric processing can be correlated to the ratio of acetylene (C2H2) to carbon monoxide (CO). This correlation remains strong despite the effects of dilution of the anthropogenically impacted air with air that is representative of clean marine air. Because these two compounds have common combustion sources they should be good markers for these combustion sources of SO2. The highest concentrations of SO2 observed east of Guam and Wake Island, appear to be the result of long-range transport from anthropogenic sources as indicated by C2H2/CO values near 1 pptv/ppbv. The highest SO2 concentrations for the altitude ranges > 10 km, 8.5 to 10 km and < 2.5 km, coincided with high values of C2H2/CO (Figure 3).

As the C2H2/CO values decreased, SO2 concentrations decreased but not to zero even though the SO2 lifetime with respect to OH is about 5 times shorter than C2H2. For C2H2/CO values <0.5 pptv/ppbv, SO2 concentrations appeared to approach an asymptotic limit, decreasing from 70 pptv at 10 km to 35 pptv below 2.5 km. This indicated that there were additional sources for SO2 in aged remote marine air that were not associated with combustion (Figure 3). For the mixed layer the source is likely to be DMS.

Figure 1. SO2 data for Pacific Exploratory Mission-West A (PEM-West A) for several flight altitudes indicating SO2 concentration increasing with altitude above the mixed layer. (a) Flights in which boundary layer SO2 was not heavily impacted by recent emissions from anthropogenic sources. (b) Flights in which boundary layer SO2 was heavily impacted by pollution and biomass burning. Symbol, mean; bars, 1 standard deviation about the mean. Precision of the measurements was <4 pptv.

Figure 2. Aerosol sulfate concentrations for the central and tropical Pacific troposphere.
The contribution of DMS to SO$_2$ can be estimated for the altitudes above 10 km. The upper limit for the average DMS concentration at this altitude was 3 pptv for the flights considered here. This included the samples in which DMS was not detected but had an upper limit of 2 pptv. If the efficiency of conversion of DMS to SO$_2$ is unity, the estimated contribution of DMS to the SO$_2$ burden would be at most 18 pptv based on the relative reaction rates with OH. For the relatively clean air cases when the C$_2$H$_2$/CO ratio was <0.5 pptv/ppbv, greater than 80 pptv of SO$_2$ was observed above 10 km. Consequently, DMS does not appear to be a major source of SO$_2$ above 10 km.

Although the tropopause for the flights around Guam and between Guam and Hawaii was 4 to 5 km above the highest aircraft altitudes, a stratospheric source of SO$_2$ cannot be ruled out. Browell et al. [this issue] show how intrusions of stratospheric air at high latitudes could be advected at high altitudes around the east side of the central Pacific high. The low sulfate aerosol concentrations for the high-altitude tropical data were accompanied by $^7$Be concentrations of 90 to 190 fCi m$^{-3}$. For $^7$Be this is more than a tenfold dilution of the stratospheric air north of 43$^\circ$N where concentrations were over 2500 fCi m$^{-3}$. The background SO$_2$ in the tropical regions may be partially from stratospherically influenced air as identified by Browell et al. [this issue]. The SO$_2$ levels ranging from 200 to 630 pptv found in the stratospheric intrusions on the flights to and from Anchorage, Alaska, had C$_2$H$_2$/CO ratios < 0.1 pptv/ppbv. Approximately a fivefold to tenfold dilution of 200-630 pptv SO$_2$ concentrations observed south of Alaska would be needed to obtain the background levels observed in the tropical regions. Thus 20-63 pptv of the SO$_2$ found in stratospherically influenced air sampled in the Hawaii to Ames mission, can be attributed to transport from the stratosphere.

The contribution of the Pinatubo volcano directly to the central Pacific troposphere cannot be evaluated easily from this data set because of the absence of suitable tracers of the volcano. Prior to the explosions of June 1991 which affected the stratosphere, SO$_2$ emissions to the troposphere were estimated at 200 to 500 t/d. Taking into account the very long photochemical half-life of SO$_2$ above 10 km (>40 days) and several weeks of high activity, the volcano could make a significant contribution to the background SO$_2$ concentration over the Pacific.

**Lifetime of $\text{SO}_2$ in the Low-Latitude Free Troposphere**

With the large suite of chemical and physical variables measured during the PEM-West A missions, Davis et al. [this issue] computed OH concentrations along the flight tracks. Combining these OH values with the pressure, temperature, and water vapor data, we computed rates for the reaction between SO$_2$ and OH,

$$\text{SO}_2 + \text{OH} \rightarrow \text{HOSO}_2$$

using the rate constant from DeMore et al. [1992].

The distribution of SO$_2$ half-lives with respect to oxidation by OH for each altitude range is shown in Figure 4. Lifetimes of SO$_2$ increased from 10-15 days in the mixed layer to greater than 30 days above 10 km. For a 1-km boundary layer the 1/e time for dry deposition to the ocean surface would be 1.2 days for a dry deposition rate of 1 cm/s for SO$_2$ [Wesely and Hicks, 1977]. This implies that homogeneous gas phase production of sulfuric acid in the marine boundary layer is not significant compared to heterogeneous losses of SO$_2$.

At wind speeds $\geq$ 20 m/s, which are typical of high altitudes, air parcels could travel around the globe at 30$^\circ$ latitude.
Figure 4. Estimated SO2 lifetimes as a function of altitude based on oxidation by OH calculated from SO2 data and model results for OH concentrations.

...by the time the SO2 concentration decreases by 1/e. This makes it difficult to determine the origin of SO2 at high altitude. With lifetimes for SO2 of 20 days or more at altitudes over 10 km, long-range transport from anthropogenic and volcanic sources in east Asia would be possible. Large-scale convective events on the continent and strong cyclonic tropical storms could provide an avenue for fast transport to the upper free troposphere. Such transport for SO2, DMS, and CS2 was observed near the top of Typhoon Mireille when it was in the vicinity of Kyushu, Japan, where the Sakat-jima and Unzen volcanoes are located [Newell et al., this issue]. The lack of other tracers of volcanic emissions adds to the uncertainty because vertical transport in convective events can effectively remove particulate material with much less effect on gases.

Estimated Production of Sulfuric Acid From SO2 Reaction With OH

The production rates of sulfuric acid were calculated using the simple mechanism defined by reaction (1) and reactions (2) and (3) below:

\[
\text{HOSO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2 \quad (2)
\]

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4(\text{g}) \quad (3)
\]

The rate constants for reactions (1)-(2) were taken from DeMore et al. [1992]. For reaction (3) a rate constant of $1 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was used, which is more conservative than the upper limit of the rate constant of Wang et al. [1988] and DeMore et al. [1992]. For the water vapor levels observed in the upper troposphere over the central Pacific Ocean in the subtropical zone, reaction (3) reaches steady state within 2 min.

A rate of production of H$_2$SO$_4$ from OH oxidation of SO$_2$ was calculated for each SO$_2$ measurement where a calculated OH concentration was available. It was assumed that the air parcel in which the measurement was made remained intact for the 12-hour period. A local meridian time was calculated for each measurement and a local noon OH level was estimated assuming a sinusoidal function centered about local noon for a 12-hour daylight period. For most of the flight periods considered here, local meridian times of 1000 to 1600 hours and the corrections to local noon maximum OH were generally small. Assuming a sinusoidal distribution of OH over a 12-hour daylight period, an average OH level was calculated.

The distribution of SO$_2$ concentrations and the resulting H$_2$SO$_4$ production rates as a function of altitude are shown in Figures 5 and 6 respectively. At altitudes over 10 km this distribution of H$_2$SO$_4$ production rates reflects the combination of long-range transport of SO$_2$ from the west and the generally lower OH concentrations. The relatively lower H$_2$SO$_4$ production rates in the 8.5 to 10 km level reflects the influence of convective clouds reaching these altitudes in the tropical and subtropical latitudes. The vertically advected air in these clouds had much lower SO$_2$ levels, which were typical of the tropical marine boundary layer (Figure 1a), resulting in lower H$_2$SO$_4$ production rates.

Despite the long half-life of SO$_2$ with respect to OH, significant production of sulfuric acid can occur above 10 km over the central Pacific (Figure 6) when concentrations of SO$_2$ of 150 to 400 pptv are present as they were between Guam and Hawaii. To put this sulfuric acid production in perspective, it can be compared to the observed sulfate data for these flights. The sulfate aerosol data for these flights ranged from 15 to 35 pptv SO$_4$$^-$ at altitudes over 10 km (Figure 2).
Radiation and the formation of condensation nuclei, which could grow to cloud condensation nuclei [Charlson et al., 1992]. Most theories for nucleation and growth of sulfuric acid particles are based on thermodynamics [Jaeger-Vidor and Mirabel, 1988; Kreidenweiss and Seinfeld, 1988]. The formation of \( \text{H}_2\text{SO}_4 \) (g) and its hydrates is not well understood. Wang et al. [1988] measured the rate constant for the reaction (3) and attempted to explain the slow rate obtained on the basis of the high activation energy of the isomerization of the \( \text{SO}_2\cdot\text{H}_2\text{O} \) adduct to \( \text{H}_2\text{SO}_4\cdot\text{H}_2\text{O} \) as derived from the ab initio quantum mechanical calculations of Chen and Plummer [1985]. Popov et al. [1995] predicted that \( \text{SO}_2\cdot\text{H}_2\text{O} \) isomerize directly to \( \text{H}_2\text{SO}_4\cdot(n-1)\text{H}_2\text{O} \) where \( n > 1 \) without the formation of \( \text{H}_2\text{SO}_4\cdot\text{H}_2\text{O} \).

Recent laboratory experiments by Nolan [1987] indicated that the formation of \( \text{SO}_2\cdot\text{H}_2\text{O} \) from \( \text{SO}_2 \), \( \text{H}_2\text{O} \), and air with light in a flow system leads to an instantaneous response in an aqueous CN counter. The rate of CN formation was first order in \( \text{SO}_2 \) and was significantly faster than nucleation theory predicts. Weber et al. [1995a,b] reported nucleation rates of ultrafine particles in ambient air very well above that predicted by classic nucleation theory.

Sulfuric acid is generally recognized as the most effective moiety leading to the formation of new CN from the gas phase. The growth of acidic sulfate CN to form new CCN is limited in part by the surface area of preexisting particles which can scavenger the CN as well as \( \text{SO}_2 \). At high altitude the number and surface area of preexisting particles is much lower than in the mixed layer [Clarke, 1992]. This would allow sufficient opportunity for large numbers of new particles to form from gas phase sulfuric acid and its hydrates.

During May and June 1990, Clarke [1992] found ultrafine CN concentrations (3- to 15-nm diameter) of \( 10^4 \text{ cm}^{-3} \) from 8 to 10.5 km over the central Pacific Ocean with only very small fractions of surface-derived CN. At high altitudes the number and size of larger particles was relatively small compared to the lower troposphere. The number of particles with diameters greater than 15 nm was less than 10 cm\(^{-3} \) between 10°S and 25°N over the western Pacific Ocean. Clarke [1992] also found a strong negative correlation of ultrafine CN concentration with the surface area of particles over 150 nm diameter. With limited surface area available, scavenging of \( \text{H}_2\text{SO}_4 \) by preexisting aerosols appeared to be slow.

With \( \text{H}_2\text{SO}_4 \) formation rates of 1000 molecules cm\(^{-3} \) s\(^{-1} \) (2 pptv/d) at high altitudes based on the PEM-West A \( \text{SO}_2 \) data, the potential for creating large numbers of new particles exists. This rate would be sufficient to generate in 1-day the \( 10^4 \) to \( 10^5 \text{ CN cm}^{-3} \) observed by Clarke [1992] in the same region of the Pacific troposphere. It is interesting to note that Clarke’s measurements occurred a year before the Pinatubo eruption. The PEM-West A data suggest that transport of \( \text{SO}_2 \) into the upper troposphere over the Pacific may be a common event not dependent on direct volcanic inputs. For the tropical region data subset considered here, the tropopause was often 5 km above the highest flight level although mixing of stratospheric air to lower altitudes could be detected in a few cases [Browell et al., this issue].

**Conclusion**

The NASA-PEM West A 1991 field experiment provided a unique opportunity to evaluate the conversion of \( \text{SO}_2 \) to sulfate over the Pacific Ocean following the Pinatubo eruptions. The major sources of the \( \text{SO}_2 \) in the central Pacific upper tro-

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**Fig. 6.** Calculated sulfuric acid production rates as a function of altitude based on \( \text{SO}_2 \) data (shown in Figure 5) and model results for OH concentrations.

The residence time for the sulfuric acid aerosols formed from \( \text{SO}_2 \) can be estimated from the ratio of the measured sulfate to the sulfuric acid production ratio. For the flights considered here at altitudes above 10 km with an average sulfate concentration of 21 pptv and a median sulfuric acid production rate of 4 pptv/d, the residence time would be 5 days. If the air mass containing the \( \text{SO}_2 \) brought to this altitude from the surface was the result of a convective cloud, the sulfate aerosol could have been effectively removed in the cloud. The time to replenish this sulfate to 20 pptv would be 5 days with a sulfuric acid production rate of 4 pptv/d.

Recent theoretical and experimental work on the formation of sulfuric acid indicates that \( \text{H}_2\text{SO}_4 \) (g) may not be formed by as simple a path as reaction (3). Popov et al. [1993, 1995] have calculated that the formation of gas phase sulfuric acid as shown in reaction (3) is kinetically hindered. The likely pathway for production of sulfuric acid appears to be through a dihydrate of \( \text{SO}_2 \) (\( \text{SO}_2\cdot\text{H}_2\text{O} \)) to the monohydrate of sulfuric acid (\( \text{H}_2\text{SO}_4\cdot\text{H}_2\text{O} \)). Morokuma and Muguruma [1994] have also predicted a second-order dependence on water for the conversion of \( \text{SO}_2 \), through reaction with water dimer (\( \text{H}_2\text{O}_2 \)) to sulfuric acid monohydrate. Kolb et al. [1994] have experimentally shown that the reaction of \( \text{SO}_2 \) with \( \text{H}_2\text{O} \) is second-order in water. The details of the conversion of \( \text{SO}_2 \) to sulfuric acid remains to be determined. The simple mechanism of reactions (1)-(3) would represent an upper limit on sulfuric acid production.

**Aerosol Production**

The formation of new aerosol particles from the oxidation of \( \text{SO}_2 \) to \( \text{H}_2\text{SO}_4 \) would have a significant impact on the energy balance of the troposphere through the direct scattering of radiation and the formation of condensation nuclei, which
posphere appeared to be anthropogenic with long-range transport and return of volcanic SO$_2$ from the stratosphere. Dimethyl sulfide did not appear to be a significant source of SO$_2$ except occasionally in the boundary layer.

At altitudes above 10 km the half-life of SO$_2$ was $> 30$ days. Based on the OH concentrations from calculations using a large suite of variables measured in situ, sulfonic acid production was estimated to have a median value of 4 pptv/d over the central Pacific above 10 km. With measured mean sulfate concentrations of 21 pptv for this region above 10 km, the replacement time for sulfate aerosol was estimated to be 5 days.

Calculated production rates of H$_2$SO$_4$ averaged 1600 molecules cm$^{-3}$ s$^{-1}$ above 8.5 km for the central Pacific troposphere. The important consequences of this significant production of sulfate aerosols would be a significant source of CN in the upper troposphere with a direct radiative cooling effect in the upper troposphere. Under the influence of the subsidence in the central Pacific gyre, entrainment of these sulfate aerosols into the moister mixed layer could lead to additional cooling effects by promoting the formation of clouds.

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