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Uptake of Formaldehyde by Sulfuric Acid Solutions: Impact on Stratospheric Ozone

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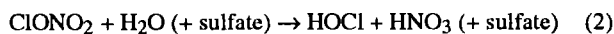
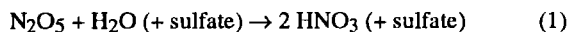
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Chemical reactions on sulfuric acid aerosols have recently been shown to play an important role in stratospheric chemistry. In particular, these reactions push odd-nitrogen compounds into HNO₃ and thereby enhance the chlorine-catalyzed destruction of ozone. It has been suggested that our current set of heterogeneous reactions may be incomplete. Indeed we show that formaldehyde, CH₂O, is rapidly and irreversibly taken up by stirred sulfuric acid solutions (60 to 75 wt % H₂SO₄ at -40° to -65°C) with uptake coefficients as large as $\gamma = 0.08$. If similar uptake occurs under stratospheric pressures of CH₂O (that is, 1000 times lower than used in the present study), then the removal of CH₂O from the gas phase can take away a significant source of odd hydrogen in the mid- and high-latitude lower stratosphere. We show here that with the inclusion of this reaction, concentrations of OH and HO₂ are reduced by as much as 4% under background levels of aerosols and more than 15% under elevated (volcanic) conditions. Further, the accumulation of CH₂O in stratospheric aerosols over a season may alter the composition and reactivity of these sulfuric acid-water mixtures.

INTRODUCTION

In the past several years, laboratory, field, and modeling studies have provided mounting evidence that heterogeneous reactions on naturally occurring stratospheric aerosols could be impacting ozone on a global scale. In particular, laboratory measurements [Mozurkewich and Calvert, 1988; Tolbert *et al.*, 1988; Van Doren *et al.*, 1991; Hanson and Ravishankara, 1991a] have shown that reactions (1) and (2) occur on sulfuric acid solutions thought to be representative of the stratospheric sulfate layer. These studies suggest that reaction (1) occurs readily under all stratospheric conditions. In contrast, reaction (2) occurs efficiently only on dilute sulfuric acid solutions.



The predominant role of reactions (1) and (2) is to push odd-nitrogen compounds, particularly NO_x (=NO + NO₂) into HNO₃. Reductions in the abundance of NO and NO₂ shift the balance of chlorine species from the inactive forms (e.g., HCl and ClONO₂) to species more active in catalyzing ozone loss (e.g., ClO). Photochemical model studies that include reaction (1) on the sulfate layer suggest that this reaction may contribute to the observed decrease in mid-latitude ozone over the past 11 years [Mather and

Brune, 1990; Rodriguez *et al.*, 1991; World Meteorological Organization (WMO), 1992]. Furthermore, modeling studies have proposed that heterogeneous reactions (1) and (2) lead to significant ozone destruction following major volcanic eruptions that inject massive amounts of sulfur into the stratosphere [Hofmann and Solomon, 1989; Brasseur *et al.*, 1990; Prather, 1992a]

Although photochemical models that include heterogeneous chemistry are able to reproduce many features in the stratosphere, there are still significant discrepancies between observations and model predictions [King *et al.*, 1991; Considine *et al.*, 1992]. For example, although Considine *et al.* [1992] found that inclusion of heterogeneous reaction (1) led to better agreement between model calculations and the Limb Infrared Monitor of the Stratosphere (LIMS) HNO₃ data, a worse fit with LIMS NO₂ resulted. In contrast, a recent intercomparison of models and measurements showed that with reaction (1) the models were able to reproduce the seasonal cycle in SAGE-II NO₂ and the large column abundances of HNO₃ in winter [Remsberg and Prather, 1992]. However, there are enough uncertainties left in these comparisons to leave open the question of missing heterogeneous chemistry.

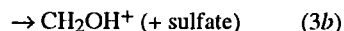
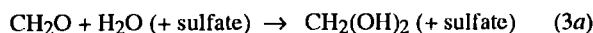
Gaseous formaldehyde (CH₂O) is formed in the stratosphere by the oxidation of methane. The cycle of methane oxidation continues to CO and provides a significant source of odd hydrogen (HO_x = OH + HO₂ + 2H₂O₂) in the lower stratosphere. If heterogeneous processes were to remove a significant fraction of stratospheric CH₂O, then reductions in HO₂ and OH could occur.

Herein, we investigate the uptake of formaldehyde, CH₂O, by low temperature sulfuric acid solutions representative of global stratospheric particulate. Previous work at room temperature [McTigue and Sime, 1963] has suggested that formaldehyde reacts in sulfuric acid according to reaction (3), where the products of (3a)

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and (3b) are methylene glycol and protonated formaldehyde,



respectively. Below, we describe experiments that measure the uptake of gaseous formaldehyde by 60 to 75 wt % sulfuric acid solutions at stratospheric temperatures. We use a photochemical model to demonstrate the first-order atmospheric impact of heterogeneous uptake of formaldehyde by sulfuric acid aerosols. Further, we propose that the presence of condensed formaldehyde in the stratospheric sulfate aerosols could have implications for the reactivity of the aerosols toward other trace species.

EXPERIMENT

The uptake of CH_2O by sulfuric acid solutions is studied using a Knudsen cell flow reactor described previously [Golden *et al.*, 1992]. Briefly, the Knudsen cell consists of two chambers separated by a 4-inch diameter butterfly valve. The sulfuric acid solutions (10 - 20 ml) are placed in the lower chamber which is cooled using thermoelectric coolers. The solutions are prepared by diluting commercial 96.5 wt % H_2SO_4 with distilled water. The final H_2SO_4 concentrations are determined by titration. The sulfuric acid is stirred using a 1-cm glass stir bar at a spinning rate of 20 rev/min. This level of stirring is very gentle and we estimate it does not increase the overall surface area of the solution by more than 20%. All of the solutions used in the present study were liquid, although the 75 wt % solution at low temperature was quite viscous and difficult to stir.

The upper chamber of the Knudsen cell is coupled to a differentially pumped mass spectrometer through a calibrated escape orifice. The mass spectrometer intensity for a given molecule is proportional to its flow, F (molecule s^{-1}), out of the Knudsen cell. CH_2O is conveniently monitored using mass peak m/e 29. In a typical experiment, gaseous CH_2O is initially routed through the upper chamber, bypassing the sulfuric acid surface. Changes in the mass spectrometer signal for mass 29 that occur when the valve is opened are used to determine the amount of CH_2O lost during exposure to H_2SO_4 . We look for gaseous reaction products by scanning the mass spectrometer over all mass peaks from m/e 1 to 68. After each exposure the reversibility of the uptake is checked by turning off the flow of CH_2O and monitoring mass peak m/e 29 while continuing to stir the sulfuric acid solutions. The mass spectrometric data and reactor temperature are acquired using a microcomputer, with one data set collected approximately every 1 - 5 s.

The experimental quantity that is measured in the present work is the time-dependent net uptake efficiency, $\gamma(t)$, defined as the fractional collision frequency that leads to CH_2O uptake by the solution. The net uptake efficiency is determined using equation (4)

$$\gamma(t) = A_h/A_s \{ (F^0 - F(t))/F(t) \} \quad (4)$$

[Quinlan *et al.*, 1990], where A_h and A_s are the areas of the Knudsen cell escape orifice and the sulfuric acid solution, respectively, and F^0 and $F(t)$ are the CH_2O flows out of the Knudsen cell in the absence and presence of the sulfuric acid, respectively. In the present experiment the surface areas were constant at $A_h = 0.45 \text{ cm}^2$ and $A_s = 26 \text{ cm}^2$. The initial CH_2O flow, F^0 , was varied in the range $1 \times 10^{14} \text{ molecule s}^{-1}$ to $8 \times 10^{14} \text{ molecule s}^{-1}$, resulting in initial CH_2O number densities from 2×10^{10} to $2 \times 10^{11} \text{ molecule cm}^{-3}$.

The CH_2O densities used in the present experiment are considerably higher than those expected in the stratosphere, $\approx 10^7$ - $10^8 \text{ molecule cm}^{-3}$. Recent laboratory work on the pressure dependence of the ClONO_2 reaction on solid PSC surfaces showed that higher reactant concentrations can lead to surface saturation and lower apparent reaction rates [Hanson and Ravishankara, 1991b]. In contrast, studies of reactions (1) and (2) on liquid sulfuric acid solutions have not shown pronounced pressure dependences. This may be due to the fact that these reactions on sulfuric acid surfaces form primarily gaseous products. If the CH_2O reaction saturates in sulfuric acid, then we would expect the uptake efficiency to decrease with time. The rate at which saturation occurs will depend on both the CH_2O density and the sulfuric acid volume. Although our experiments use much higher CH_2O densities than found in the stratosphere, we also use much larger volumes of sulfuric acid. A more detailed discussion of saturation effects is provided below.

RESULTS AND DISCUSSION

An example of the data showing the time-dependent uptake of CH_2O by 71 wt % H_2SO_4 at -61.5°C is given in Figure 1a. In this example the sulfuric acid was exposed to formaldehyde both with and without the solution being stirred. It can be seen that the time-dependent uptake is quite complex. Initially, the CH_2O flows through the upper chamber of the Knudsen cell at a rate of $1.7 \times$

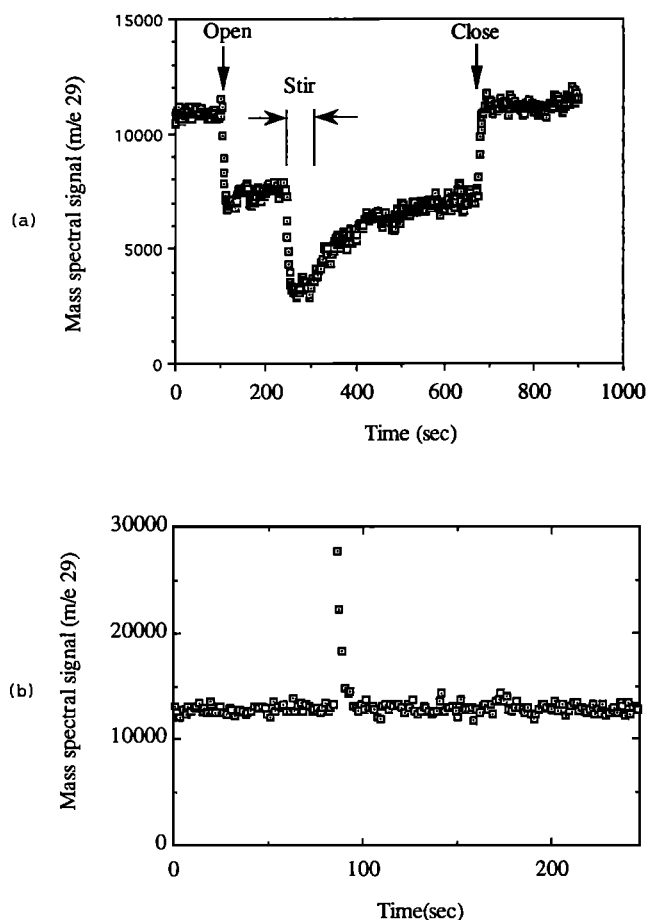


Fig. 1. Mass spectrometer signal for formaldehyde as measured using m/e 29 as a function of time during exposure of (a) $1.7 \times 10^{14} \text{ molecule s}^{-1}$ CH_2O to 71 wt % H_2SO_4 at a temperature of -61.5°C and (b) $1.8 \times 10^{16} \text{ molecule s}^{-1}$ CH_2O to an empty cell at a temperature of -56°C .

10^{14} molecule s^{-1} without being exposed to the sulfuric acid solution. After approximately 100 s, the butterfly valve is opened to expose the unstirred sulfuric acid to the CH_2O . The drop in signal indicates that CH_2O is being lost to the solution. At 220 s, the solution is gently stirred while continuing to expose it to CH_2O . Here, a major decrease in m/e 29 signal indicates that the stirring greatly increases the formaldehyde uptake. When the stirring is stopped at 300 s, the signal slowly returns to near its previous nonstirred value. Finally, when the valve is closed, the CH_2O returns to its original level, indicating that the incoming flow into the Knudsen cell was steady.

In parallel control experiments using a cold cell but without sulfuric acid present, we observed no formaldehyde uptake. For example, Figure 1b shows the signal resulting from the exposure of CH_2O to the cold cell at $-56^\circ C$. In this case, the CH_2O flow was initially 1.8×10^{16} molecule s^{-1} , approximately 2 orders of magnitude higher than used in the sulfuric acid experiments. Because formaldehyde polymerization is known to occur at high CH_2O pressures and low temperatures [Walker, 1964], the higher pressure used in the control experiment offers a more stringent test of uptake by the empty cell. At 90 s, the butterfly valve was opened to expose the cold cell to CH_2O . The signal actually increased briefly in this case, due to a small pressure burst that results from compression of the o-ring seal as the butterfly valve is opened. Similar results were obtained using lower flows of CH_2O . The lack of measurable uptake of formaldehyde on the cold empty cell suggests that the observed uptake is indeed due to the presence of the sulfuric acid. One potential problem with this conclusion lies in the fact that different water vapor pressures were present in two experiments, due to the water vapor from the sulfuric acid solution that was not present in the control experiment. However, we do not think that this is a major problem, as suggested by the stirred versus nonstirred results discussed below.

Although we always observed significant CH_2O uptake on sulfuric acid whether or not we stirred the solution, we found that we were only able to obtain reproducible results (within estimated uncertainty of $\pm 50\%$) when the solution was stirred. We have previously observed similar behavior for reaction (1) on H_2SO_4 as a function of stirring the solution [Golden *et al.*, 1992]. We believe that without stirring, the sulfuric acid surfaces are rapidly saturated due to relatively slow diffusion in the liquid and large gas concentrations. Of concern is the possibility that stirring affects the laboratory solution in a way not possible for actual stratospheric aerosols. However, stratospheric conditions of large aerosol surface to volume ratios and small gas number densities favor a much cleaner surface in the stratosphere than in the laboratory and thus real aerosols may not require stirring for high reactivity. Also stratospheric sulfate aerosols are continually undergoing evaporation/condensation in equilibrium with the background water vapor, thus ensuring a constantly renewed surface. Note also that the fact that stirring increases the observed CH_2O uptake reinforces the results of the above control experiment indicating uptake by the sulfuric acid rather than the container walls.

In what follows, we report the uptake efficiency using the signal level observed while stirring the sulfuric acid solutions. For the data in Figure 1a we obtain an uptake efficiency of $\gamma = 0.068$. Note that if we had chosen to evaluate the uptake efficiency at the pseudo stable level shown in Figure 1a without stirring, we would obtain a much lower, but still quite rapid value, $\gamma = 0.016$. The factor of 4 difference between γ for stirred versus nonstirred sulfuric acid is much larger than can be accounted for by the difference in

surface area caused by stirring (20%). For all of the solutions studied, the stable nonstirred values were in the range $\gamma = 0.01$ –0.02.

During the exposure to formaldehyde we probed the gas phase for reaction products by scanning the mass spectrometer over the range $m/e = 1$ to 68. We observed no new peaks in the mass spectrometer over this range as a result of the interaction. It therefore appears that the uptake of formaldehyde by sulfuric acid was not accompanied by release of gaseous products. After the exposure to formaldehyde we tested the reversibility of uptake by pumping on the sulfuric acid solution while stirring. We were never able to see any formaldehyde released from the solution to the gas phase at levels over our background m/e 29 signal. We thus conclude that the uptake of formaldehyde under the pressure and temperature conditions used is not reversible.

It would be very unlikely for us to have saturated the bulk sulfuric acid solution under our conditions. For the experiment in Figure 1a we added a total of approximately 7×10^{16} molecules of CH_2O to our 20 ml solution of sulfuric acid in 600 s. Thus if we assume that stirring effectively distributes the CH_2O throughout the solution, our final concentration would be 5.8×10^{-6} M. For other experiments using higher flows for longer durations, we calculate that we have made solutions as concentrated as 10^{-3} M CH_2O . These concentrations are extremely dilute when compared to CH_2O/H_2SO_4 solutions used in previous bulk studies, with CH_2O concentrations around 0.03 to 0.5 M [McTigue and Sime, 1963; Indu *et al.*, 1991]. It is thus not too surprising that we do not see release of CH_2O from the solution at our concentrations. However, in the stratosphere, if the aerosols were to become this concentrated, we might expect that either the uptake would saturate, gaseous products would be released, or that precipitation would occur. Experiments using high CH_2O densities and small sulfuric acid samples are needed to test these possibilities.

The uptake efficiencies we obtain for CH_2O on stirred 60 to 75 wt % H_2SO_4 solutions as a function of temperature are given in Figure 2. In general, the uptake efficiencies are quite large, with γ in the range 0.01 to 0.1. These are comparable to values that have been measured for the reaction of N_2O_5 on sulfuric acid [Mozurkewich and Calvert, 1988; Hanson and Ravishankara, 1991a; Van Doren *et al.*, 1991; Golden *et al.*, 1992]. It can also be seen that all the solutions exhibit a slight to moderate increase in γ at lower temperatures (with fixed wt % H_2SO_4). Similar negative temperature dependences have been observed for the uptake of HCl and HNO_3 by sulfuric acid [Watson *et al.*, 1990; Reihls *et al.*, 1990]. Perhaps the most intriguing aspect of Figure 2 is the dependence of the uptake on sulfuric acid concentration. This is shown more clearly in Figure 3, where the uptake efficiency is plotted as a function of sulfuric acid concentration for one temperature where the data overlap, $-45^\circ C$. It is clear from Figure 3 that the uptake efficiencies actually increase with increasing sulfuric acid concentration over the reported range. (An exception is the lower uptake by 67 than 60 wt % H_2SO_4 , where we believe the differences in γ are not statistically significant.) This behavior of increasing reactivity with increasing H_2SO_4 concentration has not been noted previously. For $ClONO_2$, HCl, and HNO_3 the uptake efficiency decreases with increasing sulfuric acid concentration, while there appears to be very little acid-concentration dependence for the N_2O_5 uptake. Thus from (1) the apparent irreversibility, (2) the lack of gas phase products, and (3) the dependence on wt % H_2SO_4 , the uptake of formaldehyde appears to involve very different chemistry than has been reported previously for nitrogen and chlorine compounds.

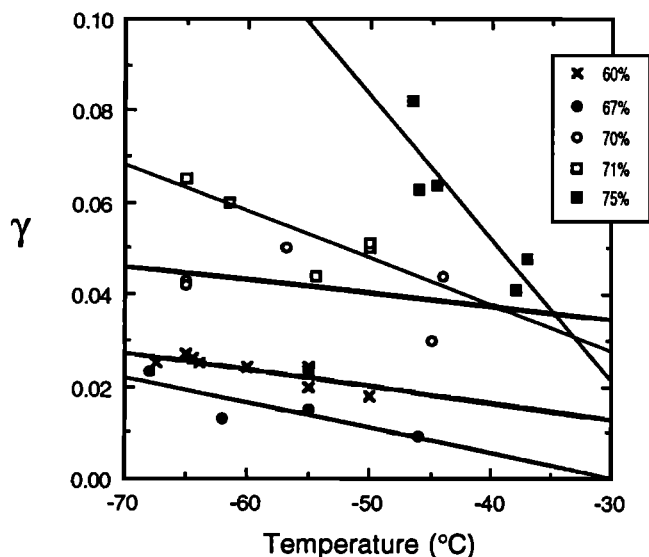


Fig. 2. Summary of the uptake efficiencies for CH_2O on 60 to 75 wt % H_2SO_4 as a function of temperature.

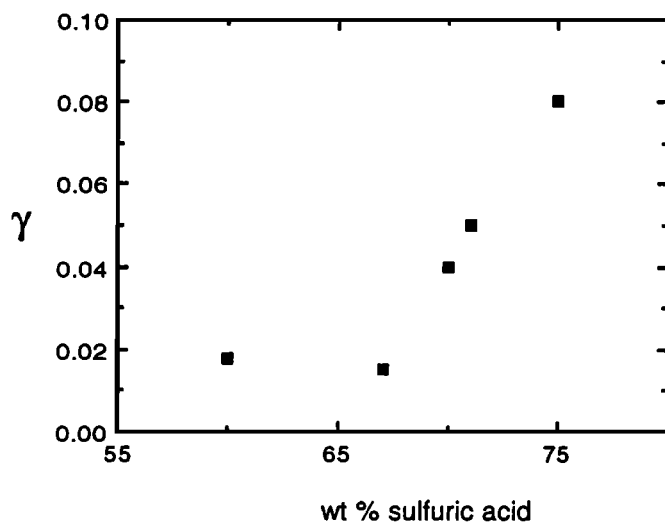


Fig. 3. Variation in the CH_2O uptake efficiency at -45°C as a function of sulfuric acid concentration.

Because we observe no gaseous products, we believe that the dramatic change in uptake efficiency near 70 wt % H_2SO_4 may be related to changes that are occurring in the condensed phase. In water it is well known that formaldehyde is found almost entirely as methylene glycol, with $K_{\text{eq}} = 2.5 \times 10^3$ for reaction (3a) [Finlayson-Pitts and Pitts, 1986]. The speciation of formaldehyde in sulfuric acid at low temperatures is not well established but has been studied at room temperature by McTigue and Sime [1963] using ultraviolet spectroscopy and condensed phase reactivity with Br_2 . They found that for sulfuric acid concentrations less than 71 wt %, methylene glycol dominated, whereas protonated formaldehyde from reaction (3b) dominated at higher sulfuric acid concentrations. Although their work was done at room temperature, it suggests that the speciation of condensed formaldehyde may change rapidly near 70 wt % H_2SO_4 , right where we observe a large change in the uptake efficiency. If the formaldehyde partitioning is similar at -45°C , then our work suggests that CH_2O uptake is enhanced by the formation of protonated formaldehyde. Another possibility is that the increase in formaldehyde uptake near 70 wt % is due to a new

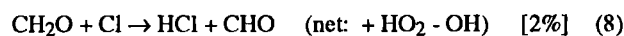
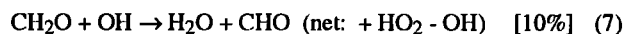
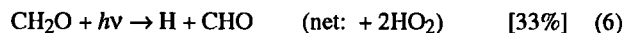
chemical reaction with some species in the sulfuric acid. For example, HSO_4^- has recently been proposed as a reactive species in stratospheric sulfate aerosols [Burley and Johnston, 1992a, b]. Experiments are currently in progress to determine the partitioning and reactivity of formaldehyde in concentrated solutions of sulfuric acid at low temperature.

All of the discussion thus far has focused on fairly dilute concentrations of formaldehyde in sulfuric acid. If the solutions of formaldehyde were to become quite concentrated in either the lab work or actual stratospheric aerosols, the possibility of formaldehyde polymerization exists. Concentrated aqueous solutions of formaldehyde (>5 wt % CH_2O) tend to form dimers and trimers, which eventually polymerize [Walker, 1964]. For example, an aqueous 5 wt % CH_2O solution (≈ 1.7 M) at 35°C has been found to contain 87.2% of the dissolved CH_2O as the monomer, with the remainder being higher polymers [Walker, 1964]. The solutions we form in the Knudsen cell experiment are 3 to 6 orders of magnitude more dilute than this, and thus they are unlikely to support polymerization. We attempted to make concentrated solutions of formaldehyde by dissolving paraformaldehyde in bulk sulfuric acid. We found that we were only able to make solutions as concentrated as 2M CH_2O in 75 wt % H_2SO_4 at room temperature using paraformaldehyde. Gaseous CH_2O uptake by sulfuric acid solutions may lead to a different apparent solubility limit. Polymerization of formaldehyde in the stratospheric sulfuric acid aerosols is still an open question because of the potential for accumulation of high concentrations of condensed formaldehyde in the very small aerosols. The Henry's law solubility of CH_2O in sulfuric acid merits further investigation.

Once dissolved in sulfuric acid, it is possible that formaldehyde may undergo condensed phase reactions with other trace species dissolved in solution. For example, it has been shown that formaldehyde in 10 to 55 wt % H_2SO_4 (that is, methylene glycol) reacts with Cl_2 [Indu et al., 1991] (or Br_2 [McTigue and Sime, 1963]) to form formic acid and HCl (or HBr). Formaldehyde has also been reported to react with concentrated HNO_3 [Walker, 1964] and NO_2 [Pollard and Wyatt, 1949] to form NO, CO_2 and water. Finally, previous work has shown that formaldehyde reacts with excess HCl in concentrated sulfuric acid to form $\text{ClCH}_2\text{OCH}_2\text{Cl}$ [Schneider, 1938]. Further experiments are needed to determine if such reactions could occur under conditions representative of those expected for stratospheric sulfate aerosols.

ATMOSPHERIC IMPLICATIONS

In the stratosphere, most CH_4 oxidation pathways lead through CH_2O . In the mid-latitude lower stratosphere there are four important paths for CH_2O loss (approximate diurnally integrated branching ratios shown):



The net HO_x change includes the subsequent reactions of H and CHO with O_2 to form HO_2 as well as the recycling of HCl by reaction with OH. Reaction (6) is the only pathway leading to net

production of HO_x and thus approximately 2/3 HO_x molecule is produced for every CH_2O molecule. The lifetime against heterogeneous CH_2O removal is calculated as $4/(\nu \alpha \gamma_3)$, where ν is the average molecular velocity (cm s^{-1}) and α is the specific surface area of the aerosol layer ($\text{cm}^2 \text{cm}^{-3}$). The photochemical lifetime of CH_2O ranges from about 6 to 24 hr, and thus the heterogeneous uptake (reaction (3)) competes with reactions (5-8) for background levels of aerosols (e.g., $\alpha = 10^{-8} \text{ cm}^2 \text{cm}^{-3}$) when the uptake efficiency, γ_3 , is of the order of 0.1.

The removal of CH_2O from the gas phase and from subsequent reactions becomes increasingly important as α increases from background levels of less than $1 \times 10^{-8} \text{ cm}^2 \text{cm}^{-3}$ to more than $50 \times 10^{-8} \text{ cm}^2 \text{cm}^{-3}$ following the Mount Pinatubo eruption [Deshler *et al.*, 1992; Dye *et al.*, 1992]. Although this loss of CH_2O perturbs the HO_x chemistry, the primary impact of increasing aerosols comes from the reduction in NO_x (reactions (1) and (2)). In Figure 4 we examine the standard aerosol chemistry (reactions (1) and (2)) and show the additional impact of heterogeneous uptake of CH_2O (reaction (3)). Calculations are appropriate for September, 75°N at 16 km altitude ($3.27 \times 10^{18} \text{ molecule cm}^{-3}$, 222.6 K, $\text{O}_3 = 2.5 \text{ ppm}$, $\text{NO}_y = 5.4 \text{ ppb}$, $\text{Cl}_y = 1.8 \text{ ppb}$, $\text{Br}_y = 15 \text{ ppt}$, $\text{H}_2\text{O} = 4 \text{ ppm}$, $\text{CH}_4 =$

1.4 ppm, $\text{CO} = 20 \text{ ppb}$, $\gamma_1 = 0.01$, $\gamma_2 = 0.0004$) and assume photochemical balance over a 24-hour cycle [Prather and Jaffe, 1990; Prather, 1992b]. Because the detailed condensed-phase chemistry has not yet been established, we assume that formaldehyde is lost to the aerosols with a uniform uptake efficiency of $\gamma_3 = 0.05$ and assume that the reaction is irreversible. Because of the limitations of these assumptions, the model simulation should only be used to illustrate the potential importance of reaction (3) as a function of effective surface area of the aerosols.

NO_x and ClO are plotted as a function of α in Figure 4a, demonstrating the importance of reaction (1) in suppressing NO_x . The transfer of NO_x into HNO_3 changes the photochemical balance (e.g., Cl/ClO ratios, OH levels) and leads to an increase in ClO levels [Mather and Brune, 1990; Rodriguez *et al.*, 1991]. Except during polar winter, reaction (2) is rarely fast enough to directly perturb the cycling between chlorine species, but has its main impact through augmenting the suppression of NO_x [Prather, 1992a]. Inclusion of reaction (3) has little impact on NO_x and ClO .

Figures 4b and 4c show the response of OH and HO_2 , respectively, to increasing aerosol area. Here the effects of heterogeneous removal of CH_2O are seen to reduce the HO_x abundances by 4% at background levels and by more than 15% for larger α . The impact becomes smaller at mid-latitudes where the CH_4 oxidation cycle is a less important part of the overall HO_x budget: at 45°N (not shown) the model predicts HO_x reductions of 1-2% at background levels and up to 10% under volcanic conditions.

In all of these model predictions we see that the largest perturbations to stratospheric chemistry caused by heterogeneous reactions are associated with changes in the NO_x - HNO_3 balance, and thus the primary uncertainty is the determination of the NO_x levels (that is, a combination of α , γ_1 , and γ_2). However, a secondary but still important perturbation to the chemistry is caused by the removal of CH_2O , as shown here. An immediate question arises as to whether other parts of the HO_x cycle can be impacted by heterogeneous chemistry. Sensitivity studies with the chemical model were used to examine the importance of heterogeneous uptake of peroxides (H_2O_2 and CH_3OOH) and peroxy radicals (HO_2 and CH_3OO). If these species are also removed at rates similar to CH_2O (reaction (3)), then the HO_x reduction can be enhanced, leading to a total reduction of as much as 50% in OH levels for volcanic conditions ($\alpha > 10 \times 10^{-8} \text{ cm}^2 \text{cm}^{-3}$) even at mid-latitudes. Note that while this article was in press, results were reported by Hanson *et al.* [1992] showing uptake efficiencies for OH and HO_2 on 28 wt % H_2SO_4 of >0.08 and >0.05 , respectively.

Although perturbations to the HO_x chemistry at mid-latitudes would appear modest under background conditions, the impact on the composition of the sulfate layer itself may be quite large. Under background levels, $\alpha = 0.3 - 1.0 \times 10^{-8} \text{ cm}^2 \text{cm}^{-3}$, about 5% of the formaldehyde produced could be taken up by the sulfate aerosols. This absorption of $1.4 \times 10^{-17} \text{ moles cm}^{-3}$ per day with background volumes of $0.1 \times 10^{-12} \text{ cm}^3 \text{cm}^{-3}$ [Dye *et al.*, 1992] would generate formaldehyde solutions of 0.14 M per day. If the uptake of CH_2O in H_2SO_4 solutions is irreversible, then the exposure of the sulfate aerosols over a season (90 days) would produce solutions with 20 wt % or more of dissolved formaldehyde. Recall, however, that we were unable to make solutions of CH_2O more concentrated than 2 M in room temperature 75 wt % H_2SO_4 . Thus the irreversibility we observe for CH_2O uptake under our experimental conditions may not be relevant for the very high CH_2O concentrations we estimate to be present in atmospheric H_2SO_4 aerosols. Nonetheless, the

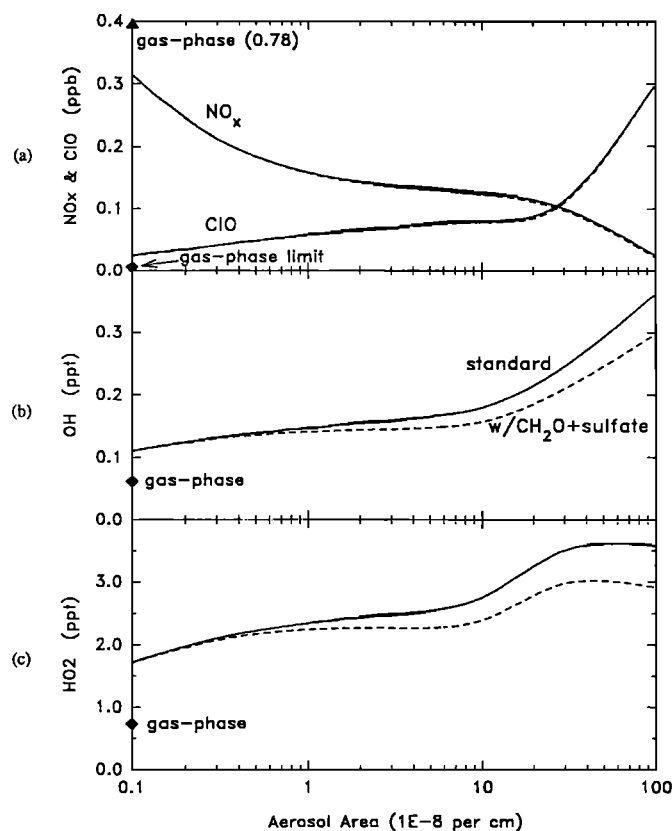


Fig. 4. Effects of sulfate layer reactions on stratospheric chemistry as a function of the aerosol surface area α , both with (dashed curve) and without (solid curve) the CH_2O reaction (3). Model calculations assume photochemical balance over a 24-hour cycle for September, 75°N at 16 km altitude ($3.27 \times 10^{18} \text{ molecule cm}^{-3}$, 222.6 K, overhead ozone column = 200 DU, $\text{O}_3 = 2.5 \text{ ppm}$, $\text{NO}_y = 5.4 \text{ ppb}$, $\text{Cl}_y = 1.8 \text{ ppb}$, $\text{Br}_y = 15 \text{ ppt}$, $\text{H}_2\text{O} = 4 \text{ ppm}$, $\text{CH}_4 = 1.4 \text{ ppm}$, $\text{CO} = 20 \text{ ppb}$, $\gamma_1 = 0.01$, $\gamma_2 = 0.0004$, $\gamma_3 = 0.05$). (a) Decline in NO_x and corresponding increase in ClO as the rate of heterogeneous reactions increase; their abundances for gas phase chemistry alone are shown by symbols on the left axis. (b) and (c) Same sequence of model simulations for the nighttime concentrations of OH and HO_2 , respectively, where the heterogeneous removal of CH_2O (dashed curves) reduces the HO_x abundances.

presence of ≈ 1 M solutions of CH_2O in stratospheric sulfate aerosols may substantially change the reactivity or solubility of other gases in the sulfate layer.

CONCLUSIONS

Knudsen cell flow experiments have shown that gaseous formaldehyde is readily taken up by stirred sulfuric acid solutions with uptake efficiencies as large as $\gamma = 0.08$. The CH_2O uptake increases with increasing sulfuric acid concentration above 70 wt %. This increase in γ coincides with formation of protonated formaldehyde in room temperature solutions as determined by *McTigue and Sime* [1963]. From a combination of the apparent irreversibility, the lack of gas-phase products, and the dependence on wt % H_2SO_4 , we believe that the uptake of formaldehyde involves very different chemistry than has been reported previously for nitrogen and chlorine compounds. If similar uptake occurs under stratospheric pressures of CH_2O (that is, 1000 times lower than used in the present study), then the removal of CH_2O from the gas phase can take away a significant source of odd hydrogen in the mid- and high-latitude lower stratosphere. We show here that with the inclusion of this reaction, concentrations of OH and HO_2 are reduced by as much as 4% under background levels of aerosols and more than 15% under elevated (volcanic) conditions. Further, the accumulation of CH_2O in stratospheric aerosols over a season, reaching ≈ 1 M solutions, will alter the composition and may even change the reactivity of these sulfuric acid-water mixtures. For example, a reaction between condensed CH_2O and HNO_3 could potentially reverse the NO_x to HNO_3 conversion caused by reaction (1) on stratospheric sulfate aerosols. Similarly, if dissolved CH_2O alters the solubility or reactivity of chlorine reservoir species (HCl , ClONO_2) in H_2SO_4 , then a change in the partitioning between active and inactive chlorine could result. Additional laboratory studies of the trace gas solubilities and condensed phase reactions for HO_x reservoir molecules such as CH_2O and H_2O_2 in sulfuric acid are needed to make these ideas more quantitative.

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