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ARTICLES

Uptake of Methanol Vapor in Sulfuric Acid Solutions†

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The uptake of gas-phase methanol by liquid sulfuric acid has been investigated over the composition range of 40−85 wt % H_2SO_4 and the temperature range of 210−235 K. Laboratory studies were performed with a flow-tube reactor coupled to an electron-impact ionization mass spectrometer to detect trace gases. While reversible uptake was the primary mechanism at low acid concentrations, an irreversible reaction between methanol and sulfuric acid at low temperatures, forming methyl hydrogen sulfate and dimethyl sulfate, was observed at all concentrations. At compositions >65 wt % H_2SO_4, more than 90% of uptake was found to be reactive. On the basis of the uptake data and the calculated liquid-phase diffusion coefficients, the product of the effective Henry's law constant (H^*) and the square root of the overall liquid-phase reaction rate (k_l) was calculated as a function of acid concentration and temperature. The results suggest that the reaction with sulfuric acid forming methyl hydrogen sulfate and dimethyl sulfate is the dominant loss mechanism of methanol and that the oxidation of methanol is only a minor source of hydroxyl radicals in the upper troposphere.

Introduction

Oxygenated hydrocarbons, particularly acetone, play an important role in atmospheric chemistry by contributing the production of HO_x free radicals and consequently increasing the formation of ozone in the upper troposphere.[1,2] Although methanol is considered to be of secondary importance in these aspects, the concentration of methanol has been found to be as high as 700 ppt at 5−10 km.[1,3] Hence, it is important to investigate the production and loss mechanisms of methanol in the atmosphere. Sources of methanol in the atmosphere include secondary reactions of hydrocarbons, biomass burning, and direct biogenic and anthropogenic emissions.[4] On the other hand, the photolytic loss of methanol is believed to be insignificant.[5] Moreover, the reaction with ice particles inside cirrus clouds is also very slow.[6] It has been thought that the only significant loss mechanism for methanol in the upper troposphere is the reaction with hydroxyl radicals. However, the heterogeneous reaction of methanol in liquid sulfuric acid has not, to this point, been considered.

Sulfate aerosols are thought to be the dominant form of aerosol in the upper troposphere. Very recently, organic acids and hydroxymethanesulfonic acid (HMSA) have been identified in situ in aerosols at altitudes of 5−19 km.[7] These organic-containing aerosols are particularly more pronounced in the tropics because of convection from the troposphere. Thus, it is intriguing to understand their formation mechanism, for example, the interaction of gas-phase organic compounds with liquid sulfuric acid.

In the upper troposphere, where ambient temperatures are in the range of 200−240 K, sulfate aerosols are mainly composed of between 40 and 80 wt % H_2SO_4.[8,9] To understand the possible importance of this system, we have examined the uptake and reactivity of methanol in liquid sulfuric acid under the temperature and acid concentration ranges of the upper troposphere and lower stratosphere.

Experimental Methods

Apparatus. Uptake measurements in this experiment were performed using a fast flow-tube reactor coupled with an electron-impact ionization mass spectrometer, which has previously been described in detail.[10,11] The reactor made of Pyrex tubing was 25 cm long with an inner diameter of 1.8 cm. The bottom of the reactor was recessed to form a trough (1.9 cm wide and 0.3 cm deep) which held the liquid sulfuric acid. The temperature during the experiments was controlled by flowing cold methanol through the outer jacket of the reactor. Helium carrier gas was admitted through a sidearm inlet, while methanol in another helium carrier was added by a movable Pyrex injector. Pressures in the reactor were monitored by a high-precision capacitance manometer (MKS Instruments, Model 390 HA, 10 Torr full scale). Typically, a total pressure of 0.47 Torr was used. Methanol was monitored at the fragmentation peak of m/e = 31 amu for higher detection sensitivity.

Materials. Methanol (Fisher Scientific; 99.9%, reagent grade) was used as received without further purification, and its purity was confirmed by mass spectroscopy. A sample vial containing the methanol was placed in a methanol/dry ice bath to control the concentration of methanol inside the reactor. The partial pressures of methanol in these experiments were in the range of 1.7×10^{-4} to 1.7×10^{-6} Torr, depending on the type of experiment. Helium (Matheson Gas Company; 99.999%, ultra-

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high purity grade) was used as shipped for both the methanol carrier gas and the main flow gas. Sulfuric acid solutions of known composition were prepared by diluting 96.2 wt % H_2SO_4 (J. T. Baker Chemical Co.) with distilled water. To ensure the constant composition of H_2SO_4 over a long period of time, the helium flow gas was humidified in a vessel with the same H_2SO_4 composition and temperature as in the reaction cell. Additionally, the acid reservoir was changed frequently, and the composition of the acid was checked before and after each set of experiments by determining the density of the acid solutions as an expedient method to check H_2SO_4 composition.[12]

Data Analysis. The uptake coefficient was determined from the methanol data according to the equation[10,11]

$$\gamma = (4k_c/\omega)(V/S) \tag{1}$$

where V is the volume of the reaction cell, S is the geometric area of the acid reservoir, ω is the mean thermal speed of the molecule, and k_c is the corrected first-order rate coefficient. This rate coefficient is related to the fractional change of the gas-phase concentration of methanol calculated by[10,11]

$$k_c = k_g(1 + k_g D_g/v^2) \tag{2}$$

where D_g is the diffusion coefficient of methanol in He (D_g = 424/p Torr cm^2 s^{-1} at 295 K) and v is the average flow velocity. A temperature dependence of $T^{1.75}$ was used for estimating D_g at other temperatures. The observed first-order rate, k_g, is calculated by the equation

$$k_g = (F_g/V)(\Delta n/n) \tag{3}$$

where F_g is the carrier gas flow rate and $\Delta n/n$ is the fractional change in the gas-phase concentration of methanol after exposure to sulfuric acid by moving the sliding Pyrex injector. Since a symmetrical, cylindrical tube was not used for the uptake coefficient measurements, correction for radial gas-phase diffusion was not taken into account in the determination of k_g because this correction was considered to be rather imprecise. However, we estimate that this correction is very small, less than 10%.

Under conditions where less than 10% of methanol is reversibly absorbed (for example, the experiments using $\geq$65 wt % H_2SO_4, see the next section), the observed uptake coefficient can be approximately represented by the reactive uptake coefficient

$$\gamma = \frac{4RTH^*}{\omega}\sqrt{k_l D_l} \tag{4}$$

where R is the gas constant (0.082 L atm mol^{-1} K^{-1}), T is temperature, H^* is the Henry's Law solubility constant, D_l is the liquid diffusion constant, and k_l is the overall rate constant for liquid-phase reactions. Using eq 4, we are able to derive $H^*k_l^{1/2}$ from γ. The details are given in the next section.

Liquid-Phase Diffusion Coefficients. The determination of the liquid-phase diffusion coefficient was performed using the method suggested by Klassen et al.[13] The diffusion coefficient of methanol in liquid sulfuric acid is given by

$$D_l = cT/\eta \tag{5}$$

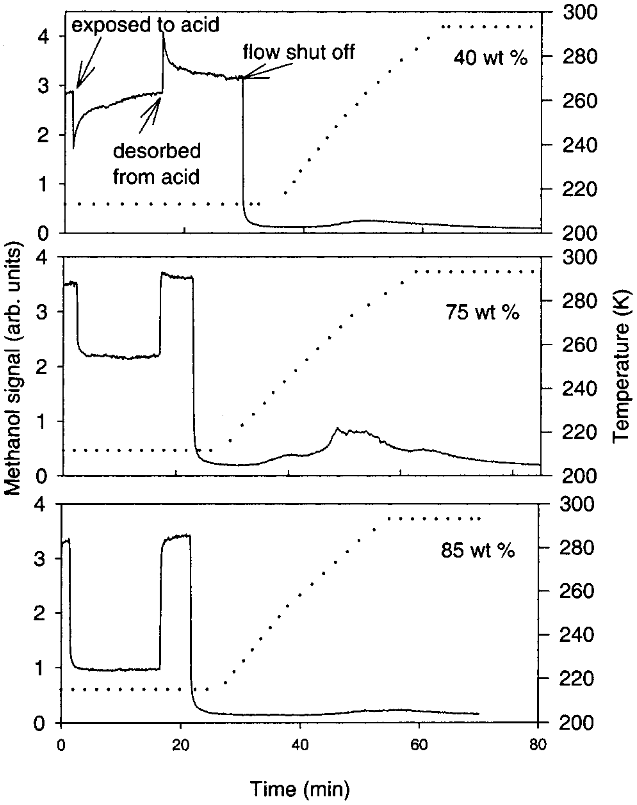

Figure 1. Uptake and desorption of methanol at 213.1 K, followed by heating to room temperature, for 40, 75, and 85 wt % H_2SO_4 (chosen as most representative data). Heating curves for each experiment are indicated by the dotted lines, scaled to the right axis. The 40 wt % H_2SO_4 shows significant low-temperature methanol desorption, only trace amounts of methanol desorbed at 75 wt %, and no desorption occurred at 85 wt % H_2SO_4 at 213.1 K. Once the methanol flow was shut off and the baseline level was achieved, the samples were heated to room temperature.

where T is the temperature, η is the viscosity of sulfuric acid, and c is a constant determined from the molar volume of methanol (Le Bas additivity rules). Wilke and Chang[14] empirically determined the value of c for the species in liquid sulfuric acid

$$c = \frac{7.4 \times 10^{-8}(\kappa_{\mathrm{solvent}})^{1/2}}{V_A^{\ 0.6}} \tag{6}$$

where $\kappa_{\mathrm{solvent}}$ is a solvent-dependent empirical factor ($\kappa_{\mathrm{solvent}}$ = 64)[13] and V_A is the Le Bas molar volume of solute A (methanol) at its normal boiling temperature (V_A = 37 cm^3/mol).[15] We calculated c to be 6.78 × 10^{-8} for methanol in H_2SO_4. In general, D_l decreases with decreasing temperature and increasing acid concentration. The square root of D_l is used in the determination of $H^*k_l^{1/2}$, and thus, the error associated with the procedure of D_l estimation is about 10−20%.

Results and Discussion

Methanol is found to exhibit some level of irreversible uptake at all the concentrations examined, and it requires a long time to reach equilibrium at concentrations dominated by reversible uptake. A relatively high pressure of methanol (1.7 × 10^{-4} Torr) was used in these experiments to facilitate the rate at which equilibrium of methanol with liquid sulfuric acid could be reached. A representative set of methanol uptake experiments is shown in Figure 1. The uptake and desorption of methanol is performed at 213.1 K for 40−85 wt % H_2SO_4. While 40 wt % H_2SO_4 shows significant low-temperature methanol desorption, only trace amounts of methanol were observed at 75 wt

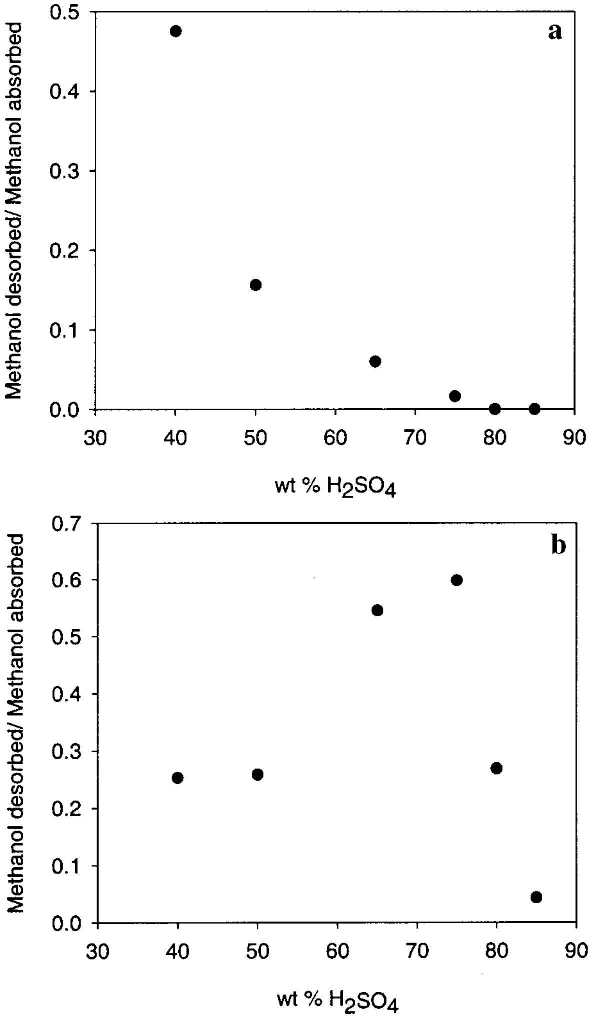

Figure 2. Low-temperature (a) and high-temperature (b) fractions of desorbing methanol at 213.1 K on a variety of sulfuric acid concentrations. As acid concentration increases, the low-temperature (nonreactive uptake) desorption fraction decreases from ~0.5 at 40 wt % H_2SO_4 to 0 at 85 wt %. High-temperature (thermally reversible reactive uptake) desorption increases from 0.25 for 40 wt % to a peak at 75 wt %, followed by a steep drop at higher concentrations. The steep drop and the total desorbing fraction of below 0.75 suggest a second reaction that is irreversible under the experimental conditions.

%, and no desorption occurred at 85 wt % H_2SO_4 at 213.1 K. To further identify the components in the sulfuric acid following methanol exposure, we heated samples to room temperature after the methanol flow was shut off and the baseline level was achieved. The heating curves for each experiment are indicated by the dotted lines, with the temperature on the right axis. Only 75 wt % H_2SO_4 shows significant high-temperature desorption upon heating, although all samples did exhibit some methanol desorption. While little methanol desorption at high temperature is expected at 40 wt % H_2SO_4 since the majority of exposed methanol is reversibly absorbed, the low yield at 85 wt % H_2SO_4 suggests a reaction, not observed at 75 wt %, that is not thermally reversible at these conditions.

To better identify the reversible and reactive components of methanol uptake by H_2SO_4, we determine the desorbing fractions of methanol both at 213.1 K and following heating to room temperature for a range of acid concentrations (40−85 wt %, see Figure 2). The desorbing fractions of methanol are shown for low temperatures (upper panel) and high temperatures (lower panel). The low-temperature data support an acid-dependent reactive component for methanol absorption. As acid concentration increases, the low-temperature (nonreactive uptake) methanol fraction decreases from ~0.5 at 40 wt % H_2SO_4 to 0 at 85 wt % H_2SO_4. Thus, under constant temperature conditions, the physical uptake is approximately 50% at 40 wt % H_2SO_4. The desorbing methanol fraction, from heating to room temperature (lower panel), increases from 0.25 at 40 wt % to a peak (~0.6) at 75 wt %, followed by a steep drop at higher concentrations.

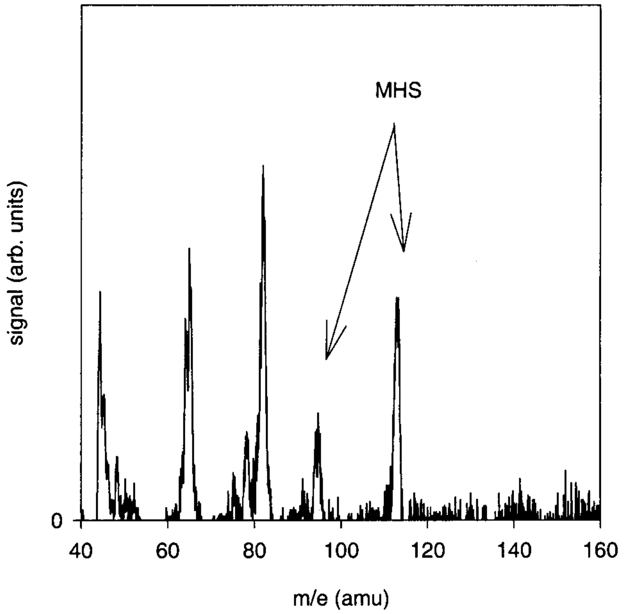

Figure 3. Mass spectrum from mixing 15 mL of H_2SO_4 with 10 mL of methanol in a vacuum. Peaks at $m/e = 112$ and 97 indicate the formation of methyl hydrogen sulfate (MHS) under these conditions. Additional peaks may be attributed to either MHS or sulfuric acid.

The most likely reaction of methanol and sulfuric acid would be the formation of methyl hydrogen sulfate (MHS)[16−20]

$$CH_3OH + H_2SO_4 \rightarrow CH_3SO_4H + H_2O \qquad (7)$$

While this product was not directly observable under the flow-tube experimental conditions, a series of experiments was conducted by mixing liquid methanol with H_2SO_4 from 40 to 85 wt % at room temperature and monitoring the reaction products by mass spectrometry. Figure 3 shows the results for 75 wt % at 295 K. Peaks at $m/e = 112$ (the parent mass of methyl hydrogen sulfate) and 97 and 81 (fragment peaks for loss of methyl and methoxy, respectively) demonstrate that MHS is a possible product from reaction at low temperature. The change in the curve at compositions >75 wt % suggests that a second reactive mechanism occurs at higher acid concentrations, as shown in Figure 2b. This reaction is not readily reversible at room temperature, and it is most likely the further reaction of methyl hydrogen sulfate with methanol to produce dimethyl sulfate[21,22]

$$CH_3SO_4H + CH_3OH \rightarrow (CH_3)_2SO_4 + H_2O \qquad (8)$$

Low vapor pressure prevents the direct observation of this product even in the mixed-liquid experiments. This reaction mechanism is in good agreement with the chemistry previously observed.[16−20]

As discussed in Experimental Methods, the fractional change in the methanol signal can be used to determine the uptake coefficient for methanol on sulfuric acid (eqs 1−3). For acid concentrations >65 wt %, all uptake can be considered

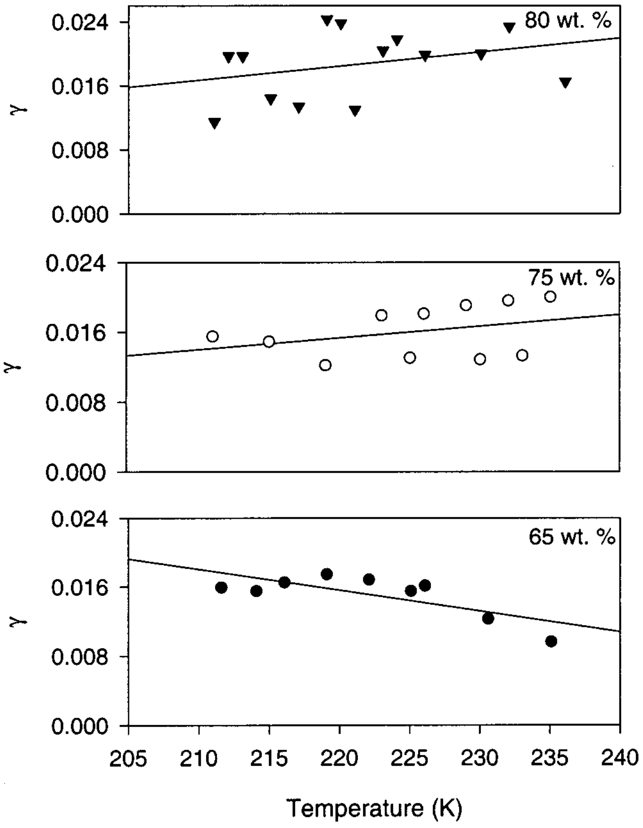

Figure 4. Calculated values for γ plotted against temperature for 65−80 wt % H_2SO_4. γ values range from 0.01 to 0.023 in the range of concentrations and temperatures observed. Solid lines are linear regression fits to the data.

irreversible. As the reactive uptake does not exhibit a recovery curve (similar to the profile of 40 wt % in Figure 1), the fractional change in the methanol signal is acquired by a stepwise increase of the distance of the glass injector inside the reaction cell allowing for sufficient time between each step to collect a good signal.[23] To better simulate atmospheric conditions in these experiments, we reduced the partial pressure of methanol to approximately 2×10^{-6} Torr. For each of three acid compositions, the value of γ was determined over a temperature range of 210−235 K. The results are plotted in Figure 4, with linear regressions of these data and each curve plotted separately. While the range of γ values is clustered between 0.012 and 0.023 in the range of concentrations and temperatures, a general trend can be observed. At very low temperatures (~210 K), the values for γ are the same regardless of acid concentration. As temperature increases, however, γ decreases for 65 wt % H_2SO_4, while it increases for 75 and 80 wt %. This also suggests a change in the reaction mechanism involved in uptake, as previously discussed.

For concentrations greater than 65 wt %, almost all uptake is reactive, and thus, the atmospherically important values of H^* and k_l can be determined from eq 4. Initially, these values are presented as a product. Figure 5 shows the results for the calculation of $H^*k_l^{1/2}$ for acid concentrations between 65 and 80 wt %. The combined product is found to increase with acid concentration and decrease as a function of temperature.

To our knowledge, the effective Henry's law constant has not been measured for acid compositions between 65 and 80%. The determination of k_l can be made by assuming the Henry's law constant of methanol to be approximately that of the value for methanol in water (based on the similar pK_a values of methanol and water).[24] The assumption is further supported by the evidence that the solubility of peroxyacetyl nitrate (PAN) in liquid sulfuric acid is nearly equal to that in water.[25] The equation for H^* of methanol in water[26−28] is

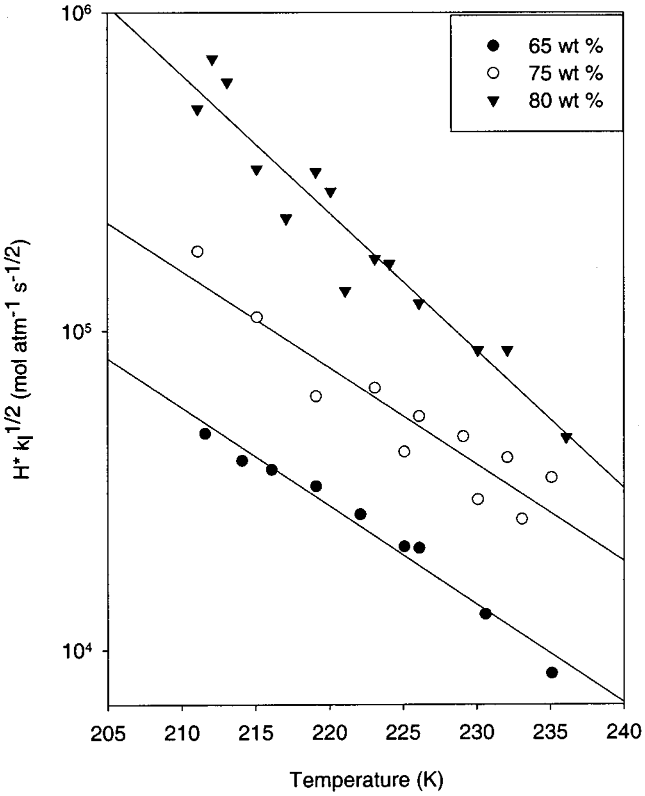

Figure 5. Determination of $H^*k_l^{1/2}$ for 65−80 wt % H_2SO_4. The combined product is found to increase with acid concentration and decrease as a function of temperature. See text for details.

$$\ln(H^*) = \ln[K_{H(T_0)}] + (\Delta H_0/R)(1/T_0 - 1/T) \qquad (9)$$

where $\ln[K_{H(T_0)}] = 5.39$, $\Delta H_0/R = -4900$ K and $T_0 = 298.15$ K. The overall rate constant for methanol in H_2SO_4 based on this assumption is shown in Figure 6. The reaction rate increases as acid concentration increases in the temperature range. The rates for 65 and 75 wt % H_2SO_4, which exhibited thermal reversibility as shown in Figure 2, increase with increasing temperature. The data collected at 80 wt % H_2SO_4, however, show a nearly constant reaction rate with respect to temperature. This also supports the further reactions of methanol and sulfuric acid to dimethyl sulfate, reactions 7 and 8, in this acidity range.

Atmospheric Implications. In Figure 6, the overall reaction rate, k_l, in the range of 0.1−10 s^{-1} suggests that it is potentially important in the upper troposphere. We adopt 10 km as a representative altitude. Using 65 wt % and 220 K, we calculate that the diffusoreactive length, $l = (D_l/k_l)^{1/2}$, is about 7 μm by assuming $D_l = 5 \times 10^{-8}$ cm^2/s and $k_l = 0.1$ s^{-1}. Since the size of stratospheric aerosols is typically submicron or smaller, we conclude that reactions 7 and 8 occur throughout the volume of aerosols and that a portion of gas-phase methanol is eventually converted into MHS and dimethyl sulfate.

To illustrate the atmospheric importance of the reaction of methanol in sulfuric acid, we need to detail the loss mechanisms and their reaction rates under typical atmospheric conditions. As noted in the Introduction, the photodissociative loss of methanol has been found to be insignificant.[5] Reactions with

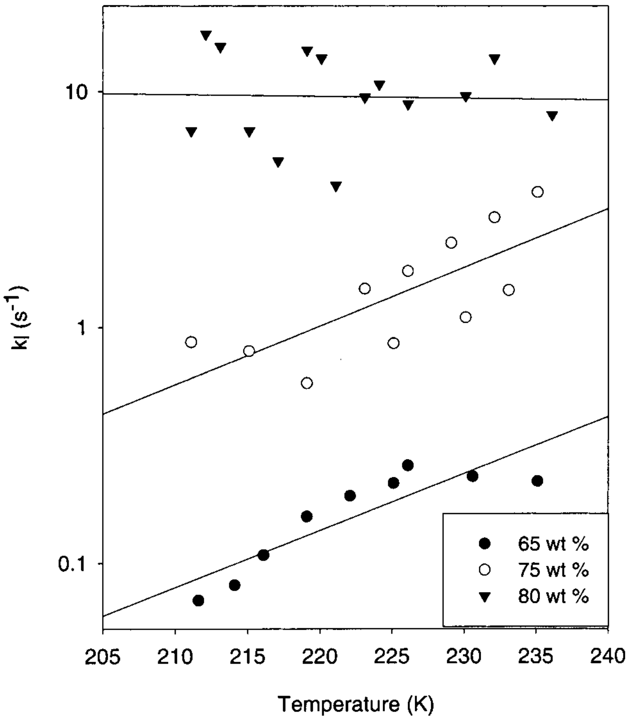

Figure 6. Rate constant for methanol uptake by 65, 75, and 80 wt % H_2SO_4. While the curves for 65 and 75 wt % show similar temperature dependence, k_l for 80 wt % is independent of temperature, indicating that the overall reaction mechanism is different than that observed for the lower acid concentrations.

liquid water or ice are also found to be very slow.[6] In addition to the reaction mechanism we have suggested, the only other significant loss mechanism for methanol is reaction with the OH radical. The estimated reaction rate for $OH + CH_3OH \rightarrow CH_3O + H_2O$ at 10 km and 220 K is $k(OH + CH_3OH) \times [OH] = 1.3 \times 10^{-7}\ s^{-1}$, and the lifetime is nearly 80 days. The rate coefficient is taken from the recommendation of the NASA Data Evaluation Panel Report,[28] and the diurnally averaged OH concentration is assumed to be 3×10^5 molecules/cm^3.[28]

To calculate the loss rate of methanol due to the reaction with sulfuric acid, we estimate the first-order rate to be $^1/_4\gamma\omega A$. The γ value is adopted from the data for 65 wt % H_2SO_4 reported in the previous section. We assume the surface-area density of sulfate aerosol at an altitude of 10 km to be about 2×10^{-7} cm^2/cm^3 for volcanic-perturbed conditions and 1×10^{-8} cm^2/cm^3 for quiescent conditions.[29,30] By using the mean thermal velocity for methanol, ω, at 220 K, we estimate the rate to be $4 \times 10^{-5}\ s^{-1}$ under perturbed volcanic conditions and $2 \times 10^{-6}\ s^{-1}$ under quiescent conditions. Thus, the reaction rate with sulfuric acid is significantly greater than the reaction rate with hydroxyl radicals. Under quiescent conditions, the lifetime of methanol is about 5 days, as compared to the average lifetime of 16 days reported by Singh et al.[1]

Although the calculations are somewhat crude, we conclude that the reaction with sulfuric acid forming methyl hydrogen sulfate and dimethyl sulfate is the dominant loss mechanism of methanol and that the oxidation of methanol is only a minor source of hydroxyl radicals in the upper troposphere. Furthermore, balancing the measured abundance of methanol and our calculated removal rates, the global source of methanol is greater than the estimated value[1] of 45 Tg/yr.

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