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Heterogeneous Chemistry of Butanol and Decanol with Sulfuric Acid: Implications for Secondary Organic Aerosol Formation

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Recent environmental chamber studies suggest that acid-catalyzed reactions between alcohols and aldehydes in the condensed phase lead to the formation of hemiacetals and acetals, enhancing secondary organic aerosol (SOA) growth. We report measurements of heterogeneous uptake of butanol and decanol on liquid H_2SO_4 in the range of 62−84 wt % and between 273 and 296 K. Both alcohols exhibit two distinct types of uptake behaviors (partially irreversible vs totally irreversible uptake), depending on the acid concentration and temperature. For the partially irreversible uptake, a fraction of the alcohol was physically absorbed while the other fraction underwent irreversible reaction. For the totally irreversible uptake, the alcohols were completely lost onto the sulfuric acid. The Henry's law solubility constant (H*) was determined from the time-dependent uptake, while the reactive uptake coefficients were calculated from the time-independent irreversible loss. Coexistence of butanol or decanol with octanal or decanal did not show enhanced uptake of the aldehydes in the sulfuric acid. Protonation and dissolution likely account for the reversible uptake, while formation of alkyl sulfate or dialkyl sulfate explains irreversible uptake of the alcohols. The results suggest that heterogeneous uptake of larger alcohols is unlikely of significant importance in the lower atmosphere except in the case of freshly nucleated aerosols that may have high acid concentrations.

Introduction

Atmospheric alcohols have received much attention[1−4] because of their likely roles in heterogeneous reactive aerosol growth. While methanol is more abundant in the atmosphere, other alcohols (mainly C2−C4) have been measured[5−9] to be in the low ppb (parts per billion) range. It is also possible for higher molecular weight alcohols to be introduced to the atmosphere by biogenic, anthropogenic, and photoreactive means.[10] Previous investigations have mainly focused on the interaction between alcohols and sulfuric acid. High levels of sulfate aerosols and alcohols in the atmosphere allow this combination to have a potentially significant impact on visibility, human health, and climate because of direct and indirect forcing.[11]

One possible reaction pathway for alcohols involving the aerosol phase is direct interaction with sulfuric acid. Such an esterification process was first reported in the 1950s.[12,13] These studies suggested formation of a complex between the alcohol and H_2SO_4 followed by a unimolecular transformation into the alkyl sulfate species. Alternatively, a bimolecular mechanism was proposed for the formation of alkyl sulfate between the alcohols and sulfuric acid as shown in reaction 1a. Elementary equations (not shown) show that possible bimolecular esterification may occur between the alcohol or its protonated ion and sulfuric acid or bisulfate ion. Further reaction of alkyl sulfate with the alcohol results in the formation of dialkyl sulfate (reaction 1b). The study of diethyl sulfate for commercial production has shown that under conditions where H_2SO_4 is in excess compared to ethanol, esterification is second-order.[14] A second-order reaction has also been attributed to the formation of dibutyl sulfate on the basis of kinetic studies.[15]

$$H_2SO_4 + ROH \rightarrow ROSO_3H + H_2O \qquad (1a)$$

$$ROSO_3H + ROH \rightarrow (RO)_2SO_4 + H_2O \qquad (1b)$$

Alcohol reaction products have been found in urban and power plant plumes. For example, dimethyl sulfate has been detected in atmospheric particulate matter for decades. Eatough et al. found concentrations of dimethyl sulfate as high as 8.7 nmol m^{-3} during a 3-day sampling period in the Los Angeles sky.[16] Dimethyl sulfate concentration has been found to increase in aerosols from power plant plumes as the plumes age.[17,18] This observation suggests that as gas-phase SO_2 emitted from fossil fuel burning has sufficient times to form H_2SO_4 in the pollution plume and alcohols from outside the plume mix with the newly formed sulfate aerosols, the reactions 1a and 1b will then occur and, at least in part, lead to the increase of dimethyl sulfate concentration.

Recently, environmental chamber and flow reactor studies suggest that reactions between alcohols and aldehydes will increase aerosol growth.[19,20] With sulfuric acid present as a catalyst, it is speculated that hemiacetals and acetals will be formed via the reactions 2a and 2b, respectively. The hemiacetals are too unstable to be isolated, but subsequent reaction between the hemiacetal and another alcohol molecule forms acetals that can be isolated. Although acetals are more stable than hemiacetals, both can revert back to their parent alcohols and aldehydes with relative ease.[21] The main factor that would hinder acetal decomposition after formation would be significant loss of water from the aerosol. Further reaction of acetals leads to high molecular weight polymers, which will remain in the condensed phase and hence increase organic aerosol growth.

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$$\mathrm{RCHO} + \mathrm{R'OH} \rightleftharpoons \mathrm{RCH(OH)(OR')} \quad (2a)$$

$$\mathrm{RCH(OH)(OR')} + \mathrm{R'OH} \rightleftharpoons \mathrm{RCH(OR')_2} + \mathrm{H_2O} \quad (2b)$$

The chemical mechanism of the interaction between the atmospheric alcohols and sulfuric acid and the role of these alcohols in the formation of secondary organic aerosol are still lacking. In this work, we report heterogeneous chemistry of butanol and decanol on liquid H_2SO_4 in the range of 62−84 wt % and between 273 and 296 K. Uptake of the alcohols on sulfuric acid was carried out using a low-pressure laminar flow reactor coupled to ion drift−chemical ionization mass spectrometry (ID-CIMS). The Henry's law solubility constant (H^*) was determined from the time-dependent uptake, and the reactive uptake coefficients were calculated from time-independent irreversible loss. Additional experiments were performed to evaluate the uptake of aldehydes in the presence of alcohols. Implications of the present results on secondary organic aerosol (SOA) formation are discussed.

Experimental Section

The uptake measurements were performed using a low-pressure laminar flow reactor in conjunction with ion drift−chemical ionization mass spectrometry (ID-CIMS) detection, similar to our previous work.[22,23] A Pyrex reactor of 50 cm in length and internal radius of 1.25 cm was used. Liquid H_2SO_4 was placed into a Pyrex vessel which was recessed to form a trough with 20 cm in length, 2.0 cm in width, and 0.7 cm in depth. A low-temperature circulator (Neslab ULT-80) was used to circulate cold methanol through the outer jacket of the inner reactor, and temperature inside the jacket was monitored with a type J thermocouple.

1-Butanol (EMD Chemicals Inc, 99%), 1-decanol (Avocado Research Chemical Ltd., 99%), octanal (Avocado Research Chemical Ltd., 98%), and 2,4-hexadienal (Aldrich, 95%) were used as received without further purification. A sample bubbler containing the alcohol was placed in a temperature bath to regulate its concentration in the flow reactor. For butanol, an ice bath was used and for decanol the bath temperature ranged from 91 to 98 °C. The alcohol purity was checked by ID-CIMS. The alcohol vapor was introduced into the flow reactor through a movable injector. Butanol in the flow reactor was estimated to be about 10^{-5} Torr and decanol was estimated to be about 10^{-6} Torr, higher than those found in the atmosphere but necessary in our investigation to allow reliable uptake measurements. All carrier flows were monitored with calibrated electronic mass flow meters (Millipore Tylan 260 Series). The flow reactor was operated under the laminar flow conditions (i.e., the Reynold number $\mathrm{Re} = 2au\rho/\mu < 2000$, where a is the internal radius of the flow reactor in cm, ρ is the density of the gas in g cm^{-3}, u is the flow velocity in cm s^{-1}, and μ is the absolute viscosity of the gas) with a pressure of about 1 Torr and typical flow velocities of 800−1000 cm s^{-1}. Liquid H_2SO_4 solutions were prepared by dilution of 96.2 wt % H_2SO_4 (EMD Chemical Inc) with deionized water. The acid reservoir was changed for each experiment and the composition of the acid was checked before and after each experiment. The acid compositions were verified by density measurements.

Details of the ID-CIMS instrumentation have been described previously.[24] Briefly, the proton-transfer reaction with H_3O^+ was used,

$$\mathrm{H_3O^+} + \mathrm{X} \rightarrow \mathrm{XH^+} + \mathrm{H_2O} \quad (3)$$

where X and XH^+ denote the alcohol species or its fragment and the corresponding protonated form, respectively. Butanol and decanol were monitored at their protonated fragmentation peaks ($m/z = 57$ for butanol and 142 for decanol, respectively) for higher detection sensitivity. The intensity of the fragment was observed to be linearly proportional to that of its parent alcohol. Octanol and 2,4-hexadienal were monitored at their protonated peaks ($C_8H_{16}OH^+$ and $C_6H_8OH^+$, respectively).

Uncertainty in the uptake measurements was primarily associated with errors such as signal shift over time, the exposed acid volume, and the changing acid concentration because of water evaporation. The acid concentration effect was greater for less concentrated acid because of a higher H_2O partial pressure.[25,26]

Gas-phase uptake by a planar liquid surface can be treated by a diffusional and reactional equation.[27,28] The uptake coefficient was calculated from the initial and time-dependent signals of the alcohol

$$\gamma(t) = \frac{4k}{\omega}\left(\frac{V}{A}\right) \quad (4)$$

where V is the volume of the flow reactor, A is the geometric area of the exposed acid, and ω is the mean thermal speed of the molecule. The first-order rate coefficient (k) is related to the fractional change ($\Delta n/n$) in the gas-phase concentration of the adsorbed/reactive molecule before and after exposure to sulfuric acid by

$$k = \frac{2F_g}{rA}\left(\frac{\Delta n}{n}\right) \quad (5)$$

where F_g is the carrier gas volume flow rate (cm^3 s^{-1}). We did not account for radial gas-phase diffusion since a symmetrical, cylindrical tube was not used for the uptake measurements. The underestimation in the uptake coefficient without the gas-phase diffusion was estimated to be less than 20% for $\gamma < 0.04$. [22]

The solution of time-dependent uptake with no chemical loss in a semi-infinite planar liquid is given as[27,28]

$$\gamma(t) = \alpha[1 - \mathrm{erf}(h\sqrt{t/D_l})]e^{h^2t/D_l} \quad (6)$$

where $h = \alpha\omega/(4RTH^*)$, α is the mass accommodation coefficient, R is the gas constant (0.082 L atm mol^{-1} K^{-1}), T is the temperature, H^* is the effective Henry's law solubility constant, D_l is the liquid-phase diffusion coefficient, and erf(x) is the Gaussian error function. Under the condition that $h(t/D_l)^{1/2} \gg 1$ (i.e., lower solubility or longer time), this solution is approximated as

$$\gamma(t) = \frac{4RTH^*}{\omega}\left(\frac{D_l}{\pi}\right)^{1/2} \quad (7)$$

Hence, eq 7 relates the measured time-dependent uptake coefficient γ to the product of the effective Henry's law solubility constant and the square root of the liquid-phase diffusion coefficient ($H^*D_l^{1/2}$). To estimate the liquid-phase diffusion coefficient, we adopted a method suggested by Klassen et al.[29]

$$D_l = c \times \frac{T}{\eta} \quad (8)$$

where c is a constant determined by the liquid and the diffusing party and η is the viscosity of the liquid.

Results and Discussion

Uptake of Butanol and Decanol on H_2SO_4. Uptake measurements were performed by exposing a certain length of the

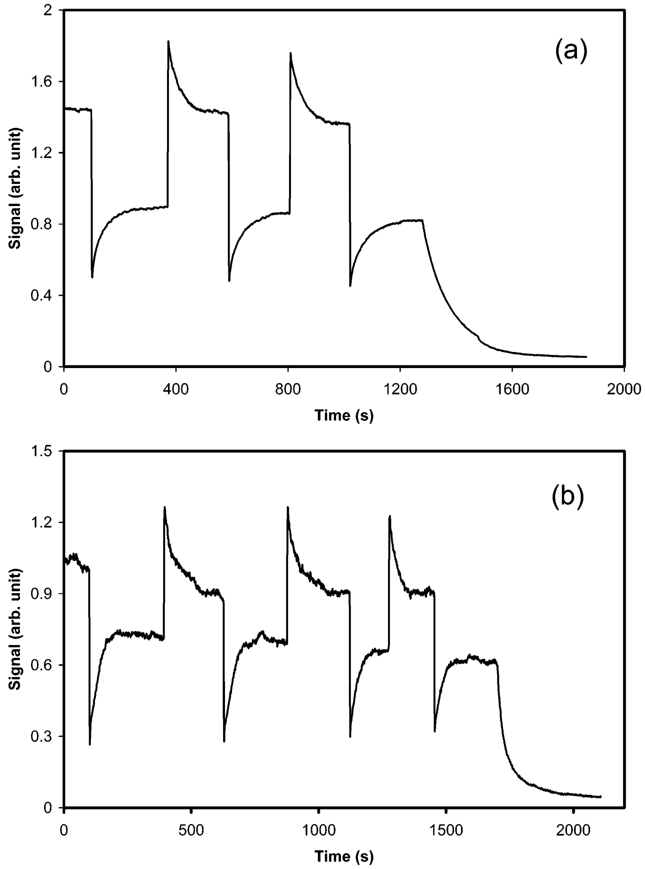

Figure 1. (a) Temporal profiles of butanol when repeatedly exposed and not exposed to a 20-cm length of sulfuric acid. The acid content of H_2SO_4 was estimated to be 73 wt %. Experimental conditions are $T = 296$ K, $P = 1.1$ Torr, and $u = 959$ cm s^{-1}. The butanol flow was terminated after 1250 s. (b) Temporal profiles of decanol when exposed and not exposed to a 20-cm length of sulfuric acid. The acid content of H_2SO_4 is 67 wt %. Experimental conditions are $T = 296$ K, $P = 1.1$ Torr, and $u = 959$ cm s^{-1}. The decanol flow was terminated after 1700 s.

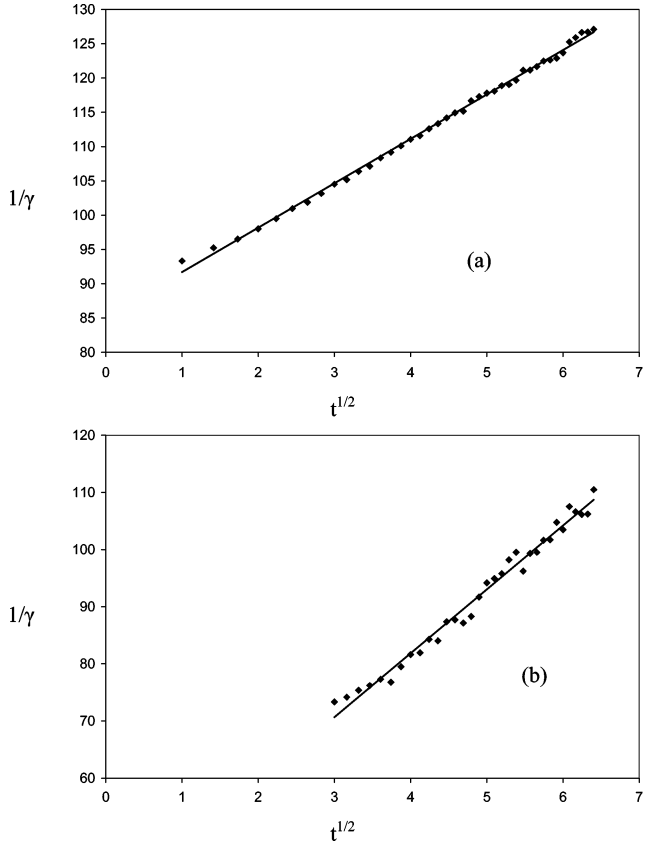

Figure 2. (a) $1/\gamma$ as a function of $t^{1/2}$ for butanol profile in Figure 1a. (b) $1/\gamma$ as a function of $t^{1/2}$ for decanol profile in Figure 1b. The line through the data is the linear least-squares fit. H^* is determined to be 89 375 M atm^{-1} for Figure 2a and 46 539 M atm^{-1} for Figure 2b.

TABLE 1: H^* Measurements of Butanol in H_2SO_4[a]

T (K)	H_2SO_4 (wt %)	H^* (10^3 M atm^{-1})
296	62.4 ± 0.9	47.4 ± 5.1
296	64.2 ± 1.1	60.0 ± 8.6
296	70.3 ± 1.4	83.8 ± 7.6
283	66.0 ± 2.9	53.8 ± 3.1
283	73.2 ± 0.6	83.9 ± 14.9
273	67.2 ± 1.4	79.3 ± 7.6
273	70.4 ± 1.2	139.2 ± 16.0

[a] Each point is the average of at least three measurements, and the error corresponds to second standard deviation (σ^2).

acid to the alcohol vapor while monitoring the alcohol signal using the ID-CIMS. Adsorption and desorption to/from H_2SO_4 in the liquid phase were evident from the decline and recovery in the alcohol signal, respectively. Figure 1a shows temporal profiles of butanol as it was repeatedly exposed and bypassed to a 20-cm length of a 73 wt % sulfuric acid at 296 K. The butanol concentration in the gas phase dropped instantly upon exposure to H_2SO_4 and recovered to approximately 40% of its original value as the H_2SO_4 liquid was saturated. Terminating the exposure resulted in an opposite peak because of desorption followed by stabilization close to the original value. The recoverable adsorption was nearly identical to the desorption, suggesting that butanol was in part physically taken up by H_2SO_4 while the lack of full recovery indicated the butanol was partially lost because of irreversible aqueous-phase reactions. This trend was observed for butanol in the acid concentration range of 62−73 wt % and temperature range of 273−296 K. Similar uptake was observed for decanol over the H_2SO_4 content of 63−69 wt % and temperature range of 273−296 K. Figure 1b shows the temporal profiles of decanol as it was repeatedly exposed and bypassed to a 20-cm length of a 67 wt % sulfuric acid at 296 K. The similar behaviors of reversible and irreversible uptakes were observed in the experiments by Timonen and Leu for uptake of ethanol on 41.1 wt % sulfuric acid.[30]

For the above conditions, the time-dependent uptake coefficients were calculated from the initial and time-dependent alcohol signals using eqs 4 and 5. Shown in Figure 2 is a plot of $1/\gamma_{obs}$ versus $t^{1/2}$, with the H^* determined from the linear least-squares fit of the data. Extrapolation of the fitting line in Figure 2 showed an offset from the origin because of an irreversible loss. The measured H^* of butanol on H_2SO_4 increased with increasing acidity and decreasing temperature as summarized in Table 1. The H^* value increased from 4.7×10^4 to 8.4×10^4 M atm^{-1} for 62−70 wt % H_2SO_4 at 296 K, while for 70 wt % H_2SO_4 H^* increased from 8.4×10^4 to 14×10^4 M atm^{-1} for 296−273 K. The measured H^* for decanol is presented in Table 2. The H^* value for decanol was lower than that of butanol under the similar acid concentration and temperature. In addition, the dependence of H^* on acidity and temperature was not clearly discerned; however, the partially reversible portion of uptake was consistently observed and both reversible and irreversible components of the uptake were clearly observed in Figure 1b. It is plausible that decanol is more sticky and viscous than butanol and hence affects the signal stability of the monitored fragment of decanol. The lower vapor pressure

TABLE 2: H^* Measurements of Decanol in H_2SO_4[a]

T (K)	H_2SO_4 (wt %)	H^* (10^3 M atm^{-1})
296	67.1 ± 0.2	46.4 ± 13.6
296	69.2 ± 1.4	33.6 ± 11.1
283	67.7 ± 0.9	17.6 ± 0.2
283	69.7 ± 0.1	16.8 ± 1.3
273	63.0 ± 0.6	40.7 ± 5.5
273	68.5 ± 0.6	60.9 ± 27.3

[a] Each point is the average of at least three measurements, and the error corresponds to second standard deviation (σ^2).

of decanol also likely caused its concentration during experimentation to be lower than that of butanol.

The increasing H^* for butanol with acidity reflects an enhanced alcohol protonation, a phenomenon covered extensively in the literature.[1,4,12,13,31,32] Higher acid activity and lower temperature favor the protonation process and hence increase the effective Henry law solubility constant H^*. While some butanol may dissolve in the solution without being protonated, under our conditions a majority of the butanol is likely protonated. Michelsen et al. estimates 10−40% of the ethanol in their sulfuric acid during experimentation is protonated in the 39−66 wt % range.[33] This protonation is considered a reversible reaction that is a potential precursor to the formation of alkyl sulfate as discussed in the Introduction section. The irreversible component can be attributed to direct formation of alkyl sulfate or dialkyl sulfate. As shown in eq 2, the reaction of butanol or decanol with sulfuric acid will form butyl sulfate and decal sulfate, respectively. Further reaction of the hydrogen alkyl sulfate (butyl sulfate or decal sulfate) with the alcohol will lead to the formation of respective dialkyl sulfate (dibutyl sulfate or didecal sufate).

In contrast to uptake on more dilute sulfuric acid, uptake of butanol and decanol on higher acid concentrations of sulfuric acid exhibited little saturation on the time scale of the experiment, indicating an irreversible loss because of the aqueous-phase reactions. Figure 3a and 3b depicts uptake measurements of butanol and decanol, respectively, on more concentrated sulfuric acid solutions (80 wt % at 273 K for butanol and 83 wt % at 296 K for decanol). No recovery signal was observed for both cases on the time scale of experiment. Additional experiments were performed to obtain the uptake coefficients of butanol and decanol on sulfuric acid under the high concentration conditions. Figure 4 demonstrates the loss of decanol (triangles) and butanol (circles) as a function of the injector position when the injector was withdrawn at a 4-cm-length interval. Both decays followed the pseudo-first-order kinetics. The pseudo-first-order rate constant can be determined from the slope of the linear least-squares fit of the data shown in Figure 4. The uptake coefficients were computed from the obtained pseudo-first-order rate constant. The uptake coefficients (γ) were determined to be 0.029 for butanol for 80 wt % H_2SO_4 at 273 K (Figure 4, circles) and 0.026 for decanol for 83 wt % H_2SO_4 at 296 K (Figure 4, triangles), respectively. Tables3 and 4 summarize the uptake coefficients for butanol and decanol, respectively. The reactive uptake coefficients are in the range of (3.2−3.6) × 10^{-2} for butanol for 80−83 wt % sulfuric acid at 273−296 K and (2.7−3.6) × 10^{-2} for decanol for 79−84 wt % sulfuric acid at 273−296 K. The measured reactive uptake coefficient of butanol slightly increased with decreasing temperature but exhibited little acid dependence over the acid range used in the experiment. For decanol, the measured reactive uptake coefficients showed weak temperature and acid dependence. In contrast, a temperature dependence inversion was observed by Kane and Leu when studying the irreversible uptake of methanol on H_2SO_4 in the 65−75 wt % range.[2] This observation was suspected to be caused by a change in the uptake reaction mechanism. The change is thought to be an increase in dimethyl sulfate formation at the expense of hydrogen methyl sulfate. It is unlikely that a similar change in reaction mechanism would occur in such a small acid composition range as studied here.

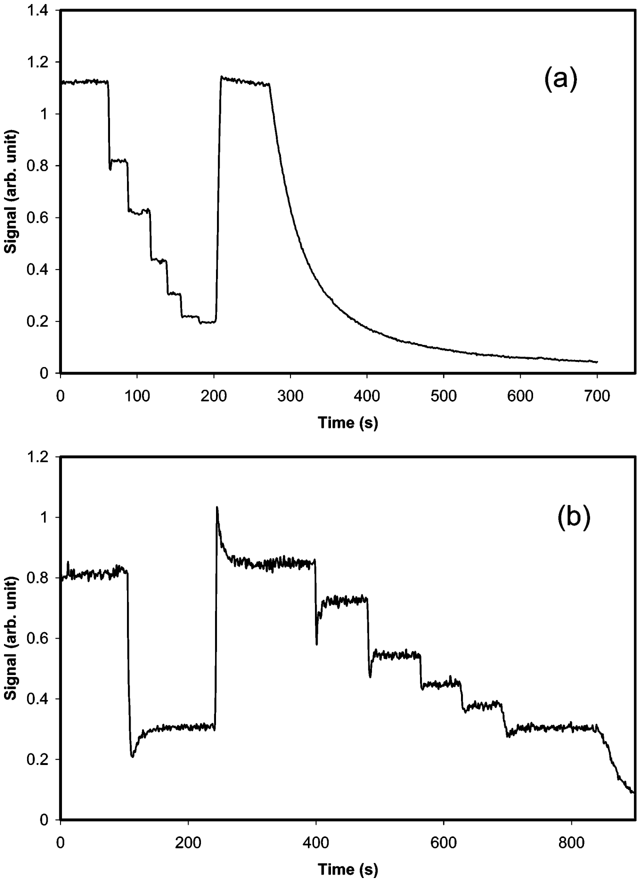

Figure 3. (a) Temporal profile of butanol with stepwise exposure in 4-cm increments to a 20-cm length of sulfuric acid. The acid content of H_2SO_4 was estimated to be 80%. Experimental conditions are T = 273 K, P = 1.0 Torr, and u = 909 cm s^{-1}. The butanol flow was terminated after 300 s. (b) Temporal profile of decanol with stepwise exposure in 4-cm increments to a 20-cm length of sulfuric acid. The acid content of H_2SO_4 was estimated to be 83%. Experimental conditions are T = 296 K, P = 1.1 Torr, and u = 974 cm s^{-1}. The decanol flow was terminated after 850 s.

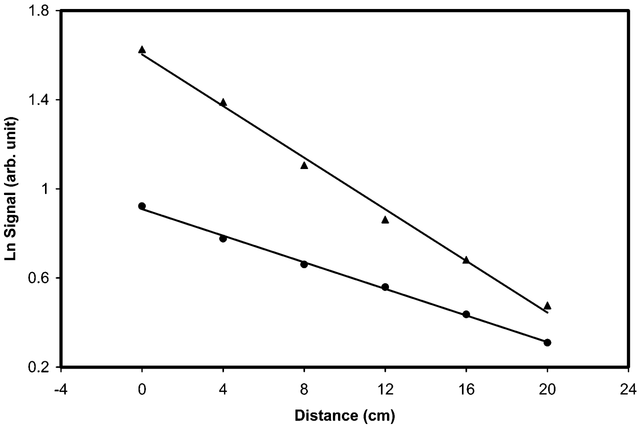

Figure 4. Intensity of alcohol signal as a function of injector distance. Solid circles identify butanol data taken from the experiment described in Figure 3a and solid triangles from that of decanol outlined in Figure 3b.

TABLE 3: γ Measurements of Butanol in H_2SO_4[a]

T (K)	H_2SO_4 (wt %)	γ (10^{-2})
283	80	3.2 ± 0.1
273	80	3.6 ± 0.4
283	81	3.4 ± 0.3
296	82	3.2 ± 0.3
283	82	3.5 ± 0.2
296	83	3.4 ± 0.2

[a] Each point is the average of at least four measurements except 80 wt % and 283 K that is the average of only two measurements. The error corresponds to second standard deviation (σ^2).

TABLE 4: γ Measurements of Decanol in H_2SO_4[a]

T (K)	H_2SO_4 (wt %)	γ (10^{-2})
273	79	2.7 ± 0.3
283	80	2.7 ± 0.3
273	80	3.4 ± 0.3
296	81	3.1 ± 0.3
283	81	2.8 ± 0.6
296	82	3.4 ± 0.7
283	82	3.2 ± 0.1
296	84	3.6 ± 1.0

[a] Each point is the average of at least three measurements, and the error corresponds to second standard deviation (2σ).

Reactive aqueous-phase reactions of butanol and decanol on more concentrated H_2SO_4 solutions lead eventually to the formation of alkyl and dialkyl sulfate (butyl sulfate or decal sulfate) as discussed above. The formation of the simplest alkyl sulfate, for example, methyl sulfate, from the reaction of methanol with sulfuric acid has been investigated in previous studies.[1,2,4,32] Similar studies have been carried out for other alkyl sulfates.[12−14,31,34] Kane and Leu have identified one reaction product as methyl hydrogen sulfate using mass spectrometery.[2] In a subsequent study, Timonen and Leu identified diethyl sulfate as a gas-phase reaction product that increased in concentration with increasing acidity.[30] Unfortunately, the reaction products (e.g., hydrogen alkyl sulfate and dialkyl sulfate) formed in this study remained in the acid solution because of their low vapor pressure and low concentration, preventing identification in the gas phase by our detection methods.

Previous investigations have determined the Henry's law solubility constant and irreversible uptake coefficient for the smaller alcohols methanol and ethanol. Iraci et al. report H^* as high as 10^7 M atm^{-1} for methanol on H_2SO_4 in the 72.2 wt % and 212−221 K range and lower values in the 10^4 M atm^{-1} range for 45.3 wt % acid at 221.8 K.[4] Reversible uptake in roughly the same range is reported for ethanol by Michelsen et al. The experimental conditions for the high uptake is 66.3 wt % H_2SO_4 and ∼217 K while the lower uptake is measured at 227−228 K in 38.5 wt % H_2SO_4.[33] Values around 10^5 M atm^{-1} are reported for ethanol and 41.1 wt % sulfuric acid and ∼223 K by Timonene and Leu.[30] Irreversible measurements by Kane and Leu using methanol found γ values between 0.01 and 0.023 for 65−80 wt % H_2SO_4 and in the temperature range of 210−235 K.[2] Timonen and Leu studied ethanol in ∼40 to ∼80 wt % sulfuric acid and found irreverisble uptake to be between 0.019 and 0.072 for acid temperatures in the 203−223 K range.[30] The values of 10^4−10^5 M atm^{-1} reported for H^* in this work are reasonable compared to the previous studies considering the larger size of the alcohols and different experimental conditions. However, our irreversible uptake values of ∼0.03 are in close agreement to those reported for methanol and ethanol at a much lower temperature.

Simultaneous Uptake of Alcohol and Aldehyde. Previous environmental chamber studies and flow reactor studies have suggested that acid-catalyzed heterogeneous reactions of carbonyls are responsible for measured SOA mass increases.[19,20,35] Several reaction mechanisms have been proposed to explain their measurements, including hydration, hemiacetal and acetal formation, polymerization, and aldol condensation. Of these reactions, the hemiacetal and acetal formation have been suggested to be facilitated in the presence of alcohols. To further survey this reaction pathway, a series of experiments were conducted to assess the role of alcohols in the uptake of octanal and 2,4-hexadienal.

In our previous work,[22] it has been shown that octanal was physically absorbed by sulfuric acid without undergoing irreversible reaction while 2,4-hexadienal irreversibly reacted with sulfuric acid. These interactions were attributed to protonation, enolization, and aldol condensation then followed by polymerization for the case of 2,4-hexadienal. The same uptake experiments as described previously[22] were performed, except that an additional flow of alcohol was introduced to the flow reactor both downstream and later upstream of the sulfuric acid reservoir while the aldehyde was introduced through the moveable injector. We observed no change in the reversible uptake of octanal when butanol was bypassed or exposed to the H_2SO_4 solution. Similar behavior was observed for all combinations between the alcohols and aldehydes studied. The results showed that the uptake of octanal and 2,4-hexadienal was not enhanced in the presence of butanol or decanol. Instead, the aldehydes and alcohols studied appeared to react independently in acidic media to form aldol condensation products and alkyl sulfate species, respectively.

Conclusions

In this work, we present the first measurements of heterogeneous uptake of butanol and decanol on liquid H_2SO_4 in the acid range of 62−84 wt % and between 273 and 296 K. Both alcohols interacted with the sulfuric acid by being physically absorbed in a reversible fashion, as well as irreversibly reacting with the sulfuric acid. The Henry's constant of butanol, because of protonation, increased with decreasing temperature when absorbed in sulfuric acid below 75 wt % and having values ranging from (32.6−95.7) × 10^3 M atm^{-1}. Above this concentration, the uptake exhibited an irreversible reactive behavior. The irreversible reaction was enhanced by decreasing the temperature or by increasing the concentration of the sulfuric acid. The Henry's constants calculated for decanol showed little acid and temperature trends as those of butanol, and the estimated values were in the same order of magnitude, but to a slightly lower extent. At roughly 80 wt %, the irreversible uptake dominated and little or no reversibility was observed for the alcohol loss. The uptake coefficient, because of formation of alkyl hydrogen sulfate or dialkyl sulfate, was enhanced by increasing sulfuric acid concentration or by decreasing temperature. The co-presence of alcohols and aldehydes did not show enhanced uptake, and the results suggest they would interact with the sulfuric acid independently. Since the acidity in particulate matter is typically small in the lower troposphere, the reversible and irreversible uptake of butanol and decanol on particulate matter will most likely be of minimal importance. In areas of high pollution, such as power plant plumes or heavily urban areas, the production of alkyl sulfates may grow to a large enough level to have a significant impact on aerosol growth. This is particularly interesting in the case of newly nucleated particles where sulfuric acid usually plays a role and acid concentrations are high.[11] Our findings are important to atmospheric chemistry because they might help explain why ultrafine aerosols sometimes contain high concentrations of organic matter.[10]

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