7458 *J. Phys. Chem. A* **2005,** *109,* 7458−7465

Surfactant Control of Gas Uptake: Effect of Butanol Films on HCl and HBr Entry into Supercooled Sulfuric Acid

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Received: January 4, 2005; In Final Form: May 27, 2005

The entry of HCl into 60−68 wt % D_2SO_4 and HBr into 68 wt % acid containing 0−0.18 M 1-butanol was monitored by measuring the fractions of impinging HCl and HBr molecules that desorb as DCl and DBr after undergoing H → D exchange within the deuterated acid. The addition of 0.18 M butanol to the acid creates butyl films that reach ~80% surface coverage at 213 K. Surprisingly, this butyl film does not impede exchange but instead enhances it: the HCl → DCl exchange fractions increase from 0.52 to 0.74 for 60 wt % D_2SO_4 and from 0.14 to 0.27 for 68 wt % D_2SO_4. HBr → DBr exchange increases even more sharply, rising from 0.22 to 0.65 for 68 wt % D_2SO_4. We demonstrate that this enhanced exchange corresponds to enhanced uptake into the butyl-coated acid for HBr and infer this equivalence for HCl. In contrast, the entry probability of the basic molecule CF_3CH_2OH exceeds 0.85 at all acid concentrations and is only slightly diminished by the butyl film. The OD groups of surface butanol molecules may assist entry by providing extra interfacial protonation sites for HCl and HBr dissociation. The experiments suggest that short-chain surfactants in sulfuric acid aerosols do not hinder heterogeneous reactions of HCl or HBr with other solute species.

Introduction

Reactions of gas-phase molecules on and in sulfuric acid aerosols can play a significant role in controlling ozone levels in the midlatitude regions of the lower stratosphere and upper troposphere.[1,2] The rates of reactions in the bulk phase depend on the probability with which the impinging gas molecules enter the droplets.[3,4] Observations of organic matter in aerosols in the upper troposphere and lowermost stratosphere prompt questions concerning how this organic material may alter the rates of gas transport and heterogeneous reactions.[5] Organic molecules that are surface active, for example, may reduce the overall reaction rates by coalescing into surface films that impede gas entry into the droplets.[6]

Ozone-depleting processes mediated by sulfuric acid aerosols include the reactions of HCl and HBr with $ClONO_2$, $BrONO_2$, HOCl, and HOBr to produce Cl_2, Br_2, and BrCl, which are then photolyzed into halogen atoms by sunlight.[2] While these reactions are most prevalent in the lower stratosphere, they also occur in the upper troposphere,[7−9] where the aerosols may contain significant amounts of organic material.[5] Our objective is to explore the behavior of HX molecules (X = Cl or Br) impinging on the surface of supercooled sulfuric acid and examine the effect of a model short-chain surfactant, 1-butanol, on the fate of HX molecules in the interfacial region. Reaction-rate calculations suggest that the surfactant coating must significantly impede HX entry to be rate-limiting. For the reaction $HCl(g) + HOCl(aq) \rightarrow Cl_2 + H_2O$ in 60 wt % H_2SO_4 at 213 K, the HCl entry probability must drop below 10^{-4} in order to limit the bulk-phase reaction rate.[10,11] This limiting value rises to $\sim 10^{-2}$ for HBr because of its higher solubility in sulfuric acid.[11,12] Long-chain surfactants pack tightly on water at room temperature and can inhibit water transport by factors exceeding 10^4,[13] but we have found that 1-butanol forms more porous surface films on supercooled sulfuric acid.[14] As described in the preceding paper,[6] D_2O evaporation from 60−68 wt % D_2SO_4 at 213 K is unaffected by butyl films comprising at least 80% of a compact monolayer (4×10^{14} cm^{-2}). We ask in this paper if the segregated butyl species can impede HX uptake into sulfuric acid or whether they remain invisible to HCl and HBr as well as to D_2O transport.[15]

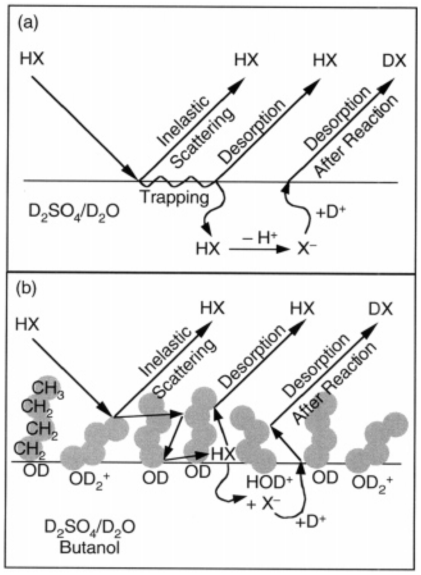

Figure 1. Observed pathways for an HX molecule (X = Cl or Br) colliding with deuterated sulfuric acid: (a) bare acid and (b) acid containing butanol.

The different pathways open to HX molecules colliding with the bare surface of deuterated sulfuric acid are illustrated in Figure 1a.[16,17] The impinging HX molecules may scatter directly from the acid in one or a few collisions, or they may fully dissipate their excess energy and become momentarily trapped

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10.1021/jp0500438 CCC: $30.25 © 2005 American Chemical Society
Published on Web 08/02/2005

at the surface, losing memory of their initial trajectories. Some of these thermally equilibrated HX molecules are then propelled into vacuum by thermal motions of the surface molecules. The remaining HX diffuse into the acid as intact molecules or as $X^-/H^+/D^+$ ions after dissociating at the interface. To characterize these different processes, we measure the fraction of thermally equilibrated HX molecules that undergo H → D exchange and desorb as DX. Regardless of whether reaction occurs in the interfacial or bulk regions of the bare acid, we find that all HX molecules that ultimately leave as DX enter and remain in the acid for long times before desorbing.[16,18] The exchange fraction therefore represents the fraction of trapped HX molecules that dissolve in the acid and become available to react with other solute species in the bulk.

How do these pathways change in the presence of a surfactant film, as depicted in Figure 1b? The addition of BuOD ($CH_3CH_2CH_2CH_2OD$) to sulfuric acid creates a surface film likely composed of BuOD and $BuOD_2^+$ in addition to small amounts of $BuOSO_3^-$ and $BuOSO_3D$.[14,19] We initially imagined that the alkyl chains would reduce HX entry by blocking adsorption sites and hindering transport to the underlying acid. We find, however, that butyl films on 60−68 wt % D_2SO_4 actually increase H → D exchange for HBr and HCl. Experiments below demonstrate that the larger HBr → DBr exchange corresponds to a larger uptake of HBr into butyl-coated acid than into bare acid. In the case of HCl, we cannot rule out that this extra exchange occurs solely within the butyl layer. The experiments suggest that H → D exchange is enhanced because the OD groups of the segregated butanol molecules provide extra interfacial sites for HCl and HBr hydrogen bonding and dissociation.

Experimental Procedure

The HCl, HBr, and CF_3CH_2OH scattering studies were conducted using the same apparatus and 60−68 wt % D_2SO_4 solutions containing 0−0.18 M BuOD described in the preceding paper.[6] Beams of 100 kJ mol^{-1} HCl were created by expanding HCl (2% mixture in H_2) through a 0.13 mm diameter glass nozzle heated to ∼80 °C to suppress dimerization. The ratio of $(HCl)_2/HCl$ in the incident beam was estimated from the H_2Cl^+/HCl^+ ratio at $m/z = 39$ and 38 because of preferential fragmentation of $(HCl)_2$ into H_2Cl^+ upon ionization in the mass spectrometer. This ion ratio was measured to be only 0.002, indicating that HCl exists predominantly as monomers in the incident beam. Beams of 150 kJ mol^{-1} HBr were similarly prepared with an H_2Br^+/HBr^+ ratio of 0.003. The beams were directed at the acid at $\theta_{inc} = 45°$, and the HCl (HBr) and DCl (DBr) species exiting the acid at $\theta_{fin} = 45°$ were monitored at $m/z = 38$ (82) and 39 (83). The HCl and DCl time-of-flight (TOF) spectra were corrected for fragment ions at $m/z = 38$ and 39 due to evaporating butanol.

Beams of 150 kJ mol^{-1} CF_3CH_2OH were created by bubbling H_2 through 20 mL of CF_3CH_2OH maintained at 8.0 °C. The nozzle was heated to 130 °C to minimize dimerization, but the incident beam may have contained a significant fraction of dimers, as the ratio of $CF_3CH_2OH_2^+/CF_3CH_2OH^+$, monitored at $m/z = 101$ and 100, was measured to be 0.6. TOF spectra of CF_3CH_2OH and CF_3CH_2OD exiting at $\theta_{fin} = 45°$ were recorded at $m/z = 31$ (CH_2OH^+) and 32 (CH_2OD^+), and were corrected for butanol desorption at these m/z values.

Results and Analysis

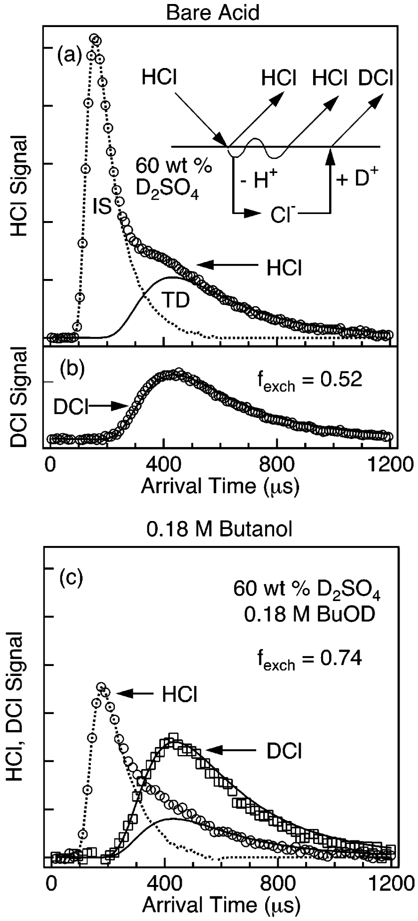

Figure 2. Time-of-flight (TOF) spectra of (a) HCl and (b) H → D exchanged DCl following collisions of 100 kJ mol^{-1} HCl with 60 wt % D_2SO_4 at $\theta_{inc} = 45°$. (c) TOF spectra of HCl (○) and DCl (□) following collisions of 100 kJ mol^{-1} HCl with 60 wt % D_2SO_4 containing 0.18 M 1-butanol (BuOD). The HCl IS channel is represented by the dotted curve, and the HCl and DCl TD components are fit by Maxwell−Boltzmann distributions (solid curves). The spectra in each panel in this figure and in Figure 3 are displayed on the same vertical scale.

Collisions of HCl with 60−68 wt % D_2SO_4. Figure 2a shows the TOF spectrum of HCl following collisions of 100 kJ mol^{-1} HCl with 60 wt % D_2SO_4 at 213 K. This spectrum, which is a plot of mass spectrometer signal versus arrival time, displays an inelastic scattering (IS) component at early arrival times (high exit energies) and a thermal desorption (TD) component at later arrival times (low exit energies). The solid curve is a Maxwell−Boltzmann distribution fit to the TD component at the acid temperature of 213 K. The DCl TOF spectrum, shown in panel b, is fit well by a Maxwell−Boltzmann curve and shows no evidence of hyperthermal DCl at short arrival times, indicating that there is no direct HCl → DCl exchange upon collision. The fraction f_{exch} of thermalized HCl molecules that undergo exchange to DCl is calculated by integrating the DCl and HCl thermal distributions according to

$$f_{exch} = \frac{\int I_{TD}^{DCl}(t)\,dt}{\int I_{TD}^{DCl}(t)\,dt + \int I_{TD}^{HCl}(t)\,dt}$$

where I_{TD} is the relative flux of thermally desorbing molecules obtained from each TOF spectrum.

The measured exchange fraction from Figure 2a,b is 0.52 ± 0.02; approximately half of the HCl molecules that thermalize on the surface undergo H → D exchange and then desorb as DCl from 60 wt % D_2SO_4, while the remaining HCl desorb

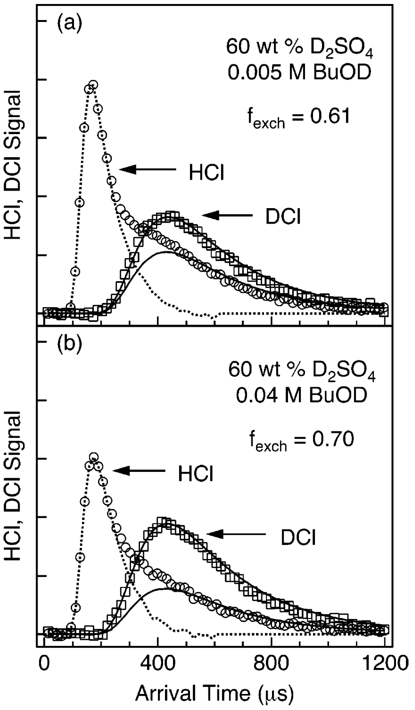

Figure 3. TOF spectra of HCl (O) and DCl (□) following collisions of 100 kJ mol^{-1} HCl with 60 wt % D_2SO_4 containing (a) 0.005 and (b) 0.04 M BuOD at 213 K. The HCl IS channel is represented by the dotted curve, and the HCl and DCl TD components are fit by Maxwell–Boltzmann distributions (solid curves).

before reaction occurs. As shown later in Figure 6, f_{exch} is the same at near-thermal collision energies of 14 kJ mol^{-1}. Uptake measurements further indicate that all thermalized HCl molecules leave the acid as either HCl or DCl within the 0.45 s time that the liquid is exposed to the vacuum.[16] Thus, the exchange fraction accounts for all HCl molecules that enter the acid.

Figure 2c shows TOF spectra of HCl and DCl following collisions of HCl with 60 wt % D_2SO_4 containing 0.18 M BuOD at 213 K. The addition of butanol suppresses inelastic scattering and shifts the IS peak to slightly later arrival times. These trends are identical to those observed for argon atom collisions in the preceding paper.[6] However, the DCl desorption signal is nearly 3 times as large as the HCl desorption signal, yielding $f_{\text{exch}} = 0.74$, a value that is *larger* than for the bare acid. Additionally, Figure 3 compares HCl and DCl TOF spectra following HCl collisions with 60 wt % D_2SO_4 at two intermediate butanol concentrations of 0.005 and 0.04 M. These spectra show that the HCl desorption signal steadily decreases and the DCl desorption signal steadily increases as more butanol is added, resulting in f_{exch} values of 0.52, 0.61, 0.70, and 0.74 at BuOD concentrations of 0, 0.005, 0.04, and 0.18 M, respectively.

The exchange fractions for HCl in collisions with 60 wt % D_2SO_4 at 213 K are plotted against butanol concentration in Figure 4. As in the preceding paper,[6] the surface excess of butyl species is plotted along the right-hand axis, calculated from surface tension measurements of 58 wt % H_2SO_4 at 294 K.[14] The f_{exch} values mirror the trend in the surface segregation of butyl species: f_{exch} increases sharply at low butanol concentrations before approaching an asymptotic value characteristic of a Langmuir adsorption curve. The similar trends in f_{exch} and butyl surface excess imply that the changes in H → D exchange with addition of butanol are caused by the presence of butyl species at the surface rather than by butyl species dissolved in the bulk.

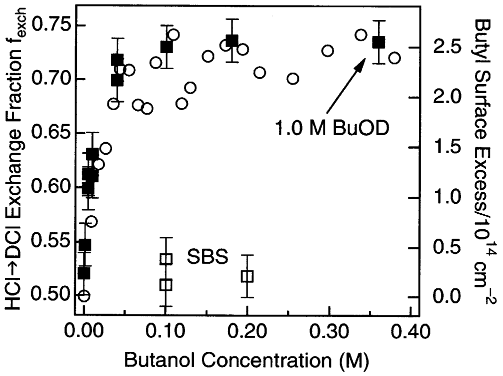

Figure 4. HCl → DCl exchange fraction f_{exch} versus butanol concentration (■) in 60 wt % D_2SO_4 at 213 K. HCl f_{exch} values for 0.10 and 0.20 M sodium 1-butanesulfonate (SBS) are shown as open squares. On the right axis is the butyl surface excess (○), calculated from surface tension measurements of butanol in 58 wt % H_2SO_4 at 294 K.[14] Additional measurements show that the maximum butyl surface coverage rises from 2.5×10^{14} to 4×10^{14} cm^{-2} as the temperature is lowered from 294 to 213 K. The uncertainties are ±0.02 in f_{exch} and $\pm 0.3 \times 10^{14}$ cm^{-2} in the surface excess.

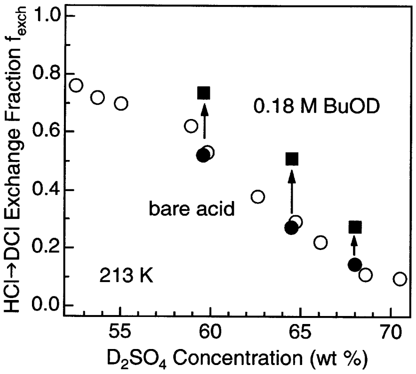

Figure 5. HCl → DCl exchange fraction versus D_2SO_4 concentration: bare acid values from ref 18 (○), bare acid values reproduced for this work (●), and values measured with acid containing 0.18 M BuOD (■). Arrows indicate the increase in f_{exch} upon addition of butanol. The uncertainties in f_{exch} (based on reproducibility) are smaller than the symbols.

The dependence of H → D exchange on the surfactant headgroup can be examined by replacing the OD group of butanol with a different functional group. As a first step in this investigation, we replaced butanol with sodium 1-butanesulfonate, $CH_3CH_2CH_2CH_2{-}SO_3^{-}Na^{+}$ (SBS), chosen because the C–S linkage eliminates the basic oxygen atom in butanol. By comparing argon atom scattering from the SBS and butanol-doped acids, we estimate that the surface concentration of SBS is roughly 2.5×10^{14} cm^{-2}, which for BuOD would increase f_{exch} from 0.52 to 0.66. The open squares in Figure 4 show that f_{exch} does not change upon addition of 0.10 or 0.20 M SBS. This invariance implies that the OD group of BuOD is necessary for enhancing HCl → DCl exchange.

The changes in f_{exch} with acid concentration for bare and butanol-doped D_2SO_4 at 213 K are summarized in Figure 5. The open circles show previous measurements[18] of HCl f_{exch} for 53–70 wt % D_2SO_4, which overlap well with the present measurements (filled circles) at 60, 64, and 68 wt % D_2SO_4. The exchange fraction rises steadily as the acid is diluted with water, increasing from 0.10 to 0.76. The addition of butanol raises f_{exch} at each acid concentration (filled squares), from 0.52 to 0.74 (60 wt % D_2SO_4), 0.27 to 0.51 (64 wt % D_2SO_4), and 0.14 to 0.27 (68 wt % D_2SO_4). These changes do not arise from bulk dilution of the acid by butanol: 0.18 M BuOD, if treated

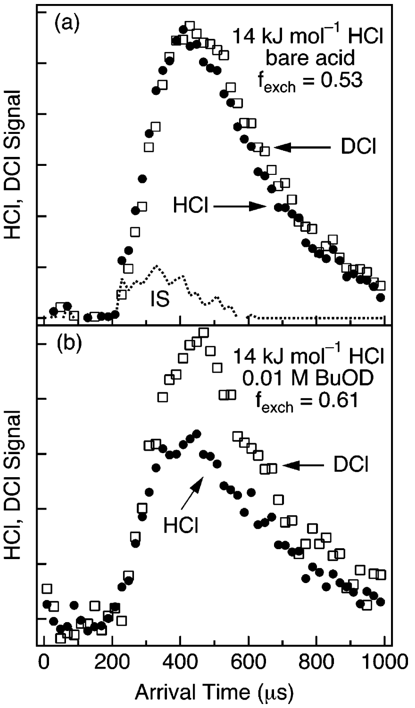

Figure 6. TOF spectra of HCl (●) and DCl (□) following collisions of 14 kJ mol^{-1} HCl with 60 wt % D_2SO_4 at 213 K: (a) bare acid and (b) acid containing 0.01 M BuOD. The dotted curve in panel a represents the inelastic scattering component of the HCl spectrum. Panels a and b are not displayed on the same vertical scale.

as D_2O, effectively lowers the acid concentration by only 0.5 wt %. We also note that the exchange fractions are independent of butanol replenishment times from 0.1 to 1.0 s, in accord with measurements in the preceding paper[6] that show that the butanol film is established within 0.1 s at all butanol concentrations used here.

High-energy HCl molecules (100 kJ mol^{-1} = $56RT_{acid}$) were employed in these experiments because their fluxes are higher than thermal-energy beams and because the high recoil velocities of directly scattered HCl enable cleaner separation of the IS and TD components and therefore more precise calculation of f_{exch}. We found in earlier studies that f_{exch} is independent of incident energy from 14 to 100 kJ mol^{-1}.[16,18] In addition, the fraction of HCl molecules that scatter directly from the surface decreases steadily as the collision energy is lowered, nearly vanishing at E_{inc} = 14 kJ mol^{-1} ($8RT_{acid}$). Figure 6a reproduces this result for bare 60 wt % D_2SO_4, where f_{exch} = 0.53 at 14 kJ mol^{-1} is unchanged from 0.52 at 100 kJ mol^{-1} (Figure 2a,b). Figure 6b illustrates the same trends upon addition of 0.01 M butanol. Nearly all HCl molecules thermalize at E_{inc} = 14 kJ mol^{-1} on the butyl-covered surface, and f_{exch} is measured to be 0.61, close to the value of 0.63 at 100 kJ mol^{-1}.

HX (X = Cl or Br) Residence Times in Bare and Butyl-Coated D_2SO_4. The interval between HX trapping and DX desorption can be investigated by measuring how long the HX and DX molecules spend in the bare and butanol-doped acids.[16,17] The enhancements in the H → D exchange fraction due to surface butyl species conceivably arise from two different pathways: (i) the butyl film assists HX molecules (as intact HX or as ions) in entering and dissolving into the bulk acid, or (ii) the butyl film itself provides an environment in which some HX molecules undergo H → D exchange and desorb as DX without ever dissolving in the bulk acid. These two pathways should occur on distinct time scales: DCl, for example, has a residence time of 130 μs in 60 wt % D_2SO_4 at 213 K,[18] whereas the time spent in the interfacial region would be less than 1 μs, assuming a depth of 10 Å and a diffusion coefficient of 4×10^{-8} cm^2 s^{-1}.[20]

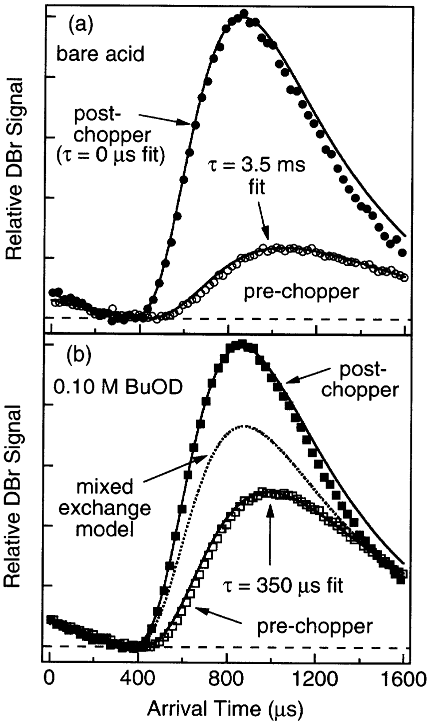

Figure 7. Comparison of post- and prechopper TOF spectra of H → D exchanged DBr following collisions of 150 kJ mol^{-1} HBr with 68 wt % D_2SO_4 at 213 K: (a) bare acid and (b) acid containing 0.10 M BuOD. The postchopper spectra in panels a and b are normalized to each other. The solid curves are simulated prechopper spectra using best-fit residence times of $\tau_{bare} = 3.5 \pm 1.5$ ms for bare acid (a) and $\tau_{BuOD} = 350 \pm 70$ μs for butanol-doped acid (b). The dotted curve in panel b is the simulated prechopper spectrum based on the mixed interfacial/bulk exchange model (model ii) described in the text.

We report pulsed-beam experiments with HBr impinging on bare and butyl-coated acid (68 wt % D_2SO_4) in addition to HCl for two reasons. First, DBr has a longer residence time (~10^{-3} s) than DCl (~10^{-4} s) in the acid, due mainly to its higher solubility. Second, the increase in f_{exch} from bare to butyl-coated acid is even more dramatic for HBr than for HCl: in 68 wt % D_2SO_4 at 213 K, f_{exch}(HBr) rises from 0.22 in bare acid to 0.65 in 0.10 M BuOD-doped acid (TOF spectra not shown). This is the largest change we have measured. These differences permit a clearer differentiation between the two pathways i and ii for HBr than for HCl.

Solute residence times are measured in two steps, as described in ref 16. The chopper wheel is first placed between the liquid and the mass spectrometer. In this postchopper position, the incident HX molecules strike the surface continuously and the arrival times depend only on the velocities of the outgoing species (as shown in Figure 1 of the preceding paper[6]). The chopper wheel is then moved before the liquid, generating 50 μs HX pulses that impinge on the acid surface. The DX arrival times at the mass spectrometer in this case depend both on the residence times of DX in the acid and on their flight times from the chopper wheel to the surface and from the surface to the mass spectrometer.

Figure 7a shows pre- and postchopper TOF spectra of H → D exchanged DBr desorbing from bare 68 wt % D_2SO_4, following thermalization of 150 kJ mol^{-1} HBr. The postchopper spectrum is fit by a Maxwell−Boltzmann distribution, which corresponds to zero residence time. The prechopper spectrum is significantly weaker and shifted to longer arrival times relative to the postchopper spectrum. This reduction in intensity and shift in time arises from molecules that diffuse deeply into the acid and emerge at later times, thus spreading the signal over a broader distribution of arrival times. The prechopper TOF spectrum is fit well with a characteristic residence time τ of 3.5 ± 1.5 ms using the fitting procedure described in ref 16. This solvation time may be expressed as[16,17]

$$\tau = D\left(\frac{4H^{*}RT}{\alpha\langle v\rangle}\right)^{2} \qquad (1)$$

where D is the solute diffusion coefficient, H^* is the combined solubility of Br^- and DBr, and $\langle v\rangle = (8RT/\pi m_{gas})^{1/2}$. The entry probability α is the fraction of thermally impinging HBr molecules that enter the acid, which we have shown for bare sulfuric acid to be equal to f_{exch}.[16] For $D = 8.5 \times 10^{-9}$ cm^2 s^{-1} and $\alpha = f_{exch} = 0.22$, we obtain $H^* = (4.7 \pm 1.1) \times 10^4$ M atm^{-1}, in good agreement with the predicted value of 5.8×10^4 M atm^{-1} for 69.8 wt % H_2SO_4 (68.0 wt % D_2SO_4).[20−22] The relation between α and f_{exch} for the butyl-coated acid is the focus of the experiments below and the first part of the Discussion.

The effect of adding 0.10 M BuOD is shown in Figure 7b. Compared to the prechopper spectrum in panel a, the prechopper spectrum in panel b is more intense and shifted to earlier times. These changes may be analyzed using the two pathways mentioned above. We first address the scenario (model i) in which the butyl film assists HBr in dissolving into the bulk acid. In this model, all HBr molecules that emerge as DBr first dissolve into the acid and the entry probability α is equal to the exchange fraction f_{exch}. Because the residence time τ varies as α^{-2}, the increase in α from 0.22 for bare acid to 0.65 for 0.1 M BuOD must be accompanied by a decrease in residence time from 3.5 ms for bare acid to $(3.5\text{ ms})(0.22/0.65)^2 = 400$ μs for 0.10 M BuOD, assuming that the alcohol does not change the solubility of HBr. The fit to the prechopper spectrum in Figure 7b yields $\tau = 350 \pm 70$ μs, in good agreement with this prediction. The change in prechopper TOF spectra from bare acid to 0.10 M BuOD is therefore consistent with the butyl film enhancing HBr entry and dissolution into the acid.

We next consider the scenario (model ii) in which some HBr molecules undergo H → D exchange in the butyl film and desorb as DBr without dissolving into the bulk acid. We first assume that the entry probability for HBr into the butyl-coated acid is the same as into bare acid, such that $\alpha(\text{butyl}) = f_{exch}(\text{bare}) = 0.22$. The molecules that enter the butyl-coated acid also have the same residence time as in bare acid, assuming that H^* does not change. A fraction (0.22/0.65) of the molecules that undergo exchange do so by entering the bulk acid, while the remaining fraction (1 − 0.22/0.65) of molecules undergo rapid, interfacial exchange followed by desorption. The prechopper spectrum then is a superposition of the signal from these two pathways: the first with $\tau \sim 3.5$ ms and the second with $\tau < 1$ μs. The simulated prechopper spectrum is depicted as the dotted curve in Figure 7b, which does not fit the data. We then varied α from 0 to its maximum value of 0.65 and recalculated τ and the prechopper spectra. The fits to the prechopper data grow steadily better as α approaches 0.65, the value that corresponds to model i. We conclude that all HBr molecules that undergo exchange fully enter the acid as intact molecules or as ions during the time between HBr trapping and DBr desorption.

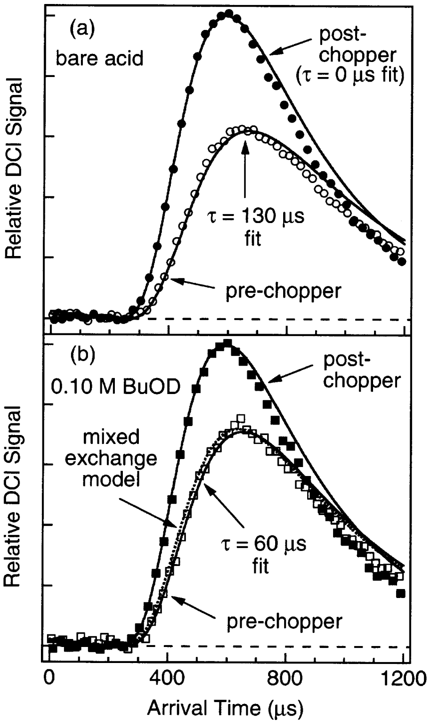

Figure 8. Same as Figure 7, but for desorption of DCl following collisions of 100 kJ mol^{-1} HCl with 60 wt % D_2SO_4 at 213 K. The best-fit residence times are $\tau_{bare} = 130 \pm 40$ μs for bare acid (a) and $\tau_{BuOD} = 60 \pm 30$ μs for butanol-coated acid (b).

The fate of HCl molecules that undergo exchange can also be investigated using residence-time measurements. Pre- and postchopper spectra for DCl are shown in Figure 8a for bare 60 wt % D_2SO_4. The prechopper spectrum is fit to a DCl residence time of 130 ± 40 μs, in good agreement with previous measurements.[18] This time and eq 1 yield $H^* = (1.5 \pm 0.3) \times 10^4$ M atm^{-1}, which overlaps the value of 1.3×10^4 M atm^{-1} obtained from thermodynamic calculations.[22] Panel b compares analogous spectra for 0.10 M butanol-doped acid. The corresponding bulk phase residence time predicted by eq 1 is 66 μs for an increase in entry probability from $\alpha = 0.52$ to 0.73 upon adding 0.10 M butanol. This prediction is in good accord with a best fit τ of 60 ± 30 μs (solid curve). The data are thus consistent with the first model in which an increase in f_{exch} corresponds to increased uptake. However, the second model, in which the 0.21 enhancement in f_{exch} is ascribed to reaction within the butyl film, predicts nearly the same distribution (dotted curve).[23] The two model predictions also converge for HCl → DCl exchange with butanol added to 64 and 68 wt % D_2SO_4. This ambiguity prohibits us from determining uniquely whether the enhancement in f_{exch} for HCl corresponds to an enhancement in uptake, as it does for HBr, or to reaction solely within the butyl film.

Collisions of CF_3CH_2OH with 60−68 wt % D_2SO_4. 2,2,2-Trifluoroethanol (TFE) is a strongly hydrogen bonding molecule that, unlike HCl or HBr, is easily protonated in sulfuric acid solutions. Its solubility is low enough, however, that almost all of the dissolved TFE evaporates within the 0.45 s time window of our experiments.[24] Figure 9a shows TOF spectra following collisions of 150 kJ mol^{-1} TFE with 60 wt % D_2SO_4.[25] The exchange fraction drops from 0.87 for bare acid to 0.85 for acid with 0.18 M BuOD, a change that is within the experimental uncertainty. The values of f_{exch} for 60, 64, and 68 wt % D_2SO_4 are displayed in Figure 9b. The data show that f_{exch} varies little over the 8 wt % acid range, with values close to 1, indicating

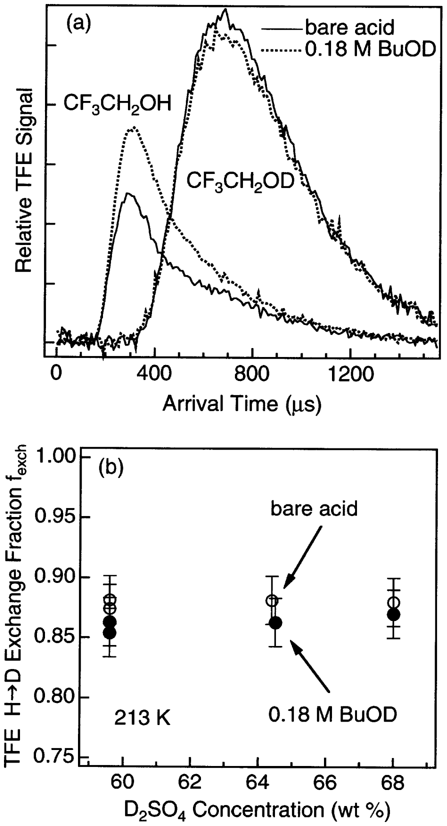

Figure 9. (a) TOF spectra of CF_3CH_2OH and CF_3CH_2OD following collisions of 150 kJ mol^{-1} CF_3CH_2OH with 60 wt % D2SO4 containing 0 and 0.18 M BuOD at 213 K. The bare acid and 0.18 M BuOD spectra are represented by solid and dotted curves, respectively. (b) H → D exchange fraction versus D_2SO_4 concentration for bare acid (○) and 0.18 M BuOD (●).

that nearly all thermalized TFE molecules undergo H → D exchange and then desorb as CF_3CH_2OD.

Discussion

The increase in H → D exchange with increasing butanol concentration implies that butanol fails to impede HCl and HBr transport across the interface, and instead enhances it. We have previously shown that the H → D exchange fraction for HCl and HBr in bare sulfuric acid can be equated with the entry probability α under thermal collision conditions.[16,18] These arguments are summarized below, followed by a discussion of whether this equality holds for the butyl-coated acid. We conclude by postulating that the enhancement in H → D exchange arises from butanol OD groups that act as interfacial hydrogen bonding and protonation sites for HCl and HBr molecules.

Equating H → D Exchange with HCl and HBr Entry. The TOF spectra in Figures 2 and 6, along with previous measurements,[16,18] indicate that the HCl trapping probability increases steadily as the collision energy is decreased and likely approaches 1 at thermal energies of $2RT = 3.5$ kJ mol^{-1}. The spectra also demonstrate that f_{exch} is independent of incident energy from 100 kJ mol^{-1} (56RT) to 14 kJ mol^{-1} (8RT). These observations are consistent with a multistep process in which the impinging HCl molecules thermalize on the surface with probability p_{trap} and lose memory of their initial trajectory. A fraction f_{exch} of the thermalized molecules then undergo H → D exchange and desorb as DCl, while $1 - f_{exch}$ leave as HCl. The overall exchange probability can then be written as the product $p_{exch} = p_{trap}f_{exch}$.

As described above and in ref 16, the interval between trapping and desorption can be investigated by measuring the times that HCl and DCl molecules spend in the acid. We found that HCl molecules that desorb as DCl, having undergone H → D exchange, first dissolve on average for 130 ± 40 μs in 60 wt % D_2SO_4 at 213 K. In contrast, HCl molecules that desorb as intact HCl dissolve for less than 1 μs, the shortest measurable time in our pulsed-beam experiments. The sharp difference in these residence times implies two distinct pathways for HCl thermalizing at the surface of bare sulfuric acid.[16,17] HCl molecules that depart without undergoing exchange do so because they are most likely propelled into the vacuum by thermal motions of solvent species at the surface before reaching a favorable hydrogen bonding configuration. In contrast, HCl molecules that enter the acid do so either as intact HCl that dissociate in the bulk or as $Cl^-/H^+/D^+$ ions after dissociating first at the surface.[26] The ions then dissolve in the acid for long times that depend on their solubility and diffusivity according to eq 1, followed by recombination of D^+ and Cl^- near the surface and desorption of DCl. This picture was also found to describe HBr → DBr exchange, the chief difference being longer solvation times of DBr than of DCl at each acid concentration.[18]

The cumulative results for HCl and HBr interacting with bare sulfuric acid imply that f_{exch} represents the fraction of thermalized molecules that enter the acid as neutral or ionic species. The entry probability α is then equal to $p_{exch} = p_{trap}f_{exch}$, and because p_{trap} approaches 1 at thermal collision energies, the entry probability can be equated with the H → D exchange fraction under thermal collision conditions.[16]

The experiments reported here demonstrate that the equality between α and f_{exch} also holds for HBr → DBr exchange in butanol-doped acid. The prechopper spectrum of DBr desorbing from butyl-coated 68 wt % acid in Figure 7b is fit best using a 350 μs residence time, implying Br^-/DBr diffusion into the acid over a depth of $(D\tau)^{1/2} \approx 200$ Å. This long time is therefore consistent with HBr entry and bulk dissolution before DBr desorption. For HCl, however, our pulsed-beam experiments cannot distinguish between extra H → D exchange solely within the butyl film and enhanced HCl/Cl^- dissolution. Anticipating the discussion below, we emphasize that HCl and HBr are each strongly acidic gases that readily bond to and protonate D_2O and BuOD. This bonding and ionization should not occur before the HCl molecules penetrate deeply into the butyl film because most butanol OD groups straddle the butyl−acid interface, as pictured in Figure 10 of the preceding paper.[6] Nearly all Cl^- and H^+/D^+ ions formed within this region might then be expected to dissolve within the acid before desorbing as DCl, in analogy with the observed pathway for HBr → DBr exchange. We note that near-interfacial DCl → HCl exchange and immediate HCl desorption does occur to a small extent in collisions of DCl with liquid glycerol,[25] and we cannot exclude the possibility that some HCl → DCl exchange in butanol-doped acid occurs solely within the butyl film as well. We hope to resolve this issue through further investigations of different surfactants and acid concentrations and temperatures.

Surfactant-Enhanced HCl and HBr Entry. Within the assumption that enhancements in f_{exch} correspond to enhancements in α, Figure 5 predicts that the addition of 0.18 M BuOD increases the entry probability of HCl into sulfuric acid at 213 K from 0.14 to 0.27 (68 wt % D_2SO_4), 0.27 to 0.51 (64 wt % D_2SO_4), and 0.52 to 0.74 (60 wt % D_2SO_4). This enhancement is larger for HBr, rising from 0.22 to 0.65 (0.10 M BuOD in 68 wt % D_2SO_4). Figure 5 also shows that the addition of water increases f_{exch} for HCl, with parallel trends for HBr.[18] Unlike butanol, however, water is not surface active in sulfuric acid: Auger spectroscopy and surface tension data show that there is little or no surface segregation of water or acid species.[27,28] We previously postulated that H → D exchange increases with dilution as more D_2O molecules become available for hydrogen bonding and protonation in the interfacial region, enabling more HCl and HBr molecules to be captured during the brief time between trapping and desorption.[18] We emphasized the role of interfacial instead of bulk-phase water because the pulsed-beam experiments indicated that the branching between desorption and dissolution of adsorbed HCl and HBr must occur within 1 μs, which corresponds to a diffusion depth of less than 10 Å in 68 wt % D_2SO_4 at 213 K.

The addition of a surfactant permits further decoupling of the interfacial and bulk regions: the Langmuir-like enhancements in H → D exchange shown in Figure 4 must be caused by interfacial rather than bulk-phase butyl species. The butyl film is likely to be dominated by BuOD and $BuOD_2^+$, with smaller amounts of $BuOSO_3^-$ and $BuOSO_3D$. The headgroups of these different species must influence the packing and conformations of the butyl chains, but we focus on the role of neutral BuOD in enhancing HCl and HBr reactivity because of its basic character. The steady increase in HCl → DCl exchange upon addition of D_2O or BuOD implies that the OD groups on each molecule act as interfacial hydrogen bonding sites that help drag HCl through the interface or as protonation sites that initiate HCl dissociation immediately at the interface. While data are not available at −60 °C, the basicity of BuOH is expected to be only slightly less than H_2O at 25 °C,[29] and primary alcohols do not readily form alkyl chlorides or bromides but are reversibly protonated by HCl and HBr.[30] Within this picture, butanol is a base like water that can bond to and be protonated by HCl and HBr, but unlike water it resides preferentially at the interface.

The essential role of interfacial butanol OD groups is further supported by HCl → DCl exchange measurements using the surfactant sodium butanesulfonate instead of butanol, as shown in Figure 4. The unchanged values of f_{exch} are consistent with the weak basicity of $R-SO_3^-$ groups, which cannot be readily protonated by HCl.

The enhancement in H → D exchange by interfacial butanol molecules also disappears when the basic molecule trifluoroethanol is substituted for HCl or HBr. Figure 9 shows that the TFE exchange fraction does not change upon addition of butanol or with acid concentration over 60−68 wt % D_2SO_4 by more than 0.02, which lies within our estimated uncertainty. The exchange fraction remains high, above 0.85, for both bare and butanol-coated acid. The high entry probability implied by these measurements is likely driven by facile protonation of TFE in the interfacial region. The trends in Figure 9 suggest that entry is only slightly impeded by the butyl film even at coverages corresponding to ~80% of maximum packing. TFE entry is not aided by the addition of butanol, as in the case of HCl or HBr, because the segregated butyl species dilute the surface region and reduce its acidity. The high transport probability of TFE through the butyl-coated surface is consistent with the unimpeded evaporation of D_2O measured in the preceding paper,[6] and shows that even large molecules may pass nearly unimpeded between the butyl chains and reach the acid subphase.

Atmospheric Implications and Conclusions

H → D exchange and residence time experiments demonstrate that short-chain alcohol surfactants such as butanol do not impede HCl uptake into 60−68 wt % D_2SO_4 at 213 K or HBr uptake into 68 wt % D_2SO_4 even when the butyl species occupy ~80% of the surface. Thus, butyl films will not impose barriers that limit reactions of HCl or HBr with dissolved HOCl or $ClONO_2$, which would occur if the HCl entry probability dropped below $\sim 10^{-4}$ on the surfactant-coated acid (or below $\sim 10^{-2}$ for HBr).[11] The butyl film is instead observed to enhance HCl uptake from 0.14 to 0.27 on 68 wt % D_2SO_4 and from 0.52 to 0.74 on 60 wt % D_2SO_4, and to enhance HBr uptake from 0.22 to 0.65 in 68 wt % D_2SO_4, within the assumption that H → D exchange and gas uptake can be equated. The data suggest that this enhancement arises because segregated butanol molecules provide extra interfacial hydrogen bonding and protonation sites that assist HX dissociation; HCl and HBr molecules can be “teased” into the acid by coating the surface with a porous but protonatable surfactant. The butyl film also does not impede the uptake of basic protic gases such as CF_3CH_2OH into sulfuric acid, and it does not impede the evaporation of D_2O, as shown in the preceding paper.[6]

Together, the HCl, HBr, CF_3CH_2OH, and D_2O experiments suggest that protic gases will enter sulfuric acid coated with butanol with nearly equal and sometimes greater probability than bare sulfuric acid. This trend appears to reverse when 1-butanol is replaced by 1-hexanol.[31] Ongoing experiments utilizing longer chain surfactants and different functional groups will determine if the entry probability can be reduced enough to alter the rates of atmospherically important processes, both for halogen-containing gases and for nonprotic species such as N_2O_5.[32,33]

Acknowledgment. We are grateful to the Air Force Office of Scientific Research for supporting this work and to the Camille and Henry Dreyfus Foundation for providing a postdoctoral fellowship in environmental chemistry to S.-C. P. We also thank a reviewer for helpful comments.

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