

## Energy and Angle-Resolved Uptake of Organic Molecules in Concentrated Sulfuric Acid

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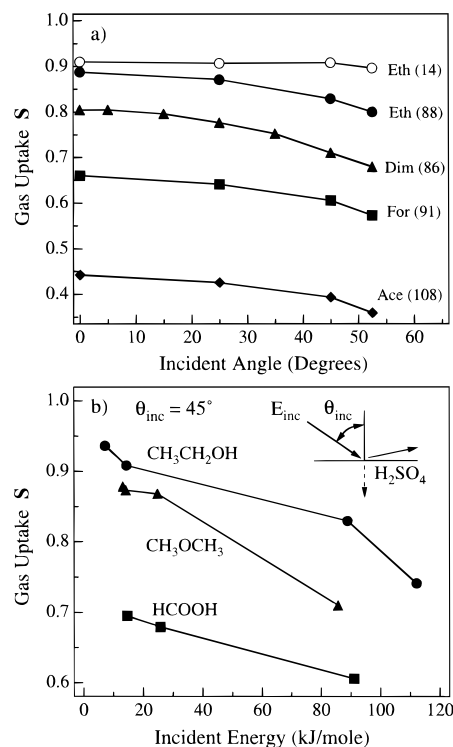
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Concentrated sulfuric acid readily protonates organic molecules with oxygen-containing functional groups.<sup>1</sup> This protonation is often strongly exothermic and shifts equilibrium between gaseous and dissolved species toward the solvated state.<sup>2,3</sup> To dissolve in the acid, an approaching gas molecule must first collide with the acid's surface. The molecule may then scatter inelastically from the surface or bind momentarily to interfacial H<sub>2</sub>SO<sub>4</sub> before evaporating or remaining behind.<sup>4</sup> The range of approach energies and angles toward the surface is broad at thermal equilibrium, spanning a Boltzmann distribution of incident energies ( $E_{\text{inc}}$ ) and a cosine distribution of incident angles ( $\theta_{\text{inc}}$ ). We explore in this letter how gas uptake in 98.8 wt % H<sub>2</sub>SO<sub>4</sub> depends on  $E_{\text{inc}}$  and  $\theta_{\text{inc}}$  for organic species of very different basicities. The molecular beam experiments demonstrate that sulfuric acid efficiently captures impinging organic molecules over a wide range of impact energies and approach directions. However, the net uptake increases sharply with basicity, indicating that strongly basic molecules undergo longtime solvation while weakly basic species return more quickly to the gas phase.<sup>5</sup>

We directed nearly monoenergetic beams of ethanol, dimethyl ether, formic acid, acetaldehyde, and propene at azeotropic sulfuric acid (98.8 wt %, 18.5 M) at  $T_{\text{liq}} = 295$  K.<sup>4,6</sup> Each species was seeded in Ar, N<sub>2</sub>, He, or H<sub>2</sub>. The mixtures were expanded through a heated pinhole to generate incident energies of 7 to 112 kJ/mol, corresponding to 1.4 to 23 times the average translational energy of a gas molecule at 295 K. Continuously renewed films of sulfuric acid were prepared in vacuum by rotating a glass wheel through a reservoir filled with acid.<sup>4</sup> A glass blade removed the outer portion of the acid on the 5.0-cm-diameter wheel, leaving a fresh acid film of 0.35 to 0.42 mm thickness at wheel speeds of 0.12 to 0.83 Hz. The film then passed by an 11-mm-diameter hole where it was exposed to the 3.2-mm-diameter molecular beam for a time  $t_{\text{exp}}$ , which could be varied from 0.30 to 0.045 s at  $\theta_{\text{inc}} = 45^\circ$ . We estimate that gas deposition rates were typically less than 0.2 monolayers/s.

The fraction of impinging molecules consumed by the acid over exposure time  $t_{\text{exp}}$  is  $S(E_{\text{inc}}, \theta_{\text{inc}}, t_{\text{exp}}) = (P_f - P_a)/(P_f - P_b)$ .<sup>7,8</sup>  $P_f$ ,  $P_a$ , and  $P_b$  are the reagent gas pressures when the incident molecules strike a Teflon flag in front of the acid, strike the bare acid, and are blocked from entering the scattering chamber, respectively. The steady-state partial pressures were measured in 10-s intervals by a mass spectrometer in the vacuum chamber.  $S = 1$  implies complete gas uptake into the acid,



**Figure 1.** (a) Gas uptake  $S$  versus  $\theta_{\text{inc}}$  for ethanol (Eth), dimethyl ether (Dim), formic acid (For), and acetaldehyde (Ace) striking 98.8 wt % sulfuric acid.  $E_{\text{inc}}$  is given in parentheses in kJ/mol. The wheel speed is 0.5 Hz ( $t_{\text{exp}} = 0.076$  s at  $45^\circ$ ). (b)  $S$  versus  $E_{\text{inc}}$  at  $\theta_{\text{inc}} = 45^\circ$  and  $t_{\text{exp}} = 0.076$  s.

while  $S = 0$  means that all molecules scatter inelastically from the surface or are trapped by the acid and desorb by time  $t_{\text{exp}}$ . The month-to-month reproducibility in  $S$  is typically  $\pm 0.03$ , while the uncertainty in trends in  $S$  with  $\theta_{\text{inc}}$  is  $\pm 0.005$  during an individual run.

Figure 1 illustrates how uptake varies with impact angle and energy for the different gases.  $S$  ranges from  $>0.9$  for ethanol at  $E_{\text{inc}} = 14$  kJ/mol to  $<0.002$  for propene at all measured  $E_{\text{inc}}$  and  $\theta_{\text{inc}}$ . For each gas, the uptake varies slowly with  $\theta_{\text{inc}}$ , decreasing monotonically with more grazing impact. This decline is smallest for low-energy molecules: at  $E_{\text{inc}} = 14$  kJ/mol,  $S$  decreases by only 0.014 for ethanol and 0.035 for dimethyl ether (not shown) from  $\theta_{\text{inc}} = 0^\circ$  to  $53^\circ$ . At higher impact energies near 90 kJ/mol,  $S$  decreases more sharply, falling by  $\approx 0.1$  from  $0^\circ$  to  $53^\circ$ .

Figure 1b shows that  $S$  decreases monotonically with impact energy at  $\theta_{\text{inc}} = 45^\circ$ . This energy dependence is weak:  $S$  drops from 0.93 to 0.74 from 7 to 112 kJ/mol for ethanol and 0.70 to 0.61 from 14 to 91 kJ/mol for formic acid. Even shallower curves are obtained at  $\theta_{\text{inc}} = 0^\circ$ , where  $S$  decreases from 0.93 to 0.83 for ethanol over the 105-kJ/mol range.

The data in Figure 1 demonstrate that gas uptake occurs extensively in sulfuric acid and depends weakly on the impinging molecule's direction of approach and translational energy.<sup>7</sup> The steady decrease in  $S$  with  $E_{\text{inc}}$  shows that gas uptake is not promoted by translational energy but is slightly hindered by it. This trend implies that high-energy gas molecules do not penetrate "ballistically" into the acid.<sup>9</sup> The decline in  $S$  with  $E_{\text{inc}}$  instead suggests that gas-surface energy dissipation is a necessary first step in reactive uptake required to bring impinging molecules momentarily to rest at the interface. These trapping events allow the gas molecule to enter the acid instead of recoiling directly from interfacial H<sub>2</sub>SO<sub>4</sub> and returning to

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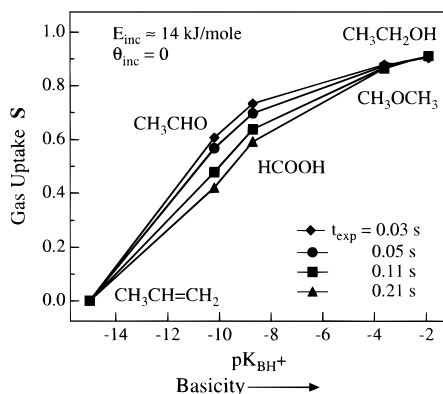
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(8)  $S$  is a time average of the instantaneous uptake  $\gamma(t)$  from  $t = 0$  to  $t_{\text{exp}}$ , corrected for gas desorption after the acid is exposed to the beam but before it reenters the reservoir. Provisionally, we set  $1/\gamma(t) = 1/\beta + (t/\tau)^{1/2}$ . See ref 5.  $\beta$  is the trapping probability leading to reaction and  $\tau$  is a characteristic residence time. The uncertainties in  $\beta$  and  $\tau$  for formic acid and acetaldehyde reflect corrections for gas desorption.

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**Figure 2.** Gas uptake  $S$  versus  $pK_{BH^+}$  at  $\theta_{inc} = 0^\circ$  and  $E_{inc} \approx 14$  kJ/mol at four exposure times  $t_{exp}$ . Similar trends are found at other  $\theta_{inc}$  and  $E_{inc}$ .

the gas phase.<sup>4</sup> Because high-incident energy molecules must dissipate more energy than low-energy molecules in order to be trapped at the interface, gas uptake decreases as  $E_{inc}$  increases.<sup>10</sup>

Collisions at more grazing impact also lead to slightly less trapping than those at more perpendicular incidence. This trend is in accord with hard sphere-like collisions between gas and surface molecules: collisions at more glancing approach angles typically occur at larger impact parameters and result in smaller momentum and energy transfers to the surface molecules.<sup>11,12</sup>

By analyzing uptake values at fixed  $E_{inc}$  and  $\theta_{inc}$  and by choosing molecules of nearly the same mass and size, we can suppress differences in the kinematics of the gas-surface collision<sup>17</sup> and investigate trends in  $S$  in terms of functional group chemistry. Figure 2 shows that  $S$  rises steadily with the solution-phase basicity of each molecule at  $E_{inc} \approx 14$  kJ/mol and  $\theta_{inc} = 0^\circ$ . We gauge the basicity by the value of  $pK_{BH^+} = -\log(K_{BH^+})$ , where  $K_{BH^+}$  is the estimated equilibrium constant for deprotonation of  $BH^+$ :  $BH^+_{(soln)} \leftrightarrow B_{(soln)} + H^+_{(soln)}$ .<sup>13</sup>

The empirical correlation between  $S$  and  $pK_{BH^+}$  provides a compact way to display the data. This trend likely reflects the relative hydrogen bonding strengths<sup>2,14</sup> between gas and surface molecules in the initial trapping process and the relative extent of protonation in the interfacial<sup>15</sup> and bulk<sup>13</sup> regions once trapping has occurred. Solutes with higher basicities (less negative  $pK_{BH^+}$ ) will favor the protonated form  $BH^+$  and remain in the acid or react further. More negative  $pK_{BH^+}$  values indicate increasing stability of the solvated neutral species  $B$ , which can desorb from solution into the vacuum. Ethanol and dimethyl ether have the highest  $S$  values of 0.91 and 0.87, reflecting their propensity for protonation in azeotropic sulfuric acid.<sup>13</sup> Formic acid and acetaldehyde have intermediate basicities and yield  $S$  values of 0.70 and 0.57 for 0.05 s exposure times, while the

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(13) Except for propene,  $[BH^+] > [B]$  in 98.8 wt %  $H_2SO_4$ .  $pK_{BH^+}$  is the half-protonation point on the respective acidity scale for each type of molecule. Dimethyl ether and formic acid: see ref 1. Ethanol: Lee, D. G.; Cameron, R. *J. Am. Chem. Soc.* **1971**, *93*, 4274. Acetaldehyde: Levy, G. C.; Cargioli, J. D.; Racela, W. *J. Am. Chem. Soc.* **1970**, *92*, 6238. Propene, rough estimate on  $H_R'$  scale: Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889. Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5408.

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uptake of the weakly basic propene is not measurable. We note that  $S$  does not track the gas-phase proton affinities of the organic molecules,<sup>16</sup> implying that protonation occurring in the interfacial region behaves more like a solution phase than gas-phase process.

The four lines in Figure 2 corresponding to  $t_{exp} = 0.03, 0.05, 0.11,$  and  $0.21$  s reveal how the residence times of the molecules in the acid increase with their basicity.  $S$ (ethanol) and  $S$ (dimethyl ether) do not vary with the exposure time of the liquid to the molecular beam: these molecules remain in the acid for times much longer than 0.21 s. This is corroborated by time-of-flight (TOF) scattering experiments which show little or no thermal desorption of accommodated ethanol or dimethyl ether during this time.<sup>6</sup> In this limit of "irreversible" absorption,  $S$  is equal to the fraction of impinging molecules that are initially trapped at the interface and remain in the acid for times longer than  $t_{exp}$ . For dimethyl ether and ethanol, these capture probabilities are near 90% at  $E_{inc} \approx 14$  kJ/mol. This trapping process is enhanced by at least three factors: efficient kinematic energy transfer due to the high mass ratio  $m_{gas}/m_{acid}$  of nearly 1/2, multiple collisions along a molecularly rough acid surface, and strong attractive forces between the gas and interfacial  $H_2SO_4$  molecules.<sup>17,18</sup>

In contrast to ethanol and dimethyl ether, formic acid and acetaldehyde display time-dependent  $S$  values, and their TOF spectra reveal that trapped molecules can desorb from solution within  $t_{exp}$ .<sup>4,6</sup> A preliminary analysis of  $S$  versus  $t_{exp}$  at  $E_{inc} = 14$  kJ/mol and  $\theta_{inc} = 0^\circ$  indicates that the trapping probabilities exceed 75% and that characteristic residence times in the acid are  $\approx 0.2$  to 2 s for formic acid and  $\approx 0.05$  to 0.5 s for acetaldehyde.<sup>8</sup> Trapping is thus much more likely than inelastic scattering for all four molecules, with trapping probabilities that rise gradually with  $pK_{BH^+}$ . Once trapped, formic acid and acetaldehyde spend less time in sulfuric acid than ethanol or dimethyl ether, as expected from their lower basicities and consequent lower solubilities.<sup>5</sup> These molecules may evaporate from the acid during the time from gas exposure to when the acid-covered wheel moves past the hole in the reservoir, which is equal to  $2.1t_{exp}$  at  $\theta_{inc} = 0^\circ$ .<sup>8</sup> The net uptake therefore decreases as  $t_{exp}$  increases, as shown in Figure 2. For weakly basic species like propene,  $t_{exp}$  greatly exceeds the solvation time, and  $S$  approaches 0 as nearly all trapped molecules return to the gas phase.

The high uptake values reported above, and their weak dependence on  $E_{inc}$  and  $\theta_{inc}$ , suggest that interfacial sulfuric acid molecules readily absorb the translational energy of impinging organic species. Most incoming molecules are trapped at least momentarily in the interfacial region, implying that gas-surface energy transfer will not usually limit the rates of reactions between organic gases and 98.8 wt %  $H_2SO_4$ . The longtime uptake of many organic species may instead be limited by their basicity, which governs the extent of protonation and the fraction of neutral species which can desorb back into the gas phase.

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(16) Gas phase proton affinities (kJ/mol): formic acid (748) < propene (751) < acetaldehyde (781) < ethanol (788) < dimethyl ether (804).

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