

# The Inhibition of N<sub>2</sub>O<sub>5</sub> Hydrolysis in Sulfuric Acid by 1-Butanol and 1-Hexanol Surfactant Coatings

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Gas–liquid scattering experiments are used to measure the fraction of N<sub>2</sub>O<sub>5</sub> molecules that are converted to HNO<sub>3</sub> after colliding with 72 wt % H<sub>2</sub>SO<sub>4</sub> containing 1-hexanol or 1-butanol at 216 K. These alcohols segregate to the surface of the acid, with saturation coverages estimated to be 60% of a close-packed monolayer for 1-hexanol and 44% of a close-packed monolayer for 1-butanol. We find that the alkyl films reduce the conversion of N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> from 0.15 on bare acid to 0.06 on the hexyl-coated acid and to 0.10 on the butyl-coated acid. The entry of HCl and HBr, however, is enhanced by the hexanol and butanol films. The hydrolysis of N<sub>2</sub>O<sub>5</sub> may be inhibited because the alkyl chains restrict the transport of this large molecule and because the alcohol OH groups dilute the surface region, suppressing reaction between N<sub>2</sub>O<sub>5</sub> and near-interfacial H<sub>3</sub>O<sup>+</sup> or H<sub>2</sub>O. In contrast, the interfacial alcohol OH groups provide additional binding sites for HCl and HBr and help initiate ionization. These and previous scattering experiments indicate that short-chain alcohol surfactants impede or enhance sulfuric acid-mediated reactions in ways that depend on the chain length, liquid phase acidity, and nature of the gas molecule.

## Introduction

The aerosol-mediated conversion of N<sub>2</sub>O<sub>5</sub> into HNO<sub>3</sub> is a key step in regulating ozone levels in the stratosphere and troposphere and in denitrifying the troposphere through wet and dry deposition of nitric acid.<sup>1–6</sup> Because N<sub>2</sub>O<sub>5</sub> is formed at night from NO<sub>2</sub> and NO<sub>3</sub> and photolyzes back into these species during the day, the reaction



effectively converts NO<sub>2</sub> and NO<sub>3</sub> into the temporary reservoir species HNO<sub>3</sub>. In the lower stratosphere, this reaction suppresses the NO/NO<sub>2</sub>-catalyzed destruction of ozone while enhancing both the HO/HO<sub>2</sub> cycle (through photolysis of HNO<sub>3</sub> into OH and NO<sub>2</sub>) and the Cl/CIO cycle (by curtailing formation of ClONO<sub>2</sub>) that reduce O<sub>3</sub>.<sup>7</sup> Inclusion of this hydrolysis reaction in models of the lower stratosphere and upper troposphere lead to better agreement between predicted and observed O<sub>3</sub> depletion rates and ratios of nitrogen oxide species.<sup>8,9</sup> In the global troposphere, N<sub>2</sub>O<sub>5</sub> hydrolysis occurs on a variety of aqueous surfaces<sup>10</sup> and is estimated to reduce NO and NO<sub>2</sub> levels by ~40% and O<sub>3</sub> levels by ~5% during winter months.<sup>11–13</sup>

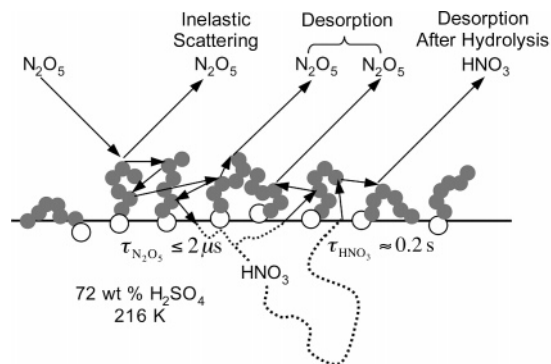
The hydrolysis of N<sub>2</sub>O<sub>5</sub> is typically mediated by submicron sulfuric acid particles in the lower stratosphere that range from 40 to 80 wt % H<sub>2</sub>SO<sub>4</sub> at temperatures from 200 to 240 K, with wider variations in acidity in the upper troposphere due to absorption of NH<sub>3</sub>.<sup>3,4</sup> Laboratory studies demonstrate that N<sub>2</sub>O<sub>5</sub> hydrolysis occurs with a probability near 0.1 in sulfuric acid aerosols over a wide range of acid concentrations at low temperatures.<sup>14–19</sup> Field measurements indicate that, in the upper troposphere and tropopause regions, these aerosol particles contain significant concentrations of organic species.<sup>20</sup> Neither

the abundance nor the speciation of these organic molecules is firmly established, but they are expected to range from small molecules such as methanol and acetone to long-chain fatty acids.<sup>21–24</sup> These molecules may segregate to the surface of the acid droplets and coat them, potentially impeding interfacial transport and suppressing N<sub>2</sub>O<sub>5</sub> hydrolysis. Organic coatings have been recently suggested to be one explanation for the variability in N<sub>2</sub>O<sub>5</sub> hydrolysis rates on acidic particles over the northeast United States.<sup>25</sup> In this article, we focus on the effects of two soluble alcohols, 1-butanol and 1-hexanol, on N<sub>2</sub>O<sub>5</sub> hydrolysis in 72 wt % H<sub>2</sub>SO<sub>4</sub> at 216 K and compare hydrolysis rates with HCl and HBr uptake into the bare and film-coated acids.

Insoluble and soluble organic species behave very differently at the surfaces of aqueous solutions. Numerous experiments show that insoluble, long-chain surfactants such as hexadecanol (C<sub>16</sub>H<sub>33</sub>OH) form compact monolayers on water and sulfuric acid that inhibit rates of water evaporation by 10<sup>4</sup> or more, with resistances that grow exponentially with chain length.<sup>26</sup> Kinks in the chain moderate this resistance substantially, as demonstrated recently by the 10-fold greater permeation of acetic acid through films of *cis*-9-octadecen-1-ol (C<sub>18</sub>H<sub>36</sub>O) on water than through the straight-chain 1-octadecanol.<sup>27</sup> Permeation data are scarce for short-chain surfactants: slightly soluble C<sub>8</sub>–C<sub>12</sub> alcohols in water may impede H<sub>2</sub>O and CO<sub>2</sub> transport,<sup>28</sup> and organic films can even enhance uptake when the gas is more soluble in the surface film than in the subphase, as shown by the adsorption of anthracene onto 1-octanol-coated water.<sup>29</sup> Conversely, recent fluorescence experiments indicate that 1-octanol films on water suppress interfacial pH changes induced by exposure to HNO<sub>3</sub> or NH<sub>3</sub>.<sup>30</sup>

Most pertinent to the present study are experiments by Thornton and Abbatt, which demonstrate that a monolayer of hexanoic acid on synthetic seawater aerosol reduces N<sub>2</sub>O<sub>5</sub> hydrolysis by 3- to 4-fold.<sup>31</sup> Further experiments by McNeill

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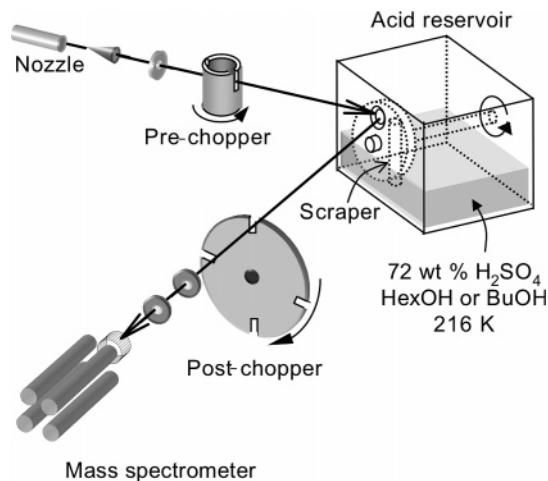
**Figure 1.** Several pathways for an  $\text{N}_2\text{O}_5$  molecule colliding into sulfuric acid containing 1-hexanol. The  $\tau$  values refer to the average liquid-phase residence times of unreacted  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$ .

et al. show that sodium dodecyl sulfate coatings on natural seawater and  $\text{NaCl}$  aerosols reduce hydrolysis of  $\text{N}_2\text{O}_5$  10-fold.<sup>32</sup> Folkers et al. and Anttila et al. also showed that aqueous sulfate particles coated with thick, multilayer films formed from monoterpene oxidation reduce  $\text{N}_2\text{O}_5$  hydrolysis by factors of 10 or more.<sup>33,34</sup>

$\text{N}_2\text{O}_5$  molecules can follow a range of pathways upon collision with a submonolayer organic film on sulfuric acid, as illustrated in Figure 1 for acid coated with hexanol molecules in different chain conformations.<sup>35,36</sup> At thermal collision energies, nearly all impinging  $\text{N}_2\text{O}_5$  molecules will be momentarily trapped at the surface, and only a small fraction will recoil directly (inelastic scattering).<sup>37,38</sup> Some of the thermalized  $\text{N}_2\text{O}_5$  may then desorb from the surface before or after moving between the hexyl chains, while others may permeate through the porous film and undergo hydrolysis near the film–acid interface or deeper into the acid.

Our previous studies of butanol and hexanol coatings on 56 to 68 wt %  $\text{D}_2\text{SO}_4$  (0.20 to 0.30 mole fraction acid) at 213 K led us to suspect that these films would not significantly inhibit  $\text{N}_2\text{O}_5$  passage into the acid because they do not form compact monolayers.<sup>37–40</sup> Each alcohol reacts with  $\text{H}_2\text{SO}_4$  to form mixtures of  $\text{ROH}$ ,  $\text{ROH}_2^+$ ,  $\text{ROSO}_3^-$ , and  $\text{ROSO}_3\text{H}$ , which are expected to be in roughly equal proportions in 70 wt %  $\text{H}_2\text{SO}_4$  at 298 K.<sup>41</sup> On the basis of surface tension measurements of 72 wt %  $\text{H}_2\text{SO}_4$  mixed with butanol and hexanol at 295 and 250 K, the total surface concentration of all alkyl species at 216 K is predicted to saturate at  $\sim 3.0 \times 10^{14} \text{ cm}^{-2}$  ( $\sim 60\%$  of a close-packed monolayer) for 1-hexanol and  $\sim 2.2 \times 10^{14} \text{ cm}^{-2}$  ( $\sim 44\%$  of a close-packed monolayer) for 1-butanol.<sup>38</sup> Our first studies indicated that butyl films on 56–68 wt %  $\text{D}_2\text{SO}_4$  at 213 K do not impede water evaporation and actually enhance  $\text{HCl}$  and  $\text{HBr}$  uptake by providing extra  $\text{OH}$  surface groups that act as protonation sites for  $\text{HCl}$  and  $\text{HBr}$  dissociation.<sup>37,39</sup> When hexanol is substituted for butanol, the entry of  $\text{HCl}$  is still enhanced, except when the acid concentration is low enough (56 wt %  $\text{D}_2\text{SO}_4$ ) to reduce the fraction of  $\text{HexOH}_2^+$  and allow the hexyl film coverage to rise to  $\sim 68\%$  of a compact monolayer.<sup>38</sup> At this higher packing,  $\text{HCl}$  uptake is reduced from 0.68 to 0.59 and water evaporation is reduced by 20%. In contrast to the enhanced uptake of  $\text{HCl}$  and  $\text{HBr}$  by the alcohol films, the uptake of the basic molecule  $\text{CF}_3\text{CH}_2\text{OH}$  is nearly 1 at all acid concentrations and is impeded by less than 4% by both butyl and hexyl films.

The observations above indicate that gas transport through surface films is controlled by the chain length of the surfactant, the identity of the gas molecule, and the underlying liquid. Hexanol and butanol films on sulfuric acid may therefore alter



**Figure 2.** Molecular beam scattering apparatus and liquid reservoir. The Teflon reservoir is sealed except for a 0.9 cm diameter hole through which the  $\text{N}_2\text{O}_5$  beam strikes the acid. Only one of the prechopper or postchopper wheels is used at one time.

$\text{N}_2\text{O}_5$  hydrolysis differently than  $\text{HCl}$  and  $\text{HBr}$  uptake, and they may act differently on sulfuric acid or other subphases. The experiments below utilize 72 wt %  $\text{H}_2\text{SO}_4$  or 70 wt %  $\text{D}_2\text{SO}_4$  at 216 K, each 0.32 mole fraction acid, which are highly viscous ( $\sim 1900$  cP) and low vapor pressure ( $\sim 2 \times 10^{-4}$  Torr) liquids.<sup>42,43</sup> They show that, although the hexyl and butyl films significantly enhance  $\text{HCl}$  and  $\text{HBr}$  uptake, the conversion of  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$  drops by 60% and 33%, respectively, indicating that submonolayer films can impede this near-surface reaction.

## Experimental Procedure

**$\text{N}_2\text{O}_5$  and Acid Preparation.**  $\text{N}_2\text{O}_5$  is synthesized by oxidizing  $\text{NO}$  with  $\text{O}_2$  and  $\text{O}_3$  consecutively at room temperature, purifying the product by distillation under  $\text{O}_3$  and storing it at 195 K.<sup>44</sup>  $\text{HNO}_3$  formation is minimized by baking the apparatus and by passing  $\text{NO}$  and dried  $\text{O}_2$  through a 195 K cold trap to remove  $\text{H}_2\text{O}$ . The melting point of the  $\text{N}_2\text{O}_5$  sample under argon was observed to be 39–42 °C, which encompasses the literature value of 41 °C.<sup>45</sup> During the scattering experiments, the sample is held at 253 K, where the  $\text{N}_2\text{O}_5$  vapor pressure is estimated to be 8 Torr.<sup>46</sup> Incident beams of 13 and 150  $\text{kJ mol}^{-1}$   $\text{N}_2\text{O}_5$  are created by expanding pure  $\text{N}_2\text{O}_5$  or  $\text{N}_2\text{O}_5$  seeded in 750 Torr  $\text{H}_2$  through an unheated, 0.13 mm diameter glass nozzle.

Surfactant/acid solutions are prepared by diluting 97 wt %  $\text{H}_2\text{SO}_4$  to 72 wt % with Millipore water, adding 1-hexanol (up to 0.1 M) or 1-butanol (up to 1 M) and immediately cooling to  $216 \pm 0.5$  K in the liquid reservoir shown in Figure 2. The alcohols (Aldrich, >99% pure) are used without further purification. Titrations indicate that the acid concentration changes by no more than 0.5 wt % during the time it is in vacuum (typically less than 3 days). The measured reductions in surface tension upon adding alcohol are those expected when adding soluble, small-molecule surfactants, indicating that the alcohols are not contaminated with long-chain insoluble species.<sup>40</sup>

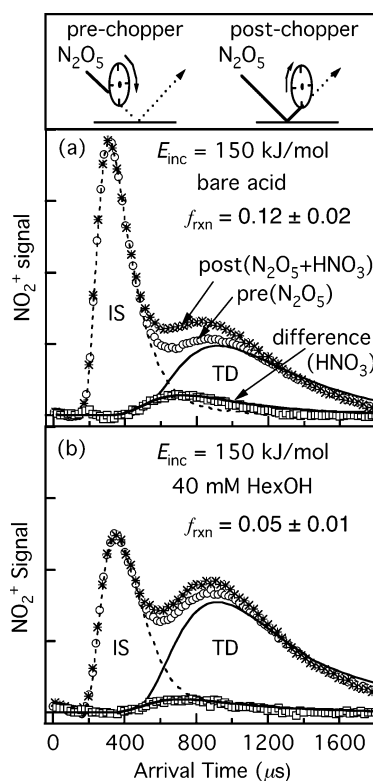
A continuously renewed, vertical liquid film is formed by rotation of a 5.0 cm diameter glass wheel partially submerged in 60 mL of the acid solution.<sup>39</sup> The acid-coated wheel is skimmed by a cylindrical Teflon scraper, which removes the outer 0.1 cm of acid and alcohol. The remaining  $\sim 0.03$  cm thick acid film then passes in front of a 0.7  $\text{cm}^2$  circular hole, where it is intercepted by the  $\text{N}_2\text{O}_5$  beam impinging at an incident

angle  $\theta_{\text{inc}}$  of 45°. At a typical wheel speed of 0.17 Hz, the time interval between scraping and exposure to the beam is 0.49 s. Argon scattering measurements show that this time is sufficient to allow the butyl and hexyl films to become reestablished at the surface of the acid, as shown previously in refs 38 and 39. The acid remains in front of the hole in the reservoir for 0.45 s and is exposed to the incident beam for a time  $t_{\text{exp}}$  equal to 0.27 s.

**Distinguishing N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> by Pre- and Postchopper TOF Analysis.** Time-of-flight (TOF) spectra of N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> exiting from the acid are recorded by a differentially pumped quadrupole mass spectrometer oriented at an angle  $\theta_{\text{fin}} = 45^\circ$ , as shown in Figure 2. Electron-impact ionization is used to detect the neutral molecules with an electron energy of 70 eV. Unfortunately, the N<sub>2</sub>O<sub>5</sub><sup>+</sup> parent ion is unstable and all stable N<sub>2</sub>O<sub>5</sub> ion fragments are also produced by HNO<sub>3</sub> ionization. Here we monitor the most abundant fragment, NO<sub>2</sub><sup>+</sup> ( $m/z = 46$ ), and employ pre- and postchopper TOF analysis to distinguish N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> by their short (<10<sup>-6</sup> s) and long (~0.1 to 10 s) residence times, respectively, in the acid. The pre- and postchopper wheels are shown in Figure 2. With the postchopper wheel in place and the prechopper wheel removed, the incident beam strikes the liquid continuously and the exiting molecules are chopped into 36 μs pulses upon exiting the acid. The arrival times of these molecules at the mass spectrometer in the postchopper spectrum therefore depend only on the velocities of the exiting molecules. In contrast, the prechopper wheel slices the incident beam into 50 μs pulses, and the total arrival time at the mass spectrometer in the prechopper spectrum depends on the residence times of the molecules in the acid solution as well as their gas-phase flight times. As described below, the HNO<sub>3</sub> signal can be obtained by subtracting the prechopper spectrum (containing only N<sub>2</sub>O<sub>5</sub>) from the postchopper spectrum (containing both N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub>).

The raw TOF signals are converted into relative N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> signals by correcting for the different ionization cross sections  $\sigma_{\text{NO}_2^+}$  for dissociative ionization of N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> into NO<sub>2</sub><sup>+</sup>. These cross-sections were calculated by multiplying the total ionization cross section  $\sigma_{\text{tot}}$  of each parent molecule by the branching ratio  $r$  for NO<sub>2</sub><sup>+</sup> formation. We used the following values to calculate  $\sigma_{\text{NO}_2^+}$ :  $\sigma_{\text{tot}}(\text{N}_2\text{O}_5) = 7.0 \text{ \AA}^2$  from ref 47,  $r(\text{N}_2\text{O}_5 \rightarrow \text{NO}_2^+) = 0.54$  from ref 48,  $\sigma_{\text{tot}}(\text{HNO}_3) = 6.3 \text{ \AA}^2$  from ref 49, and  $r(\text{HNO}_3 \rightarrow \text{NO}_2^+) = 0.60$  from ref 50. Each value is measured at an electron energy of 70 eV, which is equal to our experimental setting. Fortunately,  $\sigma_{\text{NO}_2^+}$  is 3.8 Å<sup>2</sup> for both N<sub>2</sub>O<sub>5</sub> and for HNO<sub>3</sub>. The relative intensities of HNO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> are therefore equal to the relative fluxes obtained from the TOF spectra to within an estimated uncertainty of ±15% in the ionization parameters. This systematic uncertainty is not included in the error bars reported for the hydrolysis probabilities because  $\sigma_{\text{NO}_2^+}$  does not change the ratio of probabilities for the bare and alcohol-coated acids.

**Monitoring HNO<sub>3</sub> Desorption.** The mass spectrometer is collimated to monitor a patch of the acid-coated wheel for a time equal to the exposure time,  $t_{\text{exp}}$ , of 0.27 s. This observation time is insufficient to observe the complete evaporation of the HNO<sub>3</sub> product, which desorbs over several seconds because of its high solubility of  $2 \times 10^6 \text{ M atm}^{-1}$  in 72 wt % H<sub>2</sub>SO<sub>4</sub> at 216 K (as described in the Appendix). To monitor most of the HNO<sub>3</sub> desorption, the wheel is periodically stopped for 6 s and the HNO<sub>3</sub> desorption signal is recorded. The liquid is viscous enough (1900 cP at 216 K) that it sags only slightly during this stop period; a droop in the acid film does not distort the measurements because the hydrolysis probability is determined



**Figure 3.** Pre- and postchopper TOF spectra of N<sub>2</sub>O<sub>5</sub> and their difference spectra following collisions of 150 kJ mol<sup>-1</sup> N<sub>2</sub>O<sub>5</sub> with 72 wt % H<sub>2</sub>SO<sub>4</sub> containing (a) no hexanol and (b) 40 mM hexanol. The difference spectra correspond to thermal desorption of HNO<sub>3</sub> molecules generated by N<sub>2</sub>O<sub>5</sub> hydrolysis. N<sub>2</sub>O<sub>5</sub> inelastic scattering (IS) is fit by a dotted curve. The difference spectra and the thermal desorption (TD) component of the N<sub>2</sub>O<sub>5</sub> prechopper spectra are fit by Maxwell–Boltzmann distributions shown with solid curves.

from a ratio of pre- and postchopper signals, as shown later in eq 2. The reliability of this start–stop procedure has been tested in three ways: (1) high-energy argon scattering from the stopped wheel ( $t_{\text{exp}} = 6 \text{ s}$ ) and continuously moving wheels ( $t_{\text{exp}} = 0.27 \text{ s}$ ) are identical, implying that the packing of the butyl and hexyl films remains the same on the stationary and moving films,<sup>38,39</sup> (2) measurements of the HBr → DBr and HCl → DCl exchange fractions (ranging from 0.08 to 0.60) in D<sub>2</sub>SO<sub>4</sub> using the stopped wheel differ by less than ±0.02 from measurements using a continuously moving wheel, and (3) the N<sub>2</sub>O<sub>5</sub> hydrolysis probabilities in bare 72 wt % H<sub>2</sub>SO<sub>4</sub> when measured from the stopped wheel and from the moving wheel are each  $0.15 \pm 0.02$  after correcting for the fraction of HNO<sub>3</sub> remaining in the acid, as described in the Appendix.

**Hexanol Solubility Measurements.** The solubility of hexanol in 72 wt % H<sub>2</sub>SO<sub>4</sub> was measured by comparing hexanol mass spectrometer signals from pure hexanol (of known vapor pressure<sup>51</sup>) and from 0.02 to 0.1 M hexanol in the acid at 253, 243, and 233 K. The vapor pressures varied linearly with hexanol concentration, and when extrapolated to 216 K, yield a hexanol solubility of  $3.2 \pm 0.4 \times 10^8 \text{ M atm}^{-1}$  and an enthalpy of vaporization of  $78 \pm 2 \text{ kJ mol}^{-1}$ . As discussed later, the solubility of butanol is expected to be slightly lower.<sup>52</sup>

## Results and Analysis

**Hydrolysis of N<sub>2</sub>O<sub>5</sub> by Bare Sulfuric Acid.** Figure 3a compares pre- and postchopper TOF spectra recorded at  $m/z = 46$  (NO<sub>2</sub><sup>+</sup>) following collisions of 150 kJ mol<sup>-1</sup> N<sub>2</sub>O<sub>5</sub> with uncoated 72 wt % H<sub>2</sub>SO<sub>4</sub> at 216 K. In the postchopper mode, the arrival time distribution depends only on the velocities of



**TABLE 1: N<sub>2</sub>O<sub>5</sub> Hydrolysis Probabilities and HCl and HBr HX → DX Exchange Fractions Measured for 72 wt % H<sub>2</sub>SO<sub>4</sub> or 70 wt % D<sub>2</sub>SO<sub>4</sub> at 216 K**

acid solution	N <sub>2</sub> O <sub>5</sub> $f_{\text{rxn}}$ (eq 2) <sup>a</sup>	N <sub>2</sub> O <sub>5</sub> hydrolysis probability $\gamma$ <sup>b</sup>	HCl → DCl exchange fraction <sup>c</sup>	HBr → DBr exchange fraction <sup>c</sup>
bare acid	0.12 ± 0.02	0.15 ± 0.02	0.08 ± 0.03	0.19 ± 0.02
180 mM BuOH	0.08 ± 0.02	0.10 ± 0.02	0.20 ± 0.02	0.63 ± 0.02
40 mM HexOH	0.05 ± 0.01	0.06 ± 0.01	0.16 ± 0.02	0.60 ± 0.02

<sup>a</sup> Measured in both 70 wt % D<sub>2</sub>SO<sub>4</sub> and 72 wt % H<sub>2</sub>SO<sub>4</sub>, each 0.32 mole fraction acid. <sup>b</sup> The hydrolysis probability  $\gamma$  is obtained from  $f_{\text{rxn}}$  after using eq A.1 to correct for HNO<sub>3</sub> molecules accumulating in solution and assuming no production of alkyl nitrates. <sup>c</sup> Measured in D<sub>2</sub>SO<sub>4</sub> by H → D exchange. These values are equated with the entry probability of HX, either as molecular HX or as X<sup>-</sup> and H<sup>+</sup>/D<sup>+</sup>.<sup>38</sup>

the exiting N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> molecules. Therefore, both species contribute to the TOF spectra measured at  $m/z = 46$ , regardless of their residence times in the acid. In the prechopper mode, the TOF spectrum is a convolution of the gas-phase velocities of the molecules and their residence times in the acid. The average residence time of HNO<sub>3</sub> is so long (~0.2 s), and the residence times of the individual molecules are so broadly distributed, that the desorption times of the exiting HNO<sub>3</sub> molecules are not correlated with the incident pulses. In this case, the HNO<sub>3</sub> desorption signal merges with the background. This was shown previously in Figure 3 of ref 53 for collisions of HNO<sub>3</sub> with 70 wt % D<sub>2</sub>SO<sub>4</sub> at 213 K. As described later, the residence time of N<sub>2</sub>O<sub>5</sub> lies in the opposite limit; it is shorter than the minimum 10<sup>-6</sup> s residence time that visibly alters the prechopper TOF spectrum.<sup>38,53</sup> Therefore, the prechopper spectra measured at  $m/z = 46$  in Figure 3a is composed only of unreacted N<sub>2</sub>O<sub>5</sub> molecules and is equivalent to the postchopper spectra of N<sub>2</sub>O<sub>5</sub>. By subtracting the prechopper spectrum containing only N<sub>2</sub>O<sub>5</sub> signal from the postchopper spectrum with contributions from both N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> signals, we obtain the postchopper TOF spectrum of HNO<sub>3</sub>.

The bimodal feature of the prechopper spectrum in Figure 3a reveals that N<sub>2</sub>O<sub>5</sub> molecules with high incidence energy follow two distinct pathways upon colliding with the surface, as depicted in Figure 1. The narrow, inelastic scattering (IS) peak at early arrival times (high exit velocities) corresponds to molecules that recoil directly from the surface, transferring a portion of their kinetic energy through one or a few bounces. The broader peak at later arrival times (lower exit velocities) arises from N<sub>2</sub>O<sub>5</sub> molecules that become thermalized through dissipation of their excess energy and then thermally desorb (TD). This prechopper TD component is fit well by a Maxwell–Boltzmann (MB) distribution at the acid temperature of 216 K with a mass of N<sub>2</sub>O<sub>5</sub> (108 amu) and the difference spectrum is fit well by an MB curve with a mass of HNO<sub>3</sub> (63 amu), supporting our experimental approach to identifying them.

The difference spectrum corresponds to thermalized N<sub>2</sub>O<sub>5</sub> molecules that undergo hydrolysis and then desorb as HNO<sub>3</sub>, while the prechopper TD signal represents the remaining N<sub>2</sub>O<sub>5</sub> molecules that thermally desorb before converting to HNO<sub>3</sub>. Therefore, the fraction  $f_{\text{rxn}}$  of the thermalized N<sub>2</sub>O<sub>5</sub> molecules that are converted into HNO<sub>3</sub> is calculated from

$$f_{\text{rxn}} = \frac{1/2 I_{\text{TD}}^{\text{HNO}_3}}{I_{\text{TD}}^{\text{N}_2\text{O}_5} + 1/2 I_{\text{TD}}^{\text{HNO}_3}} \approx \frac{1/2 I_{\text{TD}}^{\text{diff}}}{I_{\text{TD}}^{\text{pre}} + 1/2 I_{\text{TD}}^{\text{diff}}} \quad (2)$$

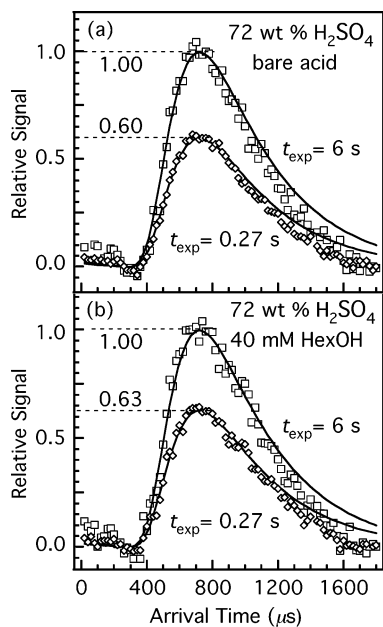
where  $I_{\text{TD}}^{\text{pre}}(I_{\text{TD}}^{\text{N}_2\text{O}_5})$  and  $I_{\text{TD}}^{\text{diff}}(I_{\text{TD}}^{\text{HNO}_3})$  are the relative fluxes of thermally desorbing molecules of the prechopper (N<sub>2</sub>O<sub>5</sub>) and the difference (HNO<sub>3</sub>) TOF spectra, respectively. The factor of 1/2 in eq 2 arises from the stoichiometry of eq 1. The measured exchange fraction from Figure 3a is 0.12 ± 0.02. The ± 0.02 error bar reflects one standard deviation in reproducibility of ±0.01 and an estimated ±0.01 uncertainty in fitting the TD

component. Finally,  $f_{\text{rxn}}$  must be corrected for those HNO<sub>3</sub> molecules that accumulate within the acid and do not desorb over the 6 s observation time. This correction, described in the Appendix, shows that 18% of the HNO<sub>3</sub> remain behind and therefore that  $I_{\text{TD}}^{\text{diff}}$  must be replaced by  $I_{\text{TD}}^{\text{diff}}/0.82$ . The corrected hydrolysis probability  $\gamma$  is then found to be 0.15 ± 0.02, as summarized in Table 1.

**Hydrolysis of N<sub>2</sub>O<sub>5</sub> by Hexyl-Coated Sulfuric Acid.** The effects of doping the 72 wt % H<sub>2</sub>SO<sub>4</sub> solution with 40 mM hexanol are displayed in Figure 3b. Surface tension measurements indicate that, at this hexanol bulk concentration, the hexyl surface concentration reaches its saturation value of 3.0 × 10<sup>14</sup> cm<sup>-2</sup>, corresponding to 60% of a compact monolayer.<sup>38,54</sup> Upon addition of hexanol, the N<sub>2</sub>O<sub>5</sub> direct scattering channel decreases and the total (N<sub>2</sub>O<sub>5</sub> + HNO<sub>3</sub>) desorption channel increases. These trends have been observed before in hyperthermal collisions of Ar, HCl, and HBr with sulfuric acid containing hexanol or butanol; they occur because the alkyl groups roughen the surface and reduce its effective mass, increasing the likelihood that N<sub>2</sub>O<sub>5</sub> will thermalize upon collision.<sup>38,39</sup>

The most important change in Figure 3b is seen in the value of  $f_{\text{rxn}}$ , which drops from 0.12 ± 0.02 to 0.05 ± 0.01 upon addition of hexanol. This reduction may be caused by at least three different factors: (1) a reduced hydrolysis efficiency imposed by the surface hexyl film, (2) a reduction in the HNO<sub>3</sub> desorption flux because the hexyl film increases the HNO<sub>3</sub> residence time in the acid, and (3) reaction of N<sub>2</sub>O<sub>5</sub> or HNO<sub>3</sub> with the hexyl species to produce hexyl nitrate. We examined the effect of added hexanol on the average HNO<sub>3</sub> residence time by measuring HNO<sub>3</sub> desorption at two different observation times of 0.27 and 6 s. These times were selected by continuously spinning the acid-coated wheel at 0.17 Hz and by stopping the wheel, respectively. As shown in Figure 4a and b, fewer HNO<sub>3</sub> molecules desorb over the 0.27 s observation time than over the 6 s period for both bare and hexyl-coated acids. The ratios of 0.60 (bare acid) and 0.63 (hexyl-coated acid) are identical to within our uncertainty, indicating that the hexyl film does not measurably impede evaporation of HNO<sub>3</sub>.

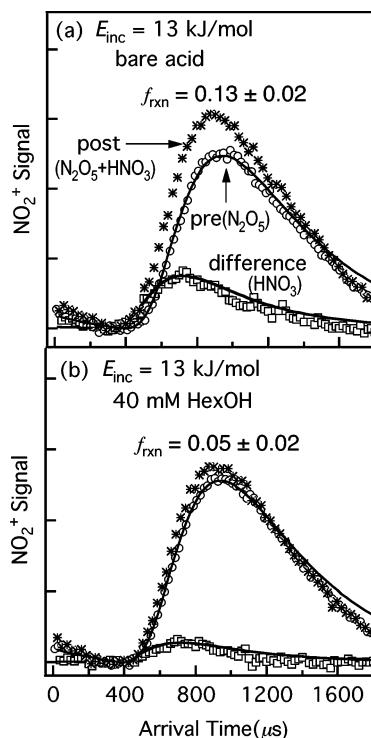
Hexyl species at the surface or in the acid may also react directly with N<sub>2</sub>O<sub>5</sub> or with HNO<sub>3</sub> generated by hydrolysis to produce hexyl nitrate, CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>ONO<sub>2</sub>, according to the reactions ROH + N<sub>2</sub>O<sub>5</sub> → RONO<sub>2</sub> + HNO<sub>3</sub> and ROH + HNO<sub>3</sub> → RONO<sub>2</sub> + H<sub>2</sub>O. Hexyl nitrate should, like hexanol itself, evaporate slowly from solution, with dominant cracks in the mass spectrometer at  $m/z = 46$ , co-incident with NO<sub>2</sub><sup>+</sup>, at  $m/z = 43$ , which does not overlap with N<sub>2</sub>O<sub>5</sub> or HNO<sub>3</sub> but does overlap with hexanol, and at  $m/z = 76$ , which is unique to hexyl nitrate. Repeated searches at each  $m/z$  value showed no evidence of a signal that could be assigned to the alkyl nitrate. We conservatively estimate that the uncertainty in these searches is ~5% of the total HNO<sub>3</sub> signal. The ratio of ionization cross sections at NO<sub>2</sub><sup>+</sup> for hexyl nitrate and nitric acid is expected to be ~1/3, based on the cracking patterns of each molecule<sup>50,55</sup>



**Figure 4.** HNO<sub>3</sub> difference spectra obtained at two beam exposure times,  $t_{\text{exp}} = 0.27$  s ( $\diamond$ ) and 6 s ( $\square$ ), following collisions of 150 kJ mol<sup>-1</sup> N<sub>2</sub>O<sub>5</sub> with 72 wt % H<sub>2</sub>SO<sub>4</sub> containing (a) no hexanol and (b) 40 mM hexanol. In each panel, the TOF signals are normalized to the signal at  $t_{\text{exp}} = 6$  s.

and assuming that the total ionization cross sections scale with the number of electrons in each molecule.<sup>49</sup> The relative TOF signals  $N$  may then be converted to relative fluxes  $I = N\langle v \rangle$  by multiplying by the ratio of their average velocities, which is  $\langle v_{\text{hexyl nitrate}} \rangle / \langle v_{\text{nitric acid}} \rangle = 0.7$ . These numbers imply that the fraction of hexyl nitrate produced should not exceed  $3 \times 0.7 \times 0.05 \approx 0.1$  of the HNO<sub>3</sub> flux. Thus, the formation of hexyl nitrate may be as high as 10% of the formation of HNO<sub>3</sub>, increasing the total loss of N<sub>2</sub>O<sub>5</sub> into the hexyl-coated acid from 0.05 to 0.055, a difference that lies within the precision of the measurement. This adjustment is not incorporated into the analysis below, but it remains a source of uncertainty in our experiments. In the absence of this nitration channel, we conclude that the reduction in HNO<sub>3</sub> desorption imposed by the hexyl film is due to a reduction in the hydrolysis of N<sub>2</sub>O<sub>5</sub>.

The TOF spectra in Figures 3 and 4 were generated by collisions of N<sub>2</sub>O<sub>5</sub> at an incident energy of 150 kJ mol<sup>-1</sup> (84  $RT_{\text{liq}}$ ), chosen because this high energy beam has a high flux (estimated to be  $6 \times 10^{14}$  cm<sup>-2</sup> s<sup>-1</sup> or approximately one monolayer s<sup>-1</sup>) and because the IS and TD components are well separated at this energy. To determine if this high collision energy skews the value of  $f_{\text{rxn}}$ , experiments were performed at the much lower incident energy of 13 kJ mol<sup>-1</sup> (7  $RT_{\text{liq}}$ ), where the N<sub>2</sub>O<sub>5</sub> flux is reduced by half. As shown in Figure 5, nearly all impinging N<sub>2</sub>O<sub>5</sub> molecules thermalize on the surface, and no IS channel can be discerned in the pre- or postchopper spectra. The measured  $f_{\text{rxn}}$  value of  $0.05 \pm 0.02$  matches the value of  $0.05 \pm 0.01$  found at high incident energy in Figure 3. The invariance of  $f_{\text{rxn}}$  with incidence energy implies that  $f_{\text{rxn}}$  may be considered to be a measurement of the hydrolysis probability  $\gamma$  that is conventionally reported for thermal-energy collisions at  $2RT_{\text{acid}} = 3.6$  kJ mol<sup>-1</sup> (neglecting any production of hexyl nitrate). As described in the Appendix, these values must be corrected for HNO<sub>3</sub> that remains behind in solution. The corrected values are listed in the third column of Table 1, which are just slightly higher than  $f_{\text{rxn}}$ . The observed reduction in the hydrolysis probability  $\gamma$  from 0.15 to 0.06 reveals that



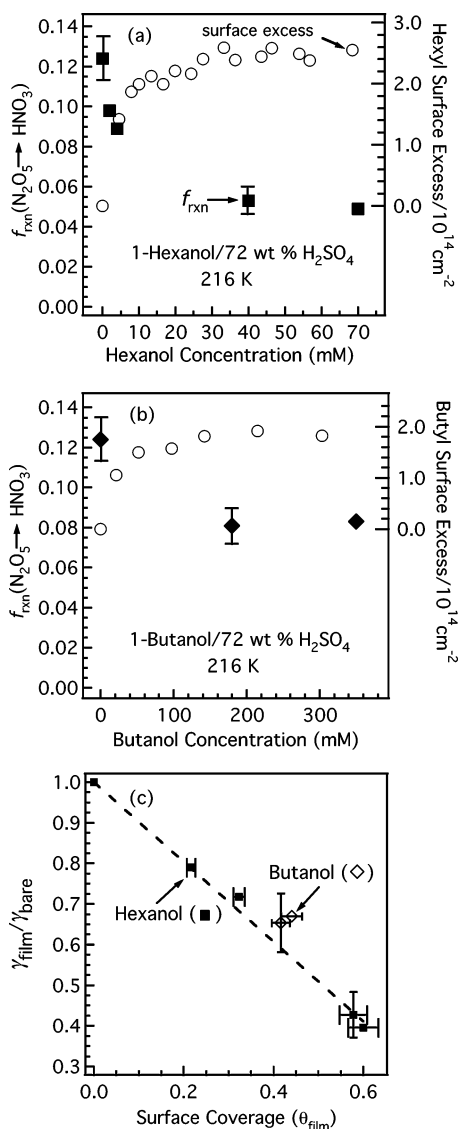
**Figure 5.** Pre- and postchopper TOF spectra of N<sub>2</sub>O<sub>5</sub> and the difference spectra following collisions of N<sub>2</sub>O<sub>5</sub> at a low incidence energy of 13 kJ mol<sup>-1</sup> with 72 wt % H<sub>2</sub>SO<sub>4</sub> containing (a) no hexanol and (b) 40 mM hexanol.

the addition of 40 mM hexanol to 72 wt % H<sub>2</sub>SO<sub>4</sub> decreases  $\gamma$  by more than half.

Figure 6a displays the dependence of  $f_{\text{rxn}}$  on the bulk-phase concentration of hexanol in 72 wt % H<sub>2</sub>SO<sub>4</sub> at 216 K. The open circles represent the surface concentration of hexyl species calculated from surface tension measurements for 72 wt % H<sub>2</sub>SO<sub>4</sub> at 295 K.<sup>54</sup> This coverage follows a Langmuir-type adsorption curve, rising rapidly at low-bulk hexanol concentrations and then plateauing near 20 mM. The production of HNO<sub>3</sub> follows an opposite trend:  $f_{\text{rxn}}$  decreases sharply and then also plateaus. The correlation between  $f_{\text{rxn}}$  and hexyl surface coverage implies that the reduction in hydrolysis with the addition of hexanol is caused by the presence of hexyl species that segregate at the surface rather than by hexyl species dissolved in the bulk.

**Hydrolysis of N<sub>2</sub>O<sub>5</sub> by Butyl-Coated Sulfuric Acid.** We also investigated changes in N<sub>2</sub>O<sub>5</sub> hydrolysis upon adding 1-butanol, a soluble surfactant that is two CH<sub>2</sub> groups shorter than 1-hexanol. Figure 6b plots  $f_{\text{rxn}}$  against the bulk concentration of butanol following collisions of 160 kJ mol<sup>-1</sup> N<sub>2</sub>O<sub>5</sub> with 72 wt % H<sub>2</sub>SO<sub>4</sub> at 216 K. The value of  $f_{\text{rxn}}$  drops from 0.12  $\pm$  0.02 for bare acid to 0.08  $\pm$  0.02 for 180 mM butanol (44% of a compact monolayer) and then does not change significantly with further increasing butanol bulk concentration. As shown in Table 1, the hydrolysis probabilities  $\gamma$  corrected for residual HNO<sub>3</sub> in the acid are 0.15 (bare acid) and 0.10 (180 mM butanol). Just as with hexanol in panel a, the trend in  $f_{\text{rxn}}$  is opposite to that of the surface segregation of butyl species (open circles).

The data in panels a and b may be used to plot  $\gamma_{\text{film}}/\gamma_{\text{bare}}$  directly against the surface coverage  $\theta_{\text{film}}$  in panel c, where  $\theta_{\text{film}} = n_{\text{surf}}/n_{\text{max}}$  is the fraction of a compact monolayer covered by the film and  $n_{\text{max}}$  is  $\sim 5 \times 10^{14}$  cm<sup>-2</sup> in the close-packed configuration.<sup>56</sup> The surface concentrations  $n_{\text{surf}}$  were obtained from the surface tension measurements at 295 and 250 K and linearly extrapolated to 216 K.<sup>39,54</sup> Panel c indicates that N<sub>2</sub>O<sub>5</sub>



**Figure 6.** Fraction  $f_{\text{rxn}}$  of  $\text{N}_2\text{O}_5$  converted to  $\text{HNO}_3$  vs (a) hexanol and (b) butanol bulk concentration in 72 wt %  $\text{H}_2\text{SO}_4$  at 216 K. The hexyl and butyl surface concentrations at 295 K are plotted against the right-hand axis as open circles. The error bars represent  $\pm 1\sigma$  for 5 measurements (bare acid), 3 (40 mM hexanol), and 3 (180 mM butanol). The other points represent single measurements. (c) The ratio of hydrolysis probabilities  $\gamma_{\text{film}}/\gamma_{\text{bare}}$  vs fractional surface coverage  $\theta_{\text{film}}$  from the data in panels a and b and the Appendix. The  $\theta_{\text{film}}$  values were obtained from surface tension data at 295 and 250 K and extrapolated to 216 K.<sup>54</sup> The dashed line is a fit to the hexanol data.

hydrolysis decreases approximately linearly with hexanol surface coverage, such that  $\gamma_{\text{hexyl}}/\gamma_{\text{bare}} = 1 - m\theta_{\text{hexyl}}$  with  $m = 1.0 \pm 0.2$  (dashed line). The single cluster of butanol values, combined with the uncertainty in determining  $\theta_{\text{film}}$ , makes it difficult to determine if the shorter-chain alcohol impedes hydrolysis less effectively at constant surface coverage.

**Collisions of HCl and HBr with Hexyl- and Butyl-Coated Sulfuric Acid.** To gauge the effects of hexyl and butyl films on HCl and HBr uptake into the acid, we also measured the extent of  $\text{HX} \rightarrow \text{DX}$  exchange following collisions of  $100 \text{ kJ mol}^{-1}$  HCl and  $150 \text{ kJ mol}^{-1}$  HBr from 70 wt %  $\text{D}_2\text{SO}_4$  at 216 K containing no surfactant, 40 mM hexanol, and 180 mM butanol. As discussed in refs 37, 38, and 53, the fraction  $f_{\text{exch}}$  of thermalized HX molecules that undergo  $\text{D} \rightarrow \text{H}$  exchange can be interpreted as the entry probability of HCl and HBr into the acid, either as molecular HX or as  $\text{X}^-$  and  $\text{H}^+$  following dissociation at the surface. Table 1 shows that, in contrast to

$\text{N}_2\text{O}_5$  hydrolysis, HCl and HBr entry is significantly enhanced by the surface films.

## Discussion

It is striking that the butyl and hexyl films on 72 wt %  $\text{H}_2\text{SO}_4$  at 216 K impede  $\text{N}_2\text{O}_5$  hydrolysis because these same films enhance HCl and HBr uptake into 70.2 wt %  $\text{D}_2\text{SO}_4$ , as shown in Table 1. H/D isotope effects are not responsible for the different outcomes; the same reduction in  $\text{N}_2\text{O}_5$  hydrolysis by the hexyl film is observed using 70 wt %  $\text{D}_2\text{SO}_4$  and 72 wt %  $\text{H}_2\text{SO}_4$ , which are each 0.32 mole fraction acid.

Previous studies in our laboratory suggest that the entry of HCl and HBr into  $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$  solutions containing hexanol at 213 K is controlled by two competing effects: hexyl chains at the surface impede gas transport through the film, while the basic hexanol OD groups assist HX entry by providing extra surface sites for HCl and HBr dissociation.<sup>38</sup> As the underlying solution is made more acidic, the hexyl and butyl films become more porous and HCl and HBr molecules can more easily reach the alcohol OD groups and protonate them. In particular, a saturated hexyl film on 68 wt %  $\text{D}_2\text{SO}_4$ , which corresponds to 62% coverage of a compact monolayer, enhances the entry of HCl from 0.14 (bare acid) to 0.23 and of HBr from 0.29 to 0.63, whereas a saturated hexyl film on 56 wt % acid, corresponding to 68% coverage, reduces HCl entry from 0.69 to 0.58.  $\text{N}_2\text{O}_5$  lacks the acidic proton of HCl and HBr and cannot follow this pathway. In 70 wt %  $\text{H}_2\text{SO}_4$  at cold temperatures,  $\text{N}_2\text{O}_5$  hydrolysis is postulated to proceed primarily through an acid-catalyzed channel consisting of  $\text{N}_2\text{O}_5 + \text{H}^+ \rightarrow \text{HNO}_3 + \text{NO}_2^+$  and  $\text{NO}_2^+ + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{H}^+$ .<sup>17,57</sup> The surface alcohol OH and  $\text{OH}_2^+$  groups could potentially substitute for  $\text{H}_2\text{O}$  and  $\text{H}^+$  as reactants and convert  $\text{N}_2\text{O}_5$  into  $\text{HNO}_3$  and alkyl nitrate. The reduction in  $\text{N}_2\text{O}_5$  hydrolysis we observe and the absence of a signal attributable to the alkyl nitrate indicate that these reactions do not readily occur and that the surface alcohol molecules instead impede the conversion of  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$ .

This reduction in  $\text{N}_2\text{O}_5$  hydrolysis may be framed within two scenarios motivated by the steady decrease in the fractional hydrolysis rate  $\gamma_{\text{hexyl}}/\gamma_{\text{bare}}$  with hexanol surface coverage  $\theta_{\text{hexyl}}$  shown in Figure 6c: (1) the hexyl chains block entry of  $\text{N}_2\text{O}_5$  into the acid, and (2) the hexyl head groups reduce the hydrolysis rate in the near-interfacial region. The steady decrease in Figure 6c is described by the relation  $\gamma_{\text{hexyl}}/\gamma_{\text{bare}} \approx 1 - (1 \pm 0.2)\theta_{\text{hexyl}}$  over the range of  $\theta_{\text{hexyl}} = 0$  to 0.6, where  $\theta_{\text{hexyl}}$  is the fraction of the surface area covered by hexyl chains in the all-trans configuration ( $\sim 20 \text{ \AA}^2$  in area and  $\sim 10 \text{ \AA}$  long).<sup>56,58</sup> Clifford et al. have recently observed, for 1-octanol films on water, that the interfacial hydrolysis of  $\text{HNO}_3$  and  $\text{NH}_3$  also decreases linearly with increasing film coverage.<sup>30</sup>

Within the first scenario, the passage of  $\text{N}_2\text{O}_5$  into the acid is limited to motions through fluctuating gaps between the hexyl chains, which become less prevalent as more hexyl species segregate to the surface at higher bulk-phase concentration and become more tightly packed. These gaps arise because, at intermediate coverages, the hexyl chains should adopt a range of configurations with varying spacings and relative positions, as pictured in simulations of butanol and heptanol on water<sup>35,36,39</sup> and inferred from neutron reflection studies of hexanol on water<sup>58</sup> and sum frequency generation studies of hexanol on 59.5 wt %  $\text{H}_2\text{SO}_4$ .<sup>59</sup> The approximate scaling between  $\gamma_{\text{hexyl}}/\gamma_{\text{bare}}$  and  $1 - \theta_{\text{hexyl}}$  implies a constant “blocking power” for each added hexyl chain. This simple correlation may be accidental, however, because the various hexyl chain conformations project different surface areas and span different lengths,



and the range of these structures becomes more restricted as the chain density increases. In particular, this scaling will likely fail as  $\theta$  approaches 1 and the chains become highly aligned and compact; for insoluble long-chain surfactants, gas permeation is observed to decrease exponentially with surface concentration at high coverage.<sup>26</sup>

The model above may be analyzed quantitatively in the limit that hydrolysis occurs far from the surfactant layer, which acts only to impede the entry of N<sub>2</sub>O<sub>5</sub> into the acid. The hydrolysis probability may then be expressed as independent resistances using  $1/\gamma_{\text{hexyl}} = 1/\alpha_{\text{hexyl}} + 1/\Gamma_{\text{react}}$ , where  $\alpha_{\text{hexyl}}$  is the probability that N<sub>2</sub>O<sub>5</sub> passes through the hexyl film and enters the acid and  $\Gamma_{\text{react}}$  is the bulk-phase reactivity.<sup>34,60,61</sup>  $\Gamma_{\text{react}}$  does not vary upon addition of hexanol because hydrolysis occurs only within the bulk acid, where little hexanol is present. The range of values of  $\Gamma_{\text{react}}$  are obtained from  $\gamma_{\text{bare}} = 0.15$  in Table 1 using the maximum value of  $\alpha_{\text{bare}} = 1$  and its minimum value of 0.15, yielding  $\Gamma_{\text{react}}(\alpha_{\text{bare}} = 1) = 0.18$  and  $\Gamma_{\text{react}}(\alpha_{\text{bare}} = 0.15) = \infty$  (every entering molecule reacts). In the latter case when  $\Gamma_{\text{react}} = \infty$ ,  $\alpha_{\text{hexyl}}$  is equal to  $\gamma_{\text{hexyl}}$  and decreases linearly with  $\theta_{\text{hexyl}}$ . When  $\Gamma_{\text{react}}$  is 0.18,  $\alpha_{\text{hexyl}}$  starts at 1 for the bare surface and drops more sharply than  $\gamma_{\text{hexyl}}$ . At the highest surface coverage of  $\theta_{\text{hexyl}} = 0.60$ , the resistance equation predicts that  $\alpha_{\text{hexyl}}$  varies between 0.09 ( $\Gamma_{\text{react}} = 0.18$ ) and 0.06 ( $\Gamma_{\text{react}} = \infty$ ). This analysis suggests that, if hydrolysis occurs far from the film region, then the saturated hexyl film must stop 90% or more of the thermalized N<sub>2</sub>O<sub>5</sub> molecules from entering the acid.

The contrasting behaviors of N<sub>2</sub>O<sub>5</sub> and HCl or HBr may be ascribed in part to their different sizes; the  $\sim 70 \text{ \AA}^3$  molecular volume of N<sub>2</sub>O<sub>5</sub> is approximately twice that of HCl and HBr, making it more difficult for N<sub>2</sub>O<sub>5</sub> to pass through gaps between the alkyl chains. Thus, HCl and HBr may permeate more easily through the film and reach the underlying acid, where they can bond to and protonate the alcohol OH groups. Size arguments alone cannot justify a lower mobility of N<sub>2</sub>O<sub>5</sub> through the film, however, because the molecular volumes of CF<sub>3</sub>CH<sub>2</sub>OH and N<sub>2</sub>O<sub>5</sub> are very similar, but CF<sub>3</sub>CH<sub>2</sub>OH passes through the hexyl and butyl films on nearly every collision.<sup>38</sup> This difference points to a potentially critical role for solute OH groups in aiding transport within the porous film, perhaps via hydrogen bonds with H<sub>2</sub>O, H<sub>3</sub>O<sup>+</sup>, or alcohol OH groups that straddle the film.<sup>62</sup>

We may also consider the opposite scenario in which N<sub>2</sub>O<sub>5</sub>, like CF<sub>3</sub>CH<sub>2</sub>OH, passes easily between the alkyl chains, but hydrolysis itself is suppressed by the interfacial alcohol species. Within this second picture, the  $1 - \theta_{\text{hexyl}}$  behavior in Figure 6c reflects the role of the hexyl head groups, rather than the hexyl chains, in reducing the rate of reaction. Previous studies indicate that N<sub>2</sub>O<sub>5</sub> hydrolysis in 70 wt % sulfuric acid is expected to occur very close to the surface.<sup>16,17,63</sup> In this region, the hexyl -OH and -OSO<sub>3</sub><sup>-</sup> end groups may locally interfere with protonation of N<sub>2</sub>O<sub>5</sub> by interfacial H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>O<sup>+</sup>, which is potentially the key step that initiates hydrolysis in acidic solutions.<sup>17,57</sup> In the limit in which hydrolysis occurs solely in the surface region and the hexyl film does not impede transport, the resistance equation reduces to  $1/\gamma_{\text{hexyl}} \approx 1/S + 1/\Gamma_{\text{surf}}$  (where  $S$ , the trapping probability, approaches 1 at thermal collision energies, as shown in Figure 5).<sup>60</sup> In this case,  $\Gamma_{\text{surf}}$  scales approximately with  $\gamma_{\text{hexyl}}$  (for  $\gamma_{\text{hexyl}} \leq 0.15$ ) and thus would be roughly proportional to  $1 - \theta_{\text{hexyl}}$ , which represents the fraction of surface area not covered by head groups.

Our experiments directly support the prediction that N<sub>2</sub>O<sub>5</sub> hydrolysis takes place in a shallow layer near the surface, potentially in the vicinity of the hexyl or butyl species. According to continuum models,<sup>17,60</sup> the average depth over

which a reaction occurs is equal to  $(D/k)^{1/2}$ , where  $D$  is the N<sub>2</sub>O<sub>5</sub> diffusion coefficient and  $k$  is the hydrolysis rate constant. Reference 17 predicts that this depth is approximately 1 Å for 72 wt % H<sub>2</sub>SO<sub>4</sub> at 216 K. In accord with this estimate, the thermal-desorption component of the prechopper TOF spectrum in Figures 4, 5, and 6 can be fit well with a Maxwell-Boltzmann distribution unconvoluted with a residence time distribution, indicating that the average bulk-phase residence time  $\tau$  of intact N<sub>2</sub>O<sub>5</sub> is less than  $2 \times 10^{-6}$  s.<sup>53</sup> In this case, the average diffusion depth of  $0.6(D\tau)^{1/2}$  is less than 10 Å for  $D \leq 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ .<sup>42,64</sup> This experimental limit implies that hydrolysis often occurs in a region containing alcohol head groups and perhaps CH<sub>2</sub> groups as well.

The data in Figure 6 therefore suggest two possible causes for the suppression of N<sub>2</sub>O<sub>5</sub> hydrolysis: the surface alkyl chains may pack tightly enough to block the entry of some N<sub>2</sub>O<sub>5</sub> molecules into the acid, while the alcohol head groups may reduce the reactivity of N<sub>2</sub>O<sub>5</sub> that do enter the acid, perhaps by reducing the concentration of both H<sub>3</sub>O<sup>+</sup> and H<sub>2</sub>O near the film-acid interfacial region.

## Conclusions and Atmospheric Implications

Hexanol and butanol dissolved in 72 wt % H<sub>2</sub>SO<sub>4</sub> at 216 K form loosely packed surface films corresponding to  $\sim 60\%$  and  $\sim 44\%$  of a compact monolayer at their asymptotic coverages, respectively. The conversion of N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> is noticeably impeded by these surface films, with reaction probabilities that drop from 0.15 to 0.06 for the hexyl film and to 0.10 for the butyl film. These changes are smaller than those observed on seawater using hexanoic acid (3- to 4-fold reduction),<sup>31</sup> most likely because the alcohol films do not pack as tightly on acidic subphases due to charge repulsion among the ROH<sub>2</sub><sup>+</sup> head groups and formation of ROSO<sub>3</sub><sup>-</sup>.<sup>40,41</sup>

The experiments demonstrate that short-chain alcohols can significantly impede N<sub>2</sub>O<sub>5</sub> hydrolysis by sulfuric acid droplets if the alcohols are plentiful enough to form saturated surface films. However, it is unlikely that butanol and hexanol are present in the background upper troposphere or lower stratosphere to reach significant surface coverages. The two shortest alcohols, methanol and ethanol, have been identified at concentrations of  $\sim 1000$  ppt and  $\sim 50$  ppt (parts per trillion by volume), respectively, in polluted regions of the upper pacific troposphere at 10–12 km.<sup>23,65</sup> Our measured solubility of hexanol in 72 wt % H<sub>2</sub>SO<sub>4</sub> at 216 K of  $3 \times 10^8 \text{ M atm}^{-1}$  permits an estimate of the gas-phase concentration required to create a saturated hexyl film. For a typical pressure of 160 Torr at an altitude of 12 km, we estimate that the  $\sim 40$  mM hexanol bulk concentration for a saturated hexyl film requires  $\sim 600$  ppt of gas-phase hexanol. The solubility of butanol should lie between the hexanol value and that of ethanol of  $2 \times 10^8 \text{ M atm}^{-1}$ ;<sup>52</sup> in this case, the  $\sim 200$  mM butanol concentration for a saturated butyl film requires  $\sim 4000$  ppt of gas phase butanol.

These minimum gas-phase concentrations rise rapidly in more dilute sulfuric acid because of lower alcohol solubilities. For 60 wt % H<sub>2</sub>SO<sub>4</sub> at 216 K, which is closer to aerosol acidities near the tropopause region,<sup>9</sup> the solubility of the alcohols is expected to be near  $\sim 4 \times 10^6 \text{ M atm}^{-1}$ .<sup>52</sup> This lower solubility requires the gas-phase hexanol concentration to increase to an even more improbable value of 50 000 ppt to create a saturated surface film. Butanol and hexanol alone are therefore not sufficiently surface active in sulfuric acid in the upper troposphere or lower stratosphere to impose barriers to N<sub>2</sub>O<sub>5</sub> hydrolysis. These short-chain alcohols are just one of many different types of organic molecules, soluble and insoluble,<sup>21–24</sup>

that may coalesce within or on aerosol droplets and segregate to the surface to form mixed monolayers of widely varying porosity and reactivity.<sup>27</sup> We hope to extend the alcohol measurements here to soluble organic molecules with different functional groups to determine their surface activity in sulfuric acid and their ability to impede or enhance gas–liquid transport and interfacial reactions.

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### Appendix: Determining the Fraction of HNO<sub>3</sub> Remaining in Solution

We determine the fraction of N<sub>2</sub>O<sub>5</sub> molecules that are converted into HNO<sub>3</sub> by measuring the relative flux of HNO<sub>3</sub> molecules that desorb from solution. Because some of the HNO<sub>3</sub> molecules created by hydrolysis remain behind in solution over the measurement time  $t_{\text{exp}}$ , the measured flux  $I_{\text{TD}}^{\text{HNO}_3}$  in eq 2 is too small. This flux can be corrected by estimating the fraction of HNO<sub>3</sub> molecules that remain dissolved in the acid. The predicted thermal-desorption flux from a fresh liquid continuously exposed for a time  $t_{\text{exp}}$  is  $I_{\text{TD}}^{\text{true}} = I_{\text{enter}}(1 - (\text{erfc}[(t_{\text{exp}}/\tau)^{1/2}] \cdot e^{t_{\text{exp}}/\tau})^{66}$  where  $I_{\text{enter}}$  is the equivalent flux of HNO<sub>3</sub> entering the solution generated by the impinging N<sub>2</sub>O<sub>5</sub> molecules. This flux depends on the characteristic residence time  $\tau$  of the HNO<sub>3</sub> molecules in solution. It is given by  $\tau = D(4H^*RT/\alpha_{\text{th}}\langle v \rangle)^2$ , where  $H^*$  is the overall solubility of HNO<sub>3</sub> in M atm<sup>-1</sup>,  $D$  is the HNO<sub>3</sub> diffusion constant,  $\alpha_{\text{th}}$  is the HNO<sub>3</sub> entry probability averaged over a Boltzmann distribution of collision energies at temperature  $T$ , and  $\langle v \rangle$  is the thermal velocity of HNO<sub>3</sub>. Over the time  $t = 0$  to  $\tau$ , the desorption flux rises from 0 to 57% of the flux entering solution. We use the values  $H^* = 2 \times 10^6$  M atm<sup>-1</sup> for HNO<sub>3</sub> in 72 wt % H<sub>2</sub>SO<sub>4</sub> at 216 K from ref 43,  $D = 7 \times 10^{-9}$  cm<sup>2</sup> s<sup>-1</sup> from ref 42, and  $\alpha_{\text{th}} = 1$  from ref 53 to obtain  $\tau = 0.2$  s.

The fraction  $f_{\text{remain}}$  of HNO<sub>3</sub> molecules that accumulate within the acid over the time  $t_{\text{exp}}$  is given by eq 8c in ref 67, where it is also graphed:

$$f_{\text{remain}}(t_{\text{exp}}) = \frac{I_{\text{enter}}t_{\text{exp}} - \int_0^{t_{\text{exp}}} I_{\text{TD}}^{\text{true}} dt}{I_{\text{enter}}t_{\text{exp}}} \\ = (\tau/t_{\text{exp}})\{\text{erfc}[(t_{\text{exp}}/\tau)^{1/2}]e^{t_{\text{exp}}/\tau} + 2(t_{\text{exp}}/\pi\tau)^{1/2} - 1\} \quad (\text{A.1})$$

For  $t_{\text{exp}} = 6$  s and  $\tau = 0.2$  s,  $f_{\text{remain}}$  is 0.18, indicating that 18% of the HNO<sub>3</sub> molecules remain in the acid even over times much longer than  $\tau$ . In this case,  $I_{\text{TD}}^{\text{diff}}$  should be divided by 0.82 in eq 2 to obtain the true relative flux. This correction increases  $f_{\text{rxn}}(\text{bare})$  from 0.12 to 0.15,  $f_{\text{rxn}}(\text{hexyl})$  from 0.05 to 0.06, and  $f_{\text{rxn}}(\text{butyl})$  from 0.08 to 0.10 in Table 1, where the corrected quantities are labeled  $\gamma$  and represent our best estimates of the hydrolysis probabilities. The ratios of  $f_{\text{rxn}}$  before and after correction remain essentially unchanged, such that  $\gamma_{\text{film}}/\gamma_{\text{bare}} \approx f_{\text{rxn}}(\text{film})/f_{\text{rxn}}(\text{bare})$ .

HNO<sub>3</sub> desorption was also measured for a much shorter observation time of 0.27 s using a continuously rotating wheel. In this case,  $f_{\text{remain}}$  rises from 0.18 to 0.52. Despite this large correction, the final value for  $\gamma(\text{N}_2\text{O}_5)$  was determined to be the same in the bare acid,  $0.15 \pm 0.02$ , suggesting that the stop–start technique may not be necessary to determine hydrolysis probabilities even when the HNO<sub>3</sub> product dissolves for long times.

No corrections are necessary for HCl dissolution in 72 wt % H<sub>2</sub>SO<sub>4</sub> at 216 K because  $\tau$  is so short ( $\tau = 2 \times 10^{-4}$  and  $f_{\text{remain}} = 0.03$ ). HBr dissolves for longer times in the bare acid ( $\tau = 0.002$  s and  $f_{\text{remain}} = 0.09$ ), but again drops to  $2 \times 10^{-4}$  s in the alkyl-coated acids because  $\alpha \approx f_{\text{exch}}$  is larger. The value for HBr entering the bare acid in Table 1 has been corrected for a 10% increase due to HBr molecules accumulating in solution over the 0.27 s exposure and observation time.

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