

Kinetics Feasibility Study of Alcohol Sulfate Esterification Reactions in Tropospheric Aerosols

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Sulfate esters have recently been identified in the secondary organic aerosol (SOA) formed in the photooxidation of biogenic hydrocarbons both in laboratory and under ambient atmospheric conditions. In the present study, the kinetics feasibility of direct reactions between alcohols and sulfuric acid to form sulfate esters in aerosol particles is explored. Nuclear magnetic resonance methods were used to monitor the bulk reaction kinetics of sulfate esterification reactions for a number of simple alcohols. The experiments were carried out at various sulfuric acid concentrations and a range of temperatures in order to estimate the rate constants of such reactions in aerosols under the previously studied laboratory conditions and under ambient atmospheric conditions. The measured rate constants did not depend greatly on the identity of the reactant alcohol, but increased strongly as a function of the sulfuric acid concentration, as predicted by excess acidity theory. Because of the strong temperature dependence of the rate constants for the direct reaction of alcohols with sulfuric acid, it appears that these reactions are kinetically infeasible for low temperature upper tropospheric sulfuric aerosols. For lower tropospheric SOA, it appears that the aerosol acidity is rarely high enough such that these reactions are likely to be responsible for the presence of sulfate esters in SOA.

Introduction

It is now recognized that secondary organic aerosol (SOA) plays an important role in the atmospheric issues of air pollution (1) and global climate change (2). Recent work suggests that acid-catalyzed particle phase chemical processes could be responsible for the enhanced SOA yields observed from the photochemical oxidation of various volatile organic compounds (VOCs). In particular, oligomerization reactions (occurring via aldol condensation reactions, among other mechanisms) have been postulated as a route by which VOCs become incorporated into SOA (3–5). More recently, organic sulfate ester products have been detected in laboratory investigations of the SOA formed from sulfuric acid seed particles and the products of the photochemical oxidation of the biogenic compounds isoprene (6, 7), α - and β -pinene (6, 8, 9), and limonene (10) in the presence of sulfuric acid seed particles. Sulfate ester products have also been identified in a laboratory investigation of the interaction of sulfuric acid aerosol with glyoxal (11), an oxidation product of aromatic VOCs. Sulfate ester products arising from isoprene,

α - and β -pinene oxidation processes have also been identified in ambient SOA in the southeastern United States (6) and Bavaria, Germany (8).

Sulfate esters have long been postulated (12) to form from the reaction of alcohols with sulfuric acid



More recent nuclear magnetic resonance (NMR) (13) and Raman spectroscopy (14) experiments have definitively shown that sulfate esters and water are the sole products of the reaction.

The potential importance of the heterogeneous reaction of gas phase alcohols with aerosol phase sulfuric acid for upper tropospheric (low temperature, highly acidic) sulfuric acid aerosols has been investigated by Iraci and co-workers via Knudsen-cell uptake experiments. As a result of their experiments with the methanol (15) and ethanol (16) systems on sulfuric acid films, Iraci and co-workers have asserted that reaction 1 is too slow to lead to appreciable amounts of sulfate esters on upper tropospheric sulfuric acid aerosols. On the other hand, because alcohols are observed as SOA constituents (17), it has been almost universally proposed that the presence of sulfate esters in SOA is due to the efficacy of reaction 1 under the relevant laboratory or atmospheric conditions. Because the origin of SOA alcohol species has generally not been definitively identified as being the result of gas and/or aerosol phase processes, it is unclear whether reaction 1 in SOA would more likely be a heterogeneous process involving gas phase alcohols or an entirely homogeneous aerosol phase process.

While there have been a few past investigations of the kinetics of sulfate esterification reactions (12, 18) there does not currently exist a sufficient database with which to estimate the rate of sulfate esterification reactions via reaction 1 for the conditions relevant to upper tropospheric sulfuric aerosols, nor for the conditions relevant to SOAs. In particular, with the exception of a sulfuric acid dependence study of the sulfate esterification reaction for the methanol system at room temperature (13), there have been no modern systematic kinetics measurements of reaction 1 as a function of sulfuric acid concentration and temperature, both of which are necessary to assess the relevance of reaction 1 to tropospheric aerosol processes. In the present study, kinetics measurements of the sulfate esterification reactions of methanol, ethanol, 1-butanol, 1,2-ethanediol (ethylene glycol), and 1,2,3,4-butanetetraol (tetrol) are performed using NMR methods. The dependence of the rate constants on both sulfuric acid concentration and temperature is determined.

Experimental Section

Due to the solvent locking requirements of ^1H NMR techniques, the experiments were performed in $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ solutions. The sulfuric acid solutions were prepared by diluting commercially obtained 96 wt% D_2SO_4 with D_2O . In one case, a mixed isotope solution was used, which was prepared by diluting 96 wt% H_2SO_4 with D_2O . Typically, solutions containing 0.5 wt% alcohol were prepared by adding a small volume (on the order of 50 μL) of the reactant alcohol (used as received from the vendor) to 5 mL of the $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ solution and vigorously mixing for 3 min. Some of this solution was transferred to a 5 mm NMR tube, and the progress of the reaction was monitored with a 400 MHz NMR spectrometer. Although each NMR spectrum took only about 30 s to collect, the auto locking and shimming procedure that preceded the collection of each spectrum limited the

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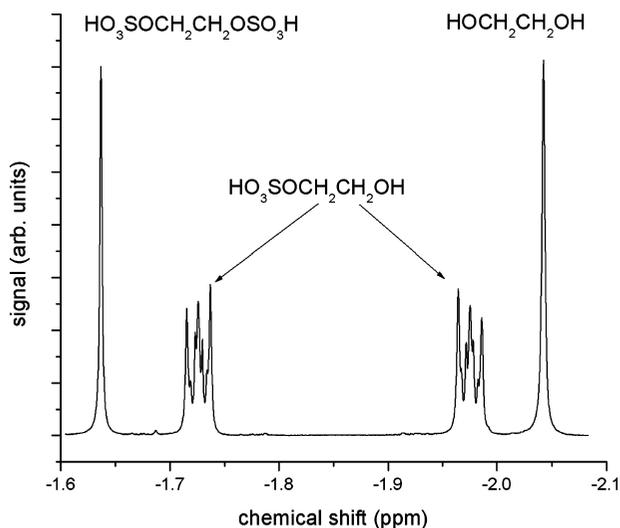


FIGURE 1. ^1H NMR spectrum of ethylene glycol in 75 wt% D_2SO_4 at 297 K at equilibrium. All resonances are due to the methylene hydrogen atoms in the reactant alcohol and the product mono and disulfate esters.

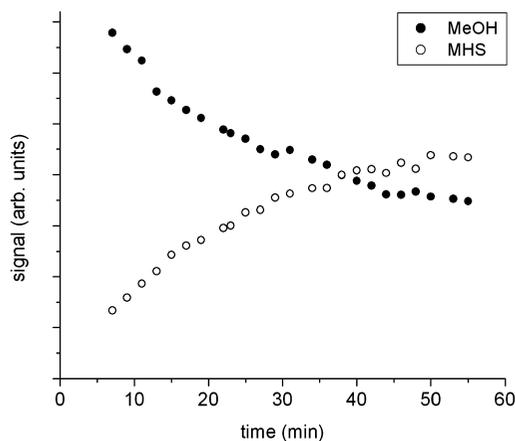


FIGURE 2. Kinetics data (circles, methanol; squares, methyl hydrogen sulfate) collected for the reaction of methanol in 75 wt% D_2SO_4 at 297 K.

time resolution of the data collection to about 3 min. For the temperature dependence measurements, the $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ solutions were prewarmed to the desired temperature before the alcohol was added, and the variable temperature feature of the NMR spectrometer maintained a fixed temperature throughout the kinetics run. The reactant and product kinetics data were obtained from integrations of the appropriate NMR signals from each NMR spectrum in the time series.

The equilibrium constants were calculated from integrations of the appropriate NMR signals after the reaction had clearly reached completion (in most cases, the experiments were performed under conditions with a reaction lifetime of about 1 h; the equilibrium constants were usually calculated from integrations obtained after about 24 h of total reaction time). Although integrated ^1H signals from different chemical species are routinely assumed to have the same linear relationship to concentration in NMR spectroscopy (unlike those for ^{13}C signals), the commercial availability of methyl hydrogen sulfate (MHS) allowed this relationship to be confirmed by direct calibration of a mixed methanol/MHS solution in (unreactive) D_2O solvent. It was assumed that the integrations for the reactants and products for the other systems were also similarly linearly dependent on concen-

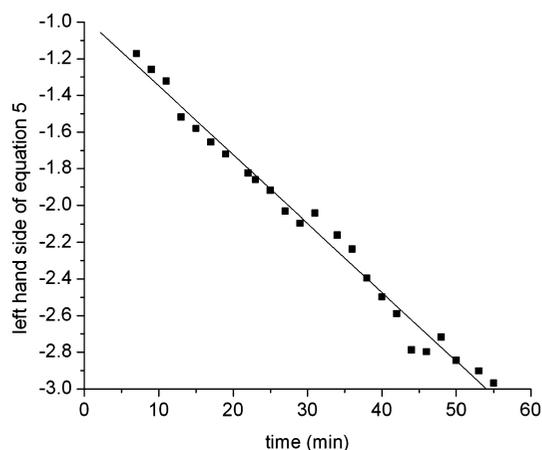


FIGURE 3. Pseudo first-order kinetics analysis for methanol data plotted in Figure 2.

tration, and the equilibrium constants were directly calculated from the appropriate reactant and product integrations.

Results and Discussion

Identification of Reaction Products. Although the chemical shifts (relative to the HDO solvent peak at 4.79 ppm) of the chemically unique protons in the reactants and products depended strongly on the concentration of the $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ solutions, the relative chemical shifts of the protons attached to the alcohol carbon atom as compared to the protons attached to the sulfate ester carbon atom were nearly constant. For example, the methyl protons in methanol and the methyl protons in MHS were usually separated by about 0.1 ppm, with the MHS signal located downfield of the methanol signal. These assignments were confirmed by comparison to NMR spectra collected for unreacted methanol and unreacted MHS (one of the few commercially available sulfate esters). Therefore, it was straightforward to identify the reactant alcohol and product sulfate ester peaks for the methanol, ethanol, and 1-butanol systems. For the diol ethylene glycol, both monoester and diester products were observed (a sample spectrum is shown in Figure 1). However, again it was straightforward to make the peak assignments, as the diester products were characterized by chemical shifts that were downfield of the monoester products. For example, in 75 wt% D_2SO_4 , the single chemically unique proton in ethylene glycol is observed to have a chemical shift of -1.45 ppm, the monoester is observed to have chemical shifts of -1.15 (for protons attached to the carbon atom adjacent to the sulfate ester functionality) and -1.35 ppm (for protons attached to the carbon atom which is geminal to the sulfate ester functionality), and the single chemically unique proton in the diester is observed to have a chemical shift of -1.05 ppm (as indicated in Figure 1). For tetrol in 75 wt% D_2SO_4 , the spectrum was too congested to make specific product assignments, but based on the downfield chemical shift signals, it was clear that at least mono- and diester products were formed.

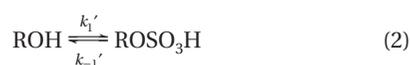
The secondary alcohol 2-butanol and the tertiary alcohol 2-methyl-2-propanol were also investigated. For 2-butanol, a small amount of sulfate ester product was formed in 75 wt% D_2SO_4 . However, unlike the primary alcohols in which the alcohol loss rate equaled the sulfate ester production rate in a stoichiometric relationship, the production rate of the sulfate ester was much lower than the overall 2-butanol loss rate, and no other products were detected via NMR. Because secondary and tertiary alcohols can undergo acid-catalyzed dehydration to form alkenes much more quickly than can primary alcohols, it is postulated most of the 2-butanol reacted to form 2-butene, which was too volatile

TABLE 1. Experimental Rate and Equilibrium Constants

system	T (K)	D ₂ SO ₄ (wt%)	(<i>k</i> ₁ ' + <i>k</i> ₋₁ ') (10 ⁻⁵ s ⁻¹)	<i>K</i> _{eq} '	<i>k</i> ₁ ' (10 ⁻⁵ s ⁻¹)	<i>k</i> ₋₁ ' (10 ⁻⁵ s ⁻¹)
methanol	297	65	6.5	0.94	3.2	3.4
	297	75	61.3	1.79	39.3	22.0
	297	85	252.0	3.29	193.3	58.7
ethanol	297	65	6.2	0.50	2.1	4.1
	297	75	55.2	0.87	25.7	29.5
	297	65	2.6	0.69	1.1	1.6
1-butanol	308	65	19.0	0.62	7.3	11.7
	313	65	37.6	0.61	14.3	23.3
	319	65	62.8	0.57	22.8	40.0
	323	65	118.0	0.55	41.9	76.1
	297	75	34.1	1.05	17.5	16.6
ethylene glycol - monoester	297	65	11.2	0.93	5.4	5.8
	297	75	103.0	2.43	73.0	30.0
ethylene glycol - diester	297	65	59.0	0.06	3.4	55.6
	297	75	210.0	0.30	48.5	161.5
tetrol	297	65			3.5	
	297	75			72.0	

to remain in solution. For 2-methyl-2-propanol in 75 wt% D₂SO₄, the dehydration reaction was apparently so fast that no organic species could be detected at all in this solution.

Pseudo First-Order Kinetics Analysis. Figure 2 shows data from a typical kinetics run for methanol in 75 wt% D₂SO₄ at 297 K. Because methanol is at very low concentrations relative to sulfuric acid and water, these kinetics traces show pseudo first-order behavior. It is also obvious from this plot that the reaction does not go to completion. Indeed, all of the systems studied had significant equilibrium concentrations of both the alcohol reactant and sulfate ester product(s). Again, because of the low concentrations of alcohol and sulfate ester in the present experiments, reaction 1 can be explicitly written as a reversible pseudo first-order reaction with forward rate constant *k*₁' and a reverse rate constant *k*₋₁':



The effective equilibrium constant *K*_{eq}' is directly related to these rate constants:

$$K_{\text{eq}}' = [\text{ROSO}_3\text{H}]_{\text{eq}}/[\text{ROH}]_{\text{eq}} = k_1'/k_{-1}' \quad (3)$$

The integrated rate law expression for such a reaction is (19)

$$\ln\left(\frac{k_1'[\text{ROH}] - k_{-1}'[\text{ROSO}_3\text{H}]}{k_1'[\text{ROH}]_0}\right) = -(k_1' + k_{-1}')t \quad (4)$$

Since [ROH]₀ = [ROH] + [ROSO₃H] at all times, eq 4 can be rearranged as follows:

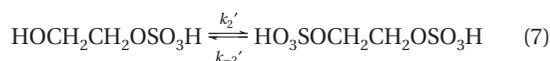
$$\ln\left(\frac{[\text{ROH}] - \left(\frac{1}{K_{\text{eq}}'}\right)([\text{ROH}]_0 - [\text{ROH}])}{[\text{ROH}]_0}\right) = -(k_1' + k_{-1}')t \quad (5)$$

Therefore, the analysis requires the time dependence of ROH loss and *K*_{eq}', and the sum of the forward and reverse rate constant is obtained as the negative of the slope of the line obtained by plotting the left-hand side of eq 5 vs time. Figure 3 shows the results of this analysis for the data given in Figure 2. Table 1 contains the values of (*k*₁' + *k*₋₁') and *K*_{eq}' determined for the systems under study in this work, as well as the *k*₁' and *k*₋₁' values calculated from these values and eq 3. The one standard deviation statistical error in the rate constants averaged about 5% for all values measured. The methanol system results are in fairly good agreement with the previous NMR study of Vinnik et al. (13), which also

utilized D₂SO₄/D₂O solutions. The methanol, ethanol, and 1-butanol rate constants measured in this study are significantly larger than those measured in the older work of Deno et al. (12) (about a factor of 5) and Clark and Williams (18) (about a factor of 2) that utilized indirect detection of the sulfate ester products and H₂SO₄/H₂O solutions.

In an attempt to determine a potential kinetic isotope effect on the rate constants due to the use of D₂SO₄/D₂O solutions, the rate constant was determined for the reaction of methanol in an isotopically mixed solution prepared by diluting concentrated H₂SO₄ with D₂O (having a composition of 65 wt% sulfuric acid), with the expectation that rapid hydrogen exchange would lead to significant quantities of both protonated and deuterated versions of the species that play a role in the reaction mechanism. The NMR data collected for this experiment were less precise, presumably due to the poorer quality lock signal resulting from the lower concentration of deuterons in the solutions. However, the rate constant determined for this system was actually slightly lower (20%) than the rate constant determined for the isotopically pure 65 wt% D₂SO₄/D₂O solution. In the case of a normal kinetic isotope effect, a larger rate constant would be expected in the mixed isotope system. In any case, based on our work, it does not appear that there is a large kinetic isotope effect for these reactions, and it may be reasonably assumed that the rate constants for H₂SO₄/H₂O solutions are similar to those determined here for D₂SO₄/D₂O solutions.

In the case of ethylene glycol, the reaction scheme can be represented by two reversible pseudo first-order reactions:



Because no analytical integrated rate law can be derived for this scheme, the ethylene glycol, monoester, and diester kinetics curves were explicitly fit to the kinetics mechanism represented in eqs 6 and 7 using a numerical kinetics solver (20) to determine the rate constants (and equilibrium constants). These values are also given in Table 1, with the reaction 6 values listed in the ethylene glycol-monoester entry and the reaction 7 values listed in the ethylene glycol-diester entry. To the best of our knowledge, there have been no previous measurements of any sulfate ester-forming rate constants for this system.

In the case of tetrol, a pseudo first order forward rate constant (*k*₁') was determined from the loss of the reactant

at early reaction times (the sulfate ester concentrations are low and the reverse reaction is negligible under these conditions) using the usual first order integrated rate law expression. These k_1' rate constants are listed in Table 1. Again, we are not aware of any previous sulfate ester-forming measurements for this system.

Excess Acidity Analysis. The excess acidity method (21) accounts for the nonideal behavior of highly acidic solutions and is necessary for the interpretation of acid-catalyzed kinetics results under the conditions of the present experiments. The excess acidity formalism is an attempt to define a linear relationship between the observed rate constant and some acidity function for an acid-catalyzed process, much like a pseudo first-order rate constant can be linearly related to the concentration of the excess reactant. The excess acidity parameter, X , is best thought of as a quantity analogous to pH for concentrated acidic solutions. In our previous study of the acid-catalyzed aldol condensation reactions of aldehydes, we found a linear relationship between $(\log k_{\text{phenom}} - \log C_{\text{H}^+} - \log a_w)$ and X , where k_{phenom} is the phenomenological rate constant, C_{H^+} is the proton concentration, and a_w is the activity parameter for H_2O , such that the data could be fit to the following expression (22):

$$(\log k_{\text{phenom}} - \log C_{\text{H}^+} - \log a_w) = mX + b \quad (8)$$

As X is analogous to $\log[\text{H}^+]$, this analysis is essentially a more sophisticated version of the "log-log" plotting exercise often used to determine reaction rate orders, but that is instead applied here to find the effective H^+ rate order (the slope, m , in eq 8) for the acid-catalyzed process. The intercept, b , in eq 8 represents the value of $\log k_{\text{phenom}}$ at infinite dilution ($X = 0$). Parameterized values for C_{H^+} , X , and a_w as a function of sulfuric acid weight percent are given in our previous work (22).

To analyze the present results in terms of the excess acidity framework, the pseudo first-order rate constants must be converted to the appropriate second order rate constants (i.e., $k_{\text{phenom}} = k_1'' = k_1'/[\text{H}_2\text{SO}_4]$). Note that this process is necessarily approximate, as an "excess hydrogen sulfate ion" formality would be needed for a more rigorous approach. In any case, the sulfuric acid molality values of 57.7, 30.6, and 18.9 m for the 85, 75, and 65 wt% sulfuric acid solutions, respectively, were used to calculate the forward bimolecular rate constants for the methanol system. For example, for methanol in 65 wt% D_2SO_4 , Table 1 indicates a value for k_1' of $3.2 \times 10^{-5} \text{ s}^{-1}$. The second order rate constant k_1'' is calculated by dividing $3.2 \times 10^{-5} \text{ s}^{-1}$ by 18.9 m to get a value of $1.7 \times 10^{-6} \text{ m}^{-1} \text{ s}^{-1}$. The excess acidity parameters for the forward reaction for methanol were determined by fitting the 65, 75, and 85 wt% sulfuric acid data to eq 8 and the values found (and one standard deviation uncertainties in parentheses) were $m = 1.022$ (0.024) and $b = -9.64$ (0.13). For the reverse reaction for methanol (using water molality values of 9.8, 18.5, and 29.9 m for the 85, 75, and 65 wt% sulfuric acid solutions, respectively, to convert to bimolecular rate constants), the excess acidity parameters were found to be $m = 1.152$ (0.007) and $b = -10.33$ (0.04). It is clear that both the forward and reverse processes are acid-catalyzed with a rate order of nearly one, as expected. Although explicit excess acidity analyses were not carried out for the other alcohols, it is clear that ethanol, 1-butanol, and the monoester-forming reactions for ethylene glycol and tetrol are also characterized by m values near one, as they show a rate constant increase from 65 to 75 wt% D_2SO_4 similar to that observed for methanol. More importantly, this parametrization allows for rate constants to be calculated for any sulfuric acid concentration, such as the lower sulfuric acid concentrations present in SOA, as will be utilized in a later section of the manuscript assessing the kinetic feasibility of these reactions in SOA.

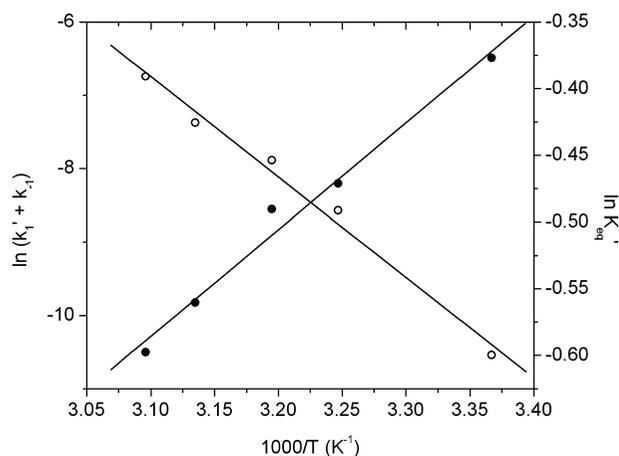


FIGURE 4. Arrhenius (open circles, left side axis) and van't Hoff (closed circles, right side) analysis of temperature-dependent data for the reaction of 1-butanol in 65 wt% D_2SO_4 .

Alcohol Dependence. The rate and equilibrium constants determined for the various alcohol systems (as a function of sulfuric acid composition and temperature) are given in Table 1. For the monoalcohols in 75 wt% D_2SO_4 , the k_1' value declined from $3.9 \times 10^{-4} \text{ s}^{-1}$ for methanol to $2.6 \times 10^{-4} \text{ s}^{-1}$ for ethanol to $1.8 \times 10^{-4} \text{ s}^{-1}$ for 1-butanol, a variability of about a factor of 2. Since polyols have been identified in SOA [such as 2-methyl-1,2,3,4-butanetetraol (2-methyl tetrol) from isoprene oxidation] (17) it is important to establish whether polyols have significantly higher sulfate ester-forming reactivity than monoalcohols. Of the systems studied, ethylene glycol was determined to have the largest k_1' value ($7.3 \times 10^{-4} \text{ s}^{-1}$) in 75 wt% D_2SO_4 , which was almost three times the value for the ethanol system ($k_1' = 2.6 \times 10^{-4} \text{ s}^{-1}$), suggesting that polyols are indeed more reactive than monoalcohols. However, tetrol was found to have k_1' values almost identical to those for ethylene glycol in 75 wt% D_2SO_4 . The similar reactivity of tetrol as compared to ethylene glycol can be rationalized if the secondary alcohol groups in tetrol (at the 2 and 3 positions) are less reactive than the primary alcohol groups (at the 1 and 4 positions). In addition, in 65 wt% D_2SO_4 , tetrol was found to have reactivity similar to that of methanol. Therefore, while the number of primary alcohol functional group sites appears to have a direct effect on the rate constant in polyols, these effects are on the order of the monoalcohol rate constant variability and smaller than the effects due to sulfuric acid composition. In any case, this result suggests that polyols do not have higher sulfate ester-forming reactivities than diols, which themselves are only slightly more reactive than monoalcohols.

Temperature Dependence. Temperature dependence measurements were made for the 1-butanol system in 65 wt% D_2SO_4 . Because of the details of the variable temperature operation of the NMR spectrometer, it was more straightforward to make kinetics measurements at temperatures above room temperature. To minimize losses due to evaporation at these elevated temperatures, 1-butanol was chosen for the temperature dependence studies. Table 1 contains the temperature dependence results for the 1-butanol system in 65 wt% D_2SO_4 . Because the equilibrium constant was only slightly temperature dependent over the range studied (24 to 50 °C), an Arrhenius analysis was performed for the temperature dependence of the sum of the rate constants: $k_1' + k_{-1}'$. A van't Hoff analysis was performed for the temperature dependence of the equilibrium constant. Both analyses are displayed in Figure 4 (left side axis, Arrhenius; right side axis, van't Hoff) and the relevant kinetic and thermodynamic parameters (and one standard deviation statistical uncertainties) were found. The activation energy was determined to be 113.8 (7.4) kJ mol^{-1} , and the thermo-

dynamic parameters were determined to be $\Delta G = +0.9$ (1.0) kJ mol^{-1} , $\Delta H = -6.7$ (0.5) kJ mol^{-1} , and $\Delta S = -25.5$ (1.6) J K mol^{-1} . The only previous study at temperatures other than room temperature were measurements made at 0 °C in the Clark and Williams study of ethanol sulfate esterification (18). As discussed earlier, the rate constants determined using their indirect methodology seem to be systematically lower than those determined in the present direct study. However, the difference between their 0 and 25 °C rate constants and equilibrium constants for the ethanol system are consistent with the activation energy and thermodynamic values determined in the present work for the 1-butanol system. The thermodynamic analysis indicates that the equilibrium constant is near unity for these reactions because the exothermicity of the sulfate ester-forming reaction is almost exactly offset by reduced entropy of the products near room temperature. The activation energy is relatively large, indicating that sulfate esterification reactions are significantly slower at the lower temperatures characteristic of the upper troposphere.

Kinetics Feasibility of Alcohol Sulfate Esterification Reactions in Upper Tropospheric Sulfuric Acid Aerosols.

Using the "typical" upper tropospheric sulfate particle parameters cited by Michelsen et al. (16) (220 K, 58 wt% H_2SO_4) and the parameters determined in the present study, the feasibility of sulfate ester-forming reactions in upper tropospheric sulfuric acid aerosols can be estimated. Methanol is used as the representative alcohol for these calculations, since it is the most abundant alcohol in the atmosphere, and its solubility characteristics are well-known (15). Under these conditions, and assuming an average tropospheric gas phase methanol concentration of 1 ppb, the physical dissolution of methanol is predicted to lead to an aerosol particle that is about 0.001 wt% methanol. As has been pointed out previously by Iraci et al., the physical partitioning of gaseous methanol into such particles is a negligible sink as compared to other loss processes (15); these much faster sinks (gas phase photochemical loss by OH reaction is the largest) are responsible for methanol's atmospheric lifetime of about 7 days (23). Using the excess acidity analysis and the parameters determined for the methanol system and the activation energy determined for the 1-butanol system as described above, the bimolecular rate constant under these conditions is calculated to be $6.9 \times 10^{-14} \text{ m}^{-1} \text{ s}^{-1}$. Assuming a sulfuric acid molality of 13.3 *m* for 58 wt% H_2SO_4 , the pseudo first-order forward rate constant (k_1') is calculated to be $9.1 \times 10^{-13} \text{ s}^{-1}$. This corresponds to a lifetime of more than 12 million days for the conversion of aerosol phase methanol to methyl hydrogen sulfate! Obviously, the earlier conclusion by Iraci and co-workers that the sulfate esterification reactions of alcohols are too slow to occur on upper tropospheric sulfuric acid aerosols is strongly supported by these results (15, 16). On the other hand, the new results are at odds with rate constants measured via methanol uptake experiments in a wetted wall flow reactor (24). In the experiments of Kane and Leu, a rate constant of 0.1 s^{-1} was determined for methanol at 220 K and 65 wt% H_2SO_4 ; the present work predicts a rate constant of only $4.5 \times 10^{-12} \text{ s}^{-1}$ under these conditions.

Kinetics Feasibility of Alcohol Sulfate Esterification Reactions in Laboratory Secondary Organic Aerosol Studies.

In the previous laboratory investigations of sulfate esterification reactions in SOA, direct measurements of the sulfuric acid content of the aerosols were not possible. However, the relative humidity was controlled in these experiments, and (assuming the aerosols were fully equilibrated), the sulfuric acid content of the aerosols can be calculated from a thermodynamic model (25).

In the isoprene and α -pinene SOA experiments of Surratt et al. (6, 7), a relative humidity of 30%, which corresponds

to an equivalent sulfuric acid content of 52.5 wt% at 298 K, and a total reaction time of 24 h were utilized. Using the excess acidity parameters for methanol determined in this work (because they are better determined than those for tetrol, but similar to those expected for tetrol), the second order rate constant under these conditions is calculated to be $k_1'' = 2.9 \times 10^{-7} \text{ m}^{-1} \text{ s}^{-1}$. The predicted lifetime for the reaction under these conditions (obtained by calculating the pseudo first-order rate constant k_1' from $[\text{H}_2\text{SO}_4] = 9.8 \text{ m}$) is 96 h. Therefore, even though the reaction time of the experiments was somewhat less than the calculated lifetime for the sulfate esterification reaction, the presence of some sulfate ester products in the SOA experiments of Surratt et al. is consistent with the present kinetics results.

In the β -pinene and limonene SOA experiments of Iinuma et al. (8, 10), a relative humidity of about 50%, which corresponds to a sulfuric acid content of about 43 wt% at 298 K, and a total reaction time of 2.5 h were utilized. Again, using the excess acidity parameters for methanol determined in this work, the second order rate constant under these conditions is calculated to be $k_1'' = 5.2 \times 10^{-8} \text{ m}^{-1} \text{ s}^{-1}$. The predicted lifetime for the reaction under these conditions (obtained by calculating the pseudo first-order rate constant k_1' from $[\text{H}_2\text{SO}_4] = 6.3 \text{ m}$) is 864 h. In this case, it does not appear that the presence of sulfate ester products due to alcohol sulfate esterification reactions in the Iinuma et al. SOA experiments is consistent with the present kinetics results.

Kinetics Feasibility of Alcohol Sulfate Esterification Reactions in Ambient Secondary Organic Aerosol.

In the measurement of ambient SOA, the chemical complexity of the particles does not allow for a direct comparison to the laboratory studies in which sulfuric acid content is controlled in the seed aerosol particles or bulk solutions. However, Zhang et al. have used measurements of the concentrations of the ionic components of the aerosols (such as sulfate, nitrate, chloride, and ammonium) to estimate the acidity ($[\text{H}^+_{\text{aerosol}}]$) of SOA particles in the Pittsburgh area (26). Zhang et al. then used the thermodynamic model of Clegg et al. (25) to calculate an average pH value for the SOA sampled. In their measurements, the pH of SOA usually ranged from about 4.0 to 1.5, but values as low as 0.0 were sometimes observed. To allow comparison with the present results, the Clegg et al. model can be used to convert these pH values to an equivalent sulfuric acid aerosol composition. For example, a pH of 0.0 corresponds to a sulfuric acid content of about 43 wt%, and a pH of 1.5 corresponds to a sulfuric acid content of about 14 wt%. As was calculated in the previous paragraph for the laboratory studies of Iinuma et al., the lifetime of the methanol sulfate esterification reaction under the conditions of 43 wt% H_2SO_4 and 298 K is 864 h (36 days). Therefore, even under the most acidic conditions observed in the Pittsburgh study, the methanol sulfate esterification lifetime is predicted to be significantly longer than the overall atmospheric lifetime of methanol (7 days) (23). The wet deposition lifetime of SOA is also on the order of a few days (27). Thus, even if the actual alcohols in SOA have longer atmospheric lifetimes than methanol or are themselves the result of aerosol-phase processes, the SOA lifetime would be the limiting factor in determining whether alcohol sulfate esterification reactions have sufficient time to occur. For the more routinely observed pH of 1.5, the equivalent 298 K sulfuric acid composition is 14 wt% (3.0 *m*). For these conditions, the excess acidity analysis predicts a k_1'' value of $8.3 \times 10^{-10} \text{ m}^{-1} \text{ s}^{-1}$, and a k_1' value of $2.5 \times 10^{-9} \text{ s}^{-1}$, which corresponds to a lifetime of 4600 days. Assuming that the atmospheric lifetime argument described above holds for the actual alcohols present in SOA, it would seem that the kinetics feasibility of alcohol sulfate esterification reactions in SOA is marginal even for the most extreme acidity conditions observed. Furthermore, under

the more typical acidities observed in the Pittsburgh study (pH = 4.0 to 1.5), alcohol sulfate esterification reactions in SOA are predicted to be completely kinetically insignificant.

As mentioned in the Introduction, most previous work has invoked sulfate esterification reactions involving alcohols as the most likely mechanism to explain the existence of sulfate esters in SOA. Based on the present results, this pathway may not be kinetically efficient enough to explain the observation of sulfate esters in either laboratory generated or ambient SOA. However, Iinuma et al. have also suggested that epoxides known to form in the oxidation of monoterpenes could react with sulfuric acid to form sulfate esters (8). Since it is well-known that epoxides are rapidly hydrolyzed under mildly acidic conditions (28), it is possible that sulfate esters could form under conditions in which HSO_4^- can compete with H_2O in role of the nucleophile in the traditional epoxide hydrolysis mechanism. The traditional epoxide hydrolysis mechanism leads to diols, which are also often observed in SOA. Therefore, if the epoxide hydrolysis pathway were a kinetically important one in SOA formation, it could explain the presence of both diols and sulfate esters in SOA. In any case, further study of alternative (and more kinetically efficient) sulfate ester forming mechanisms is warranted.

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