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Kinetic study of esterification of sulfuric acid with alcohols in aerosol bulk phase

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Abstract

In this study, we hypothesize that the formation of organosulfates through the reactions between sulfuric acid and alcohols in the aerosol bulk phase is more efficient than that in solution chemistry. To prove this hypothesis, the kinetics of the organosulfate formation was investigated for both aliphatic alcohol with single OH group (e.g., 1-heptanol) and the multialcohols ranging from semivolatiles (e.g., hydrated-glyoxal and glycerol) to nonvolatiles (e.g., sucrose) using analytical techniques directly monitoring aerosol bulk phase. Both the forward (k_1) and the backward (k_{-1}) reaction rate constants of organosulfate formation via the particle phase esterification of 1-heptanol with sulfuric acid were estimated using a Fourier Transform Infrared (FTIR) spectrometer equipped with a flow chamber under varying humidities. Both k_1 and k_{-1} are in orders of $10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$, which are three orders of magnitude higher than the reported values obtained in solution chemistry. The formation of organosulfate in the H₂SO₄ aerosol internally mixed with multialcohols was studied by measuring the pro-

- ¹⁵ ton concentration of the aerosol collected on the filter using a newly developed Colorimetry integrated with a Reflectance UV-Visible spectrometer (C-RUV). The formation of organosulfate significantly decreases aerosol acidity due to the transformation of H_2SO_4 into dialkylsulfates. The forward reaction rate constants for the dialkylsulfate formation in the multialcohol- H_2SO_4 aerosols were also three orders of magnitude greater than the reported values in solution chemistry. The water content (M_{12} a) in the
- ²⁰ greater than the reported values in solution chemistry. The water content (M_{H_2O}) in the multialcohol- H_2SO_4 particle was monitored using the FTIR spectrometer. A large reduction of M_{H_2O} accords with the high yield of organosulfate in aerosol. Based on this study, we conclude that organosulfate formation in atmospheric aerosol, where both alcohols and sulfuric acid are found together, is significant.





1 Introduction

Sulfuric acid, which is typically produced from the photooxidation of sulfur dioxide, is one of the major inorganic components for the ambient aerosol. It can either be neutralized by ammonia forming ammonium salt, or react with certain atmospheric organic compounds (e.g., alcohols and aldehydes) producing organosulfates in aerosol (Eqs. 1

and 2) (Deno and Newman, 1950; Minerath et al., 2008).

 $ROH + H_2SO_4 \rightleftharpoons ROSO_3H + H_2O$

 $ROH + ROSO_3H \rightleftharpoons ROSO_2OR + H_2O$

- Field studies have shown that organosulfate is ubiquitous in ambient aerosols collected at various locations in US (Surratt et al., 2007a; Hatch et al., 2011), Asia (Maria et al., 2003; Stone et al., 2012), and Europe (Gomez-Gonzalez et al., 2008; linuma et al., 2007; Kristensen and Glasius, 2011). For example, Hatch et al. (2011) have reported that organosulfate signal was detected in negative-ion spectra of most ambient submicron aerosols collected during the 2002 Aerosol Nucleation and Characterization Experiment (ANARChE) and the 2008 August Mini-Intensive Gas and Aerosol Study (AMIGAS). Organosulfates have also been identified in free tropospheric aerosols characterized by single particle mass spectrometry in airborne field campaigns (Froyd et al., 2010).
- In order to identify the source of organosulfates in aerosol and their reaction mechanisms, laboratory studies have been conducted using both model compounds and laboratory generated secondary organic aerosol (SOA). Some studies suggested that organosulfates form through the direct reactions of sulfuric acid with organic compounds such as alcohols, aldehydes, and epoxides. For example, Liggio et al. (2005)
- have reported organosulfate formation from the reactive uptake of glyoxal onto acidic sulfate particles. Using the HPLC/(-)ESI-IMS-QTOFMS analysis, linuma et al. (2009)



(1)

(2)



identified orgnaosulfates from the reactive uptake of monoterpene oxides on acidic sulfate particles. Surratt et al. (2010) showed organosulfates formation through the acidcatalyzed reactive uptake of isoprene epoxydiols (IEPOX). Lal et al. (2012) detected organosulfate produced from the reaction of α -pinene oxide with sulfuric acid solution

- ⁵ using NMR. In addition to the mechanisms via the direct reactions between sulfuric acid and organic compounds, organosulfates can also be formed through the reaction of organic compounds (e.g., aldehydes and oxygenated alkenes) with SO⁻₄ radicals produced from photo-irradiation of sulfate. For example, Galloway et al. (2009) found irreversible organosulfate products when glyoxal was photoirradiated in the presence
- of wet ammonium sulfate aerosol. The structures of resulting irreversible organosulfate products (e.g., glycolic acid sulphate) in their study are different from reversible organosulfate products (sulfate esters) found by Liggio et al. (2005). Noziere et al. (2010) also suggested that radical reactions would be a plausible origin for the atmospheric organosulfates.
- ¹⁵ Most kinetic studies for organosulfate formation using model compounds (e.g., alcohols) have been conducted in solution. Among organic compounds, the reaction rates of epoxides with sulfuric acid are considerably fast while those of both alcohols and aldehydes with sulfuric acid in solution chemistry are relatively too slow to produce organosulfates within the atmospheric lifetime of aerosol. For example, the reported
 ²⁰ forward reaction rate constant for esterification of alcohols in high concentration of sulfuric acid solution (65 wt %) is slow (e.g., 5.7 × 10⁻⁶ L mol⁻¹ min⁻¹ for 1-butanol) (Minerath et al., 2008) suggesting that the lifetime of alcohol for sulfate esterification is 4600 days at pH = 1.5.

However, it is disputable whether the reaction rate constants observed in solution ²⁵ chemistry are applicable to the aerosol bulk phase. Foremost, water molecules produced as by-products of organosulfate formation (Eqs. 1 and 2) can be evaporating from the aerosol leaving less volatile organosulfates in aerosol. Both water evaporation and the formation of hydrophobic organosulfates (compared to sulfuric acid) would possibly promote the forward reactions, increasing organosulfate yields (Eqs. 1 and 2).



Thus, we hypothesize that the esterification between sulfuric acid and alcohols in the aerosol bulk phase is more efficient than that in solution chemistry. To prove this hypothesis, the direct analysis of aerosol bulk phase calls for.

- The investigation of kinetics and quantification of aerosol phase organosulfates have been limited due to the lack of both analytical methods and the reversibility of organosulfates during the solvent extraction procedure. For example, it has been known that alkyl bisulfates decompose on heating before reaching to their boiling points (Kirk et al., 1991). Therefore, a conventional mass spectrometer, which requires heating at high temperature for evaporation of an extracted sample and chemical injection, is not appropriate to measure those organosulfates. In the aerosol mass spectrometer, most organosulfates manifest as separate organic and sulfate components due to the low
- organosulfates manifest as separate organic and sulfate components due to the low thermal stability, with little difference in fragmentation from inorganic sulfate (Farmer et al., 2010). In addition to poor thermal stability, the organosulfates produced from aldehydes are unstable during solvent extraction that often uses water, methanol or
- acetonitrile, indicating that they cannot be detected by the LC/MS (Galloway et al., 2009). Stone et al. (2012) have recently reported that the uncertainty of organosul-fate quantification using ultra-performance LC (UPLC) with quadrupole time-of-flight tandem mass spectrometry (QTOFMS) is estimated to be within a factor of five due to the lack of internal standards. They have also suggested that the quantification of multifunctional organosulfate products containing nitrate and carboxylate groups can be underestimated using the UPLC OTOEMS method due to the invitation of other
- be underestimated using the UPLC-QTOFMS method due to the ionization of other functionality.

In this study, the kinetics of the formation of organosulfate in the aerosol bulk phase was investigated using nondestructive in situ methods for both aliphatic alcohol with single OH group (e.g., 1-heptanol) and multialcohols (MOH). The esterification between 1-heptanol and sulfuric acid was directly monitored using particle samples in situ with a Fourier Transform Infrared (FTIR) spectrometer connected with a flow chamber with time. Organosulfates were also produced directly in the aerosol comprising of sulfuric acid with multialcohols such as sucrose, glyoxal, and glycerol. These multialcohols are





capable of producing thermodynamically stable 5- or 6-membered cyclic dialkylsulfates due to the proximity of OH groups within a molecule. The formation of dialkylsulfates was measured using a Colorimetry integrated with Reflective UV-Visible spectrometer (C-RUV) (Jang et al., 2008; Li and Jang, 2012). The C-RUV is a non-destructive optical technique that permits the direct measurement of aerosol acidity for the aerosol filter sample where organosulfate formation progresses. Sucrose and glycerol, as major sugar compounds in atmospheric aerosols, are byproducts of biomass combustion and components of soil debris (Simoneit et al., 2004), and have relatively low volatility. Glyoxal is ubiquitous in the ambient air with a global budget of 45 Tg yr⁻¹ (Fu et al., 2008)
due to the atmospheric oxidation of various volatile organic compounds. Glyoxal is also observed in aerosol due to the formation of oligomeric products in aerosol (Ervens and Volkamer, 2010).

2 Experimental methods

2.1 FTIR experiment

- To investigate the kinetics of organosulfate formation via the reaction of 1-heptanol on the surface of sulfuric acid particle, the FTIR (Nicolet Magma 560) equipped with a flow chamber (0030-104, Thermo Spectra-Tech), which holds an optical silicon disk (13 × 2 mm, Sigma Aldrich) (Jang et al., 2010), was used (Fig. 1). Sulfuric acid solution (0.01 M) was atomized using a nebulizer (LC STAR, Pari Respiratory Equipment) and impacted on the silicon disk for FTIR analyses. The FTIR disk was weighed using an analytical balance (MX5 Mettler-Toledo Ltd.) before and after particle impaction to measure the sulfuric acid particle mass. The relative humidity (RH) inside the flow chamber was controlled by combining humid air from a water bubbler and dry air from an air tank (Breathing air, Airgas) with a total air flow rate of 0.6–1.2 L min⁻¹. RH and temperature of the chamber air was measured with a hygrometer (Dwyer series 485).
- Gaseous 1-heptanol was introduced into the FTIR chamber by passing the tank air





though pure 1-heptanol standing in a water bath (Fig. 1). The gaseous 1-heptanol was collected using an impinger with acetonitrile (99%, Sigma Aldrich) and transferred to a small vial for gas chromatography mass spectrometer (GC-MS, Varian model CP-3800 GC, Saturn model 2200 MS) analysis. The GC temperature was set at 80°C. The concentrations of 1-heptanol were determined by the calibration curve with an internal

⁵ concentrations of 1-neptanol were determined by the calibration curve with an internal standard (1-nananol). FTIR spectra of sulfuric acid particles exposed to gaseous 1-heptanol using the flow chamber were measured in the absorption mode as a function of time. FTIR scan number is 32 and wavelength ranges from 400 to 4000 cm⁻¹. Table 1 shows the experimental conditions to study the kinetics of organosulfate formation via
 the esterification of sulfuric acid particles with 1-heptanol using FTIR.

To monitor the aerosol water content change during the orgnaosulfate formation reactions, the sucrose particle, glyoxal particle, glycerol particle, and the internally mixed sucrose-H₂SO₄ particle, glyoxal-H₂SO₄ particle, or glycerol-H₂SO₄ particle was collected and monitored the same way as the sulfuric acid particle. To produce internally mixed H₂SO₄ (96%, Acros organics) particles with sucrose (99%, Sigma Aldrich), glyoxal (40% *w/w* aq., Alfa Aesar), or glycerol (99%, Sigma Aldrich), the aqueous solutions of sulfuric acid (0.01 M), and sucrose (0.01 M), glyoxal (0.01 M), or glycerol (0.01 M) were mixed just before atomizing the particles. The experimental conditions and results for aerosol water content monitored using FTIR were listed in Table 2.

20 2.2 Indoor chamber experiment

All chamber experiments shown in Table 3 were conducted in a 2 m³ indoor Teflon film chamber (Czoschke and Jang, 2006) and described in Sect. S1 in the Supplement. The internally mixed sucrose-H₂SO₄ aerosol, glyoxal-H₂SO₄ aerosol, or glycerol-H₂SO₄ aerosol was generated the same way as mentioned in the Sect. 2.1 (FTIR Experi-²⁵ ment) above and introduced into the chamber. The reduction of aerosol acidity due to organosulfate formation was measured using a C-RUV (Jang et al., 2008, 2010; Li and Jang, 2012). The internally mixed multialcohol-H₂SO₄ aerosol was collected on a 13 mm diameter filter (Gelman Science Palflex, TX40H120-WW) that was dyed with an



indicator (0.02% aqueous solution of metanil yellow, Sigma Aldrich). The acidity of the resulting aerosols was analyzed by UV-Visible spectroscopy (Lambda 35 UV WinLab V5.2, PerkinElmer, Shelton) associated with an integrating sphere attachment (50 mm integrating Sphere Lambda 2–40).

5 3 Results and discussion

3.1 Kinetic study of esterification of sulfuric acid with an aliphatic alcohol

3.1.1 Product analysis using FTIR-flow chamber

The kinetics of the formation of organosulfate via esterification of sulfuric acid with an alcohol was monitored in situ for the aerosol collected on the silicone disk using FTIR equipped with a flow chamber (Fig. 1 and Table 1). 1-Heptanol, a model compound, can be easily volatilized (vapor pressure is 15 Pa at 20 °C) using the air stream at ambient temperature but its volatility is still enough to provide a significant concentration in particle phase under high gaseous concentrations. The gaseous concentration of 1-heptanol was controlled by changing the level of temperature for the water bath in which the flask stands and measured by GC-MS.

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The FTIR absorbance of organosulfate functional groups (-COS-) in particle appears at 876 cm⁻¹, but overlaps with the peak originating from bisulfate (HSO₄⁻), which appears in the range of 806–960 cm⁻¹ (Maria et al., 2003). Thus, the amount of organosulfate was monitored using the absorption of C-H stretching band at 2917 and 2848 cm⁻¹ (Fig. 2). The FTIR absorbance of the C-H stretching band gradually increases over the course of reaction and reaches to a plateau (Fig. 2a). A decay of the C-H stretching band was also observed by purging the flow chamber, where the particle sample is located, with clean air (Fig. 2b). The complete removal of the C-H stretching band suggests that organosulfate formation is controlled by an equilibrium process. The formation of organosulfate (OS) is operated by partitioning of 1-heptanol





between the gas (g) and particle (p) phases followed by the reaction in the particle phase as described below:

$$CH_3(CH_2)_6OH(g) \rightleftharpoons CH_3(CH_2)_6OH(p)$$

5
$$CH_3(CH_2)_6OH(p) + H_2SO_4 \rightleftharpoons OS + H_2O$$

To ensure that the gas-particle partitioning process is insignificant for the absorbance of the C-H stretching band in FTIR spectra, the same experiment was conducted for MgSO₄ particles as a control. No C-H stretching band has appeared in the MgSO₄ particle system even 30 min after the experiment began indicating that the C-H stretching band is mainly originating from organosulfate products in particle phase.

Stearic acid $[CH_3(CH_2)_{16}COOH]$ that has relatively low volatility (vapor pressure = 8.54×10^{-6} Pa at 25 °C) was used as a reference compound, to quantify the alkyl group in the organosulfate formed in the particle. Stearic acid was dissolved in hexane and atomized using a nebulizer. The resulting aerosol was impacted on the FTIR disk. Table 4 shows the mean of a method was dissolved in the particle state.

¹⁵ ble 1 shows the mass of organosulfate at the end of reaction after reaching to a plateau (assuming that organosulfate forms as $CH_3(CH_2)_6OSO_3H$, Minerath et al., 2008).

3.1.2 Kinetics of organosulfate formation in 1-heptanol-sulfuric acid particle

To advance the kinetics of organosulfate formation, the determination of the particle phase concentration of 1-heptanol $([CH_3(CH_2)_6OH]_p, Eq. 3)$ is necessary. $[CH_3(CH_2)_6OH]_p$ is estimated from the gas phase concentration $([CH_3(CH_2)_6OH]_g)$ and the partitioning coefficient (K_{in}) of an organic compound onto an inorganic particle medium (in) at a given experimental condition.

$$CH_3(CH_2)_6OH]_p = K_{in} \times [CH_3(CH_2)_6OH]_g \times M_{in}$$

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(3)

(4)

(5)



 $M_{\rm in}$ (µgm⁻³) is the mass concentration of inorganic aerosol, which is calculated from the sulfuric acid aerosol mass normalized by the volume of the flow chamber (1.33 × 10⁻⁵ m³).

As shown in Eq. (4), the formation of organosulfate is governed by both forward reaction rate constant (k_1) and backward reaction rate constant (k_{-1}) . The reaction rate is described as below:

$$\frac{d[OS]_{p}}{dt} = k_{1}[CH_{3}(CH_{2})_{6}OH]_{p}[H_{2}SO_{4}]_{p} - k_{-1}[OS]_{p}[H_{2}O]_{p}$$
(6)

where $[OS]_p$, $[H_2SO_4]_p$, and $[H_2O]_p$ are the concentrations of organosulfate, sulfuric acid, and water in the particle at reaction time (*t*), respectively. If Eq. (6) is combined with Eq. (5), the solution for $[OS]_p$ has the form of:

$$[OS]_{p} = \frac{k_{1}[CH_{3}(CH_{2})_{6}OH]_{g}K_{in}M_{in}[H_{2}SO_{4}]_{p}}{k_{-1}[H_{2}O]_{p}}\left(1 - e^{-k_{-1}[H_{2}O]_{p}t}\right)$$
(7)

The $[H_2SO_4]_p$ and $[H_2O]_p$ at the beginning of each reaction (no organics) is estimated using E-AIM model II (Clegg et al., 1998). K_{in} is estimated using the Pankow's absorptive partitioning equation (Pankow, 1994).

15
$$K_{\rm in} = \frac{f_{\rm in}760RT}{MW_{\rm in}\gamma p_{l,i}^0 10^6}$$

where f_{in} is the weight fraction of the absorbing inorganic phase, *R* is the gas constant, *T* is the temperature (K), MW_{in} is the mean molecular weight of the absorbing inorganic medium, γ is the activity coefficient of a compound (*i*) in the inorganic medium, $p_{l,i}^0$ is the vapor pressure of *i* at the temperature of interest. γ of 1-heptanol in sulfuric acid aerosol is estimated using the thermodynamic model (e.g., AIOMFAC) (Zuend et al., 2011) by

is estimated using the thermodynamic model (e.g., AIOMFAC) (Zuend et al., 2011) by presupposing that the activity of 1-heptanol in gas phase equals that of 1-heptanol in

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aerosol phase under the given 1-heptanol concentration in the gas phase (Table 1). k_1 , and k_{-1} in Eq. (7) were determined by fitting to experimentally measured $[OS]_p$ using six experimental data, which were obtained from two different reaction time (less than 5 min) with three different $CH_3(CH_2)_6OH(g)$ levels at given RH (20%, 40% and 5 60%, Table 1). The $[OS]_p$ measured by FTIR is plotted vs. the $[OS]_p$ semiempirically predicted using Eq. (7) at given experimental conditions (Fig. 3). A good agreement ($R^2 = 0.96$) was observed between the measurements and the predictions. The error associated with the estimation of k_1 , and k_{-1} is ±40% due to the uncertainties in the K_{in} estimation and experimental measurements.

¹⁰ Both k_1 and k_{-1} increase as RH increases: from $3.10 \times 10^{-3} \text{ Lmol}^{-1} \text{ min}^{-1}$ at RH = 20% to $5.25 \times 10^{-3} \text{ Lmol}^{-1} \text{ min}^{-1}$ at RH = 60% for k_1 and from $5.53 \times 10^{-3} \text{ Lmol}^{-1} \text{ min}^{-1}$ at RH = 20% to $8.26 \times 10^{-3} \text{ Lmol}^{-1} \text{ min}^{-1}$ at RH = 60% for k_{-1} . The increased water content at the higher RH will decrease the viscosity of the particle medium (Maples, 2000). Olea and Thomas (1988) suggested that the dif-¹⁵ fusion coefficient of a solute in liquid media is inversely related to the square root of the solvent viscosity. The RH dependency of k_1 and k_{-1} suggests that the organosulfate formation is a diffusion-controlled reaction.

 $CH_3(CH_2)_6OSO_2O(CH_2)_6CH_3$ may form through further equilibrium reactions of $CH_3(CH_2)_6OSO_3H$ with gaseous 1-heptanol as $CH_3(CH_2)_6OSO_3H$ produces. It is expected that $CH_3(CH_2)_6OSO_3H$ produces is hydrophabile due to the long alignatic

²⁰ pected that CH₃(CH₂)₆OSO₂O(CH₂)₆CH₃ is hydrophobile due to the long aliphatic carbon chain. For example, diethyl sulfate (CH₃CH₂OSO₂OCH₂CH₃), a simple dialkylsulfate, not only has poor solubility in water: 0.7 g per 100 g of water at 20 °C, but also shows no significant water absorption in the FTIR spectrum (Fig. S1). If formed, CH₃(CH₂)₆OSO₂O(CH₂)₆CH₃ will have much lower solubility in water than diethyl sulfate and may build up a separated organic layer. The backward reaction of CH₃(CH₂)₆OSO₂O(CH₂)₆CH₃ (Eq. 2) can be unfavorable due to the low water content in the organic layer. The rapid reduction of the intensity of the C-H stretching band (Fig. 2b), however, suggests that there is little or no dialkylsulfate in the aerosol. The major product formed via the reaction between 1-heptanol and sulfu-





ric acid should be $CH_3(CH_2)_6OSO_3H$ (Eq. 4), which is reversible. The predicted boiling point of $CH_3(CH_2)_6OSO_3H$ is 306 °C, which is estimated using group contribution (e.g., -SO₃H: 131 °C from the comparison between ethanol and ethyl bisulfate). Thus, $CH_3(CH_2)_6OSO_3H$ is a semivolatile organic compound with low volatility and mostly stays in the particle during the experiment.

3.1.3 Aerosol bulk phase vs. solution chemistry: aliphatic alcohol-sulfuric acid

 k_1 and k_{-1} reported by Minerath et al. (2008) using NMR for esterification of sulfuric acid with an alcohol in solution chemistry were 5.7×10^{-6} and 3.2×10^{-5} L mol⁻¹ min⁻¹, respectively (equivalent RH = 10%). In this study, the observed k_1 and k_{-1} values from

¹⁰ 1-heptanol-sulfuric acid particle are 3.10×10^{-3} and $5.53 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$ (RH = 20%), respectively (Table 1) and are three orders of magnitude higher than those reported in solution chemistry. The fast reaction rate observed in 1-heptanol-sulfuric acid particle supports our hypothesis, fast esterification in the aerosol bulk phase.

3.2 Formation of dialkylsulfates in multialcohol-sulfuric acid aerosol

15 3.2.1 Measurements of dialkylsulfates using C-RUV

To produce esters from the reaction of sulfuric acid with multialcohols, sucrose, glyoxal (glyoxal forms a gem-diol via hydration in aqueous solution), and glycerol are chosen. The organosulfate formed in the internally mixed multialcohol-H₂SO₄ aerosols is measured by the change of acidity via esterification of H₂SO₄ using the C-RUV technique (Jang et al., 2008, 2010; Li and Jang, 2012). C-RUV measures the proton concentration ([H⁺], mol L⁻¹) of the aerosol directly collected on the filter without modifying aerosol compositions due to solvent extraction. C-RUV can also measure organosulfate formation over the course of the reaction because it requires short measurement time with the low detection limit using the optical technique.





The first dissociation ($pK_{a1} = -3.0$, from H_2SO_4 to bisulfate) of sulfuric acid is generally not affected by the presence of organic compounds. The second dissociation ($pK_{a2} = 2.0$, from bisulfate into sulfate, negligible compared to the first dissociation) is slightly affected by the coexisting organic compounds in the aerosol. For example, the dissociation of bisulfate into sulfate in a mixture of malonic acid and H_2SO_4 aerosol (1 : 1.6 in mole) is reduced by 5.4 % at RH = 50 % (Clegg and Seinfeld, 2006). Thus, the impact of multialcohols on the acidity of sulfuric acid should be little since the acidity of sulfuric acid aerosol is mainly determined by the first dissociation.

The pK_a of methyl bisulfate (CH₃OSO₃H), an alkyl bisulfate, is -3.5 (King, 2006), suggesting that alkyl bisulfates are even stronger than sulfuric acid ($pK_{a1} = -3.0$) and more likely exist as dissociated forms. Therefore, the formation of an alkyl bisulfate will not reduce acidity of the multialcohol-H₂SO₄ aerosol. The change of acidity accompanies with the formation of dialkylsulfates, neutral organosulfates. The yield of dialkylsulfates (Y_{diOS}) in the aerosol can be described as below:

¹⁵
$$Y_{diOS} = \frac{[H^+]_0 - [H^+]_t}{[H^+]_0}$$

 $[H^+]_0$ is the initial proton concentration (mol L⁻¹) of the aerosol and $[H^+]_t$ is the measured proton concentration (mol L⁻¹) in aerosol at reaction time (*t*) using the C-RUV technique. The $[H^+]_0$ of the internally mixed aerosol is estimated as:

$$[\mathsf{H}^+]_0 = \frac{n_0(\mathsf{H}^+)}{V_{\rm conc} V_{\rm chamber}} \tag{10}$$

²⁰ where $n_0(H^+)$ is the number of moles of proton introduced into the chamber (from dissociation of H₂SO₄, E-AIM output, Clegg et al., 1998), V_{conc} is the volume concentration (L m⁻³) of the aerosol (monitored using a scanning mobility particle sizer, SMPS), and $V_{chamber}$ is the volume of the indoor chamber (2 m³).



(9)

Figure 4 illustrates the time profile of aerosol acidity ($[H^+]$, mol L⁻¹) measured using the C-RUV technique over the course of the reaction of H₂SO₄ with three different organic reactants (sucrose, glyoxal, and glycerol). The resulting Y_{diOS} at the end of each experiment was estimated using Eq. (9) and reported in Table 3. In all the multialcohol-H₂SO₄ aerosols, organosulfate formation rapidly progresses and completes within 60 min. The dialkylsulfate fractions of the total sulfates are significantly high at given experimental conditions. For example, Y_{diOS} in glyoxal-H₂SO₄ aerosol ranges from 72 ± 7.2 to 79 ± 7.9 % under different RH levels. Y_{diOS} in glyceol-H₂SO₄ aerosol ranges from 80 ± 8.0 to 88 ± 8.8 %. For the sucrose-H₂SO₄ aerosols, Y_{diOS} is less than those in in glyoxal-H₂SO₄ aerosols or in glycerol-H₂SO₄ aerosols. Neighboring OH groups in both glycerol and glyoxal hydrate are capable of creating thermodynamically stable 5-membered cyclic dialkylsulfates (Fig. S1). However, most sucrose's OH groups are *trans* in geometric structures and less favorable to form a 5-membered diakylsulfate are variable of creating thermodynamically stable 5-membered cyclic dialkylsulfates in LOP.

fate, resulting in low Y_{diOS} values in sucrose-H₂SO₄ aerosols (Fig. 5).

3.2.2 Kinetics of dialkylsulfate formation

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Similar to Eq. (4), the cyclic dialkylsulfate (cy-diOS) formation in glyoxal- H_2SO_4 aerosol and glycerol- H_2SO_4 aerosol can be expressed as shown in Fig. 6. The consumption of sulfuric acid is governed by both forward reaction rate constant (k_2) and backward reaction rate constant (k_{-2}). The consumption rate of sulfuric acid is described as below:

$$\frac{d[H_2SO_4]}{dt} = -k_2[MOH]_t[H_2SO_4]_t + k_{-2}[cy-diOS][H_2O]$$
(11)

where $[MOH]_t$, $[H_2SO_4]_t$, and [cy-diOS] are the concentrations of multialcohol, sulfuric acid, and cy-diOS in aerosol at reaction time *t*, respectively.



Similar to 1-heptanol, MOH is distributed between the gas phase and the aerosol phase depending on the volatility. The [MOH]_t is estimated using K_{in} , M_{in} , the total mass concentration of MOH ($M_{MOH,t}$) at reaction time t in the chamber, and V_{conc} .

$$[MOH]_{t} = \frac{K_{in}M_{in}}{(1 + K_{in}M_{in})V_{conc}MW_{MOH}}M_{MOH,t}$$
(12)

The K_{in} of glycerol partitioning onto sulfuric acid aerosol is estimated using Eq. (8). 5 The activity coefficient of glycerol in sulfuric acid aerosol is estimated using AIOMFAC (Zuend et al., 2011) under experimental conditions. The K_{in} of glyoxal onto wet aerosol was reported to be $1.43 \times 10^{-3} \,\mu\text{g}^{-1}\text{m}^3$ (Ip, 2010). Term $\frac{K_{\text{in}}M_{\text{in}}}{1+K_{\text{in}}M_{\text{in}}}$ is defined as α (α is unit for sucrose due to its low volatility), then, the analytical solution of [H₂SO₄]_t can be derived as: Eq. (13) 10

$$[H_2SO_4]_t = -\frac{M_{MOH,0}}{2V_{conc}MW_{MOH}} + \frac{[H_2SO_4]_0}{2} - \frac{k_{-2}[H_2O]}{2k_2\alpha} + \frac{\beta(1+\epsilon)}{2k_2\alpha(\epsilon-1)}$$
(13)

The derivation of the analytical solution of Eq. (11) is described in Sect. S4 in the Supplement. For deriving Eq. (13), the wall loss of MOH was not counted. $M_{MOH,0}$ is the initial total mass concentration of MOH in the chamber, MW_{MOH} is the molecular weight of MOH, and $[H_2SO_4]_0$ is the initial concentration of sulfuric acid in aerosol. $[H_2SO_4]_0$ and $[H_2O]$ in particle at the beginning of each reaction (no organics) are estimated using E-AIM model II (Clegg et al., 1998). Both $\beta(k_2, k_{-2})$ and $\epsilon(k_2, k_{-2})$ in Eq. (13) are constants but changed by k_2 , and k_2 (Sect. S4 in the Supplement). k_2 , and k_2 were determined by fitting the predicted $[H_2SO_4]_t$ (Eq. 13) to experimentally measured $[H_2SO_4]_t$ (C-RUV data) using the initial data point for each set of experiment (Table 3). 20

 k_2 of glycerol-H₂SO₄ at RH = 54.2% is 2.26×10^{-2} L mol⁻¹ min⁻¹. For glycerol, the error associated with the estimation of k_2 and k_{-2} is $\pm 30\%$ due to the uncertainties in the K_{in} estimation and experimental measurements. k_2 of glyoxal-H₂SO₄ aerosol at

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RH = 41.8% is $3.62 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}$. Although glyoxal itself is very volatile, the apparent Henry's law constant of glyoxal appeared to be high as $4.19 \times 10^5 \text{ M atm}^{-1}$ (Ip et al., 2009) due to its oligomerization in aerosol. The hydrated forms of glyoxal and their oligomers will react with sulfuric acid. As esterification progresses, the oligomeric glyoxal will produce monomeric glyoxal hydrate that can increase the consumption of sulfuric acid. k_2 of sucrose-H₂SO₄ aerosol (1 : 4 in mole) at RH = 25.8% is $8.9 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$. k_{-2} of all the multialcohol-H₂SO₄ aerosols are nearly zero, indicating the hydrolysis (backward reaction) of cy-diOS is not favorable in aerosol. As shown in Table 3, k_2 values increase with high RH for all the three alcohols. The similar result has been observed in FTIR studies (Sect. 3.1, Kinetic study of esterification of sulfuric acid with an aliphatic alcohol) for 1-heptanol-H₂SO₄ aerosol.

3.3 Aerosol bulk phase vs. solution chemistry: multialcohol-sulfuric acid

A large discrepancy appeared in rate constants of organosulfate formation between this study that characterizes the aerosol bulk phase and the previous study observed for solution chemistry. In solution chemistry using ¹H-NMR, Minerath et al. (2008) have recently reported that the yields of organosulfate from ethylene glycol were 2.8 % in 65 wt % D₂SO₄-D₂O solution (D₂SO₄ excess condition at ethylene glycol: D₂SO₄ = 1:82 with equivalent RH = 10 % at 298 K) and 17.5 % in 75 wt % D₂SO₄-D₂O solution (ethylene glycol: D₂SO₄ = 1:95 with equivalent RH = 2 % at 298 K). In their solution chemistry at pH = 1.5, the lifetime of alcohol for sulfate esterification was 4600 days, making these reactions negligible in aerosols. Nevertheless, with the less amount of sulfuric acid of our study, the yields of organosulfate from glycerol-H₂SO₄ aerosol are very high ranging from 91 to 99 % under RH = 32–60 %. In addition to large organosulfate yields, the reaction rapidly progressed and reached to completion within 60 min.

²⁵ High yields and the rapid formation of organosulfate in aerosol bulk phase comprising of sulfuric acid and a mulfialcohol (glycerol, glyoxal, or sucrose) also support our hypothesis, fast esterification in the aerosol bulk phase.



3.4 Impact of organosulfate on aerosol hygroscopic property

3.4.1 Aerosol water content

Water is one of the major components for hygroscopic inorganic aerosol. Water is also a reactant for various hydrolysis reactions: e.g., the backward reactions in Eqs. (1), (2), and (4), and Fig. 6. To better understand production of organosulfate in aerosol, the water mass (M_{H_2O} , µg) in the multialcohol- H_2SO_4 particles was monitored over the course of the reaction using an FTIR spectrometer. The FTIR peak at 1652 cm⁻¹ is exclusive for the bending motion of a water molecule and was used to monitor the water content in the aerosol impacted on a silicon disk (Jang et al., 2010; Laporta et al., 1999). To calibrate the FTIR method, NaCl particle was used as reference. M_{H_2O} in

- ¹⁰ 1999). To calibrate the FTIR method, NaCl particle was used as reference. M_{H_2O} in NaCl particle was theoretically estimated using E-AIM (Clegg et al., 1998). The correlation between the theoretical M_{H_2O} of the NaCl particles and the measured FTIR intensity at 1652 cm⁻¹ (A₁₆₅₂) permits the calculation of the water content in particle samples.
- ¹⁵ $M_{\rm H_2O} = \zeta \times A_{1652}$

20

where ζ is the correlation coefficient ($\zeta = 1.7 \times 10^3 \,\mu$ g). In this way, FTIR spectra of H₂SO₄ particle, glyoxal particle, glycerol particle, and sucrose particle were monitored at a given RH to estimate $M_{\rm H_2O}$ of these particles. The resulting data are shown in Table 2. All three multialcohol-H₂SO₄ particle systems showed a considerable reduction of $M_{\rm H_2O}$ by organosulfate formation (Fig. S3). For example, the water loss fraction of the total $M_{\rm H_2O}$ was 67.9 % for sucrose-H₂SO₄ aerosol, 59.1 % for glyoxal-H₂SO₄ aerosol, and 73.4 % for glycerol-H₂SO₄ aerosol at RH = 50 % (Table 2).

3.4.2 Evaporation of water from alcohol-sulfuric acid aerosol

Although solution chemistry can mimic the bulk phase reaction with a large amount of reactants to meet the need for the detection limits of analytical instruments such as



(14)



NMR, solution chemistry is restricted to describe aerosol-bulk phase reactions combining with water evaporation. The diffusion characteristic time (τ) of a molecule in media can be described as:

$$\tau = \frac{dp^2}{4\pi^2 D_l}$$

⁵ where D_l is the diffusion coefficient of solute (e.g., water) in a solvent (e.g., glycerol), dp is the particle diameter. For example, the diffusion coefficient of water in glycerol is 8.3×10^{-8} cm² s⁻¹ (Lees and Sarram, 1971). When the particle diameter is 0.1 µm, the estimated diffusion characteristic time of a water molecule in glycerol is 3.1×10^{-5} s, while that is 85 h for a water molecule diffuses over 1 cm distance in the NMR tube (the length of a NMR tube is 5 cm). M_{H_2O} considerably decreases via organosulfate formation in aerosol bulk phase (Table 2), while the major inorganic composition comprising of water and sulfuric acid remains almost constant in solution chemistry.

As water evaporates efficiently from aerosol, the equilibriums shown in Eqs. (1), (2), and (4), and Fig. 6 shift to the right side (forward), producing more organosulfate prod-

- ucts (Fig. 5). At the same time, poor solubility of hydrophobic organosulfate products in water can significantly reduce backward reactions (Laporta et al., 1999). Both the organosulfate formation in aerosol and water evaporation from the aerosol increase the aerosol's average molecular weight, which affects both viscosity and solidity with time. In the study of aerosol solidity using an electrical low pressure impactor and an electron microscopy, Virtanen (2010) have reported an analogous observation showing that SOA particles under ambient conditions are most likely in the glassy state, which
 - may influence the particles' ability to accommodate water.

The rapid reduction of aerosol water content (M_{H_2O}) in multialcohol- H_2SO_4 aerosol accords with the observation in Sects. 3.1 (Kinetic study of esterification of sulfuric acid ²⁵ with an aliphatic alcohol) and 3.2 (Formation of dialkylsulfates in multialcohol-sulfuric acid aerosol), supporting our hypothesis that orgnaosulfate formation is more efficient in the aerosol phase. The similar result has been reported in the study by Nguyen et al.



(15)



(2012). They observed that the formation of light absorbing products in the mixture of sulfuric acid and SOA aqueous extracts that were subject to evaporation is faster by at least three orders of magnitude than the same reaction in aqueous solution.

4 Conclusion and atmospheric implication

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In this study, kinetics of alkyl bisulfate formation through the esterification of 1-heptanol with sulfuric acid particles were investigated using FTIR equipped with a flow chamber, and dialkylsulfates formation in the internally mixed aerosol comprising sulfuric acid and a multialcohol (glyoxal, glycerol or sucrose) was studied using the C-RUV method. In both works, the reaction of H₂SO₄ with an alcohol or a hydrated aldehyde efficiently produces an ester in submicron sulfuric acid aerosol. The formation of hydrophobic organosulfate products and the evaporation of water from the aerosol promote the fast reaction and high yields of organosulfates. The reaction rate of organosulfate formation increases with increasing RH, which influences on the amount of water in aerosol. The increased aerosol water content at higher RH will reduce aerosol viscosity and in

In both urban and rural areas, both organic carbon and sulfate are major constituents of fine particulate matter (Zhang et al., 2007). Among SOA products, alcohols and hydrated-aldehydes are commonly identified. For example, the significant fraction in isoprene SOA is multialcohols (e.g., 2-methyltetrol) (Claeys et al., 2004; Surratt et al., 2007b; Gilardoni et al., 2009; Carlton et al., 2009). In particular, methyltetrol derived

- organosulfates have been identified in filed studies (Surratt et al., 2007a). Epoxytdiols is suggested as an important precursor for the organosulfates from methyltetrols while the direct reactions of sulfuric acid with methyltetrols, multialcohols or aldehydes have been overlooked due to the low reaction rate constants posted in solution chemistry.
- ²⁵ However, our study suggests that the formation of organosulfates will not be limited to epoxydiols but can be produced from the reactions of sulfuric acid with various alcohols and aldehydes in aerosol. According to the k_1 and k_{-1} values from the 1-heptanol-





 H_2SO_4 particle and the gas-particle partitioning (K_{in}) of an alcohol, the alkyl bisulfate possibly forms from the alcohol that has the carbon number equals or greater than six. All multialcohols may contribute to the formation of organosulfate due to their solubility in aqueous phase and their high reactivity (Table 3).

- ⁵ The organosulfate formation is synergistically related to the reduction of aerosol hygroscopicity as shown in Sect. 3.3. In addition to the formation of hydrophobic organosulfate, the reduction of hygroscopic sulfuric acid can considerably reduce aerosol hygroscopicity. The reduction of water in aerosol phase prohibits hydrolysis of organosulfate. Furthermore, based on our study, reexamination of SOA yields in
- the presence of sulfuric acid seeded aerosol calls for. The SMPS data, which is typically used for the estimation of aerosol volume concentrations, can underestimate SOA yields. The organic mass that equals to the volume of the water evaporated from the aerosol cannot be counted in SMPS data. In consequence, the effect of aerosol acidity on SOA formation can also be underestimated.
- ¹⁵ Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/13/23217/2013/ acpd-13-23217-2013-supplement.pdf.

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Discussion Paper

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reaction of sulfunc acid particle with r-neptation using a now reactor integrated with FTIR.										
Set	Particle	$M_{\rm p}^{\rm a}$	[1-heptanol]g ^b	RH	[H ₂ SO ₄] _p ^c	[H ₂ O] _p ^d	γ ^e	$M_{\rm OS}{}^{\rm f}$	$k_1 \times 10^{-3}$	$k_{-1} \times 10^{-3}$
		μg	mol m ⁻³	%	mol L ⁻ '	mol L ⁻ '	×10 ⁻³	μg	L mol ⁻ ' min ⁻ '	Lmol ⁻ 'min ⁻ '
1	H_2SO_4	65	0.35	20	8.6	11.4	53.9	43	3.10	5.53
2	H ₂ SO ₄	72	0.72	20	8.6	11.4	7.22	66	3.10	5.53
3	H₂SO₄	54	1.21	20	8.6	11.4	1.52	82	3.10	5.53
4	H ₂ SO ₄	53	0.35	40	6.7	39.7	53.9	20	4.37	6.75
5	H₂SO₄	56	0.72	40	6.7	39.7	7.22	38	4.37	6.75
6	H₂SO₄	50	0.35	60	5.0	44.0	53.9	15	5.25	8.26
7	H ₂ SO ₄	51	0.72	60	5.0	44.0	7.22	27	5.25	8.26
8	Mg ₂ SO ₄	75	0.35	50	n.a.	48.9 ^g	3.36	0	n.a. ^h	n.a.

Table 1. Experimental conditions for studies of kinetics of the formation of organosulfate via the reaction of sulfuric acid particle with 1-heptanol using a flow reactor integrated with FTIR.

^a The mass of particle (M_p) was obtained by weighing the silicon disk mass before and after sampling. The error associated with the particle mass is ±1 µg.

^b Concentrations of 1-heptanol in the gas phase ([1-heptanol]_g) was measured using GC-MS. The error associated with 1-heptanol concentration is 15 %.

^c Concentration of sulfuric acid ([H₂SO₄]_p) in the particle was estimated using E-AIM model II (Clegg et al., 1998).

^d Concentration of water ([H₂O]_n) in the sulfuric acid particle was estimated using E-AIM model II (Clegg et al., 1998).

^e Activity coefficient of 1-heptanol in sulfuric acid aerosol was estimated using AIOMFAC (Zuend et al., 2011).

^f The mass (M_{OS}) of organosulfate when the reaction of 1-heptanol and sulfuric acid reach equilibrium.

^g Concentration of water in the magnesium sulfate particle was estimated using data reported by Zhao et al. (2006). ^h not applicable.





Particle composition	M _{Total} ^a μg	RH %	M _{H₂O} b μg	M _{OC} ^c μg	M _{H₂SO4} ^d μg	δf _{H20} e %
Sulfuric acid	117	53	71.0	0	46.0	n.a. ^f
Sucrose	85	50	13.8	71.2	0	n.a.
Glyoxal	65	50	10.0	55.0	0	n.a.
Glycerol	81	50	13.2	67.8	0	n.a.
Sucrose-H ₂ SO ₄	123	50	27.9	44.3	50.8	67.9
Glyoxal-H ₂ SO ₄	88	50	28.5	16.2	43.3	59.1
Glycerol-H ₂ SO ₄	169	50	37.2	46.9	84.9	73.4

Table 2. Experimental conditions to study aerosol water content using FTIR.

^a The total mass (M_{Total}) of particle was obtained by weighing the silicon disk mass before and after sampling. The error associated with the particle mass is ±1 µg.

^b Mass of water ($M_{\rm H_2O}$) in the aerosol was estimated using Eq. (14). The error associated with aerosol water content is 10 %.

^c Mass of organic compounds (M_{OC}) before reaction.

^d Mass of sulfuric acid $(M_{H_2SO_4})$ before reaction.

^e The water loss fraction (δf_{H_2O}) of the total aerosol water before reaction.

^f not applicable.



Table 3. Experimental conditions for monitoring aerosol acidity and the dialkylsulfates yield of H_2SO_4 in sucrose- H_2SO_4 aerosol, glyoxal- H_2SO_4 aerosol, and glycerol- H_2SO_4 aerosols using the C-RUV technique.

Aerosol composition	RH %	$V_{\rm conc}^{a}$	$[H^+]_0^{b}$	Y _{diOS} ^c ⁰∕	$k_2 \times 10^{-2}$	k_{-2}
by mole	70	CIII III	THOLE	/0		
Sucrose-H ₂ SO ₄ (1:2)	26.1	1.51×10^{-4}	5.26	86 ±8.6	0.96	~0
Sucrose-H ₂ SO ₄ (1:4)	25.8	1.58 ×10 ⁻⁴	6.72	79 ±7.9	0.89	~0
Sucrose-H ₂ SO ₄ (1:6)	25.4	1.53 ×10 ⁻⁴	7.41	74 ±7.4	0.96	~0
Sucrose-H ₂ SO ₄ (1:9)	24.8	1.56 ×10 ⁻⁴	7.95	56 ± 5.6	0.82	~0
Glyoxal-H ₂ SO ₄	70.0	1.60 ×10 ⁻⁴	4.47	72 ±7.2	6.03	~0
Glyoxal-H ₂ SO ₄	41.8	1.53 ×10 ⁻⁴	6.08	77 ±7.7	3.62	~0
Glyoxal-H ₂ SO ₄	22.5	1.51 ×10 ⁻⁴	7.20	79 ±7.9	2.58	~0
Glycerol-H ₂ SO ₄	60.3	1.52 ×10 ⁻⁴	4.38	80 ±8.0	5.30	~0
Glycerol-H ₂ SO ₄	54.2	1.81 ×10 ⁻⁴	4.68	84 ±8.4	2.26	~0
Glycerol-H ₂ SO ₄	32.1	1.66 ×10 ⁻⁴	7.04	88 ±8.8	1.12	~0

^a The volume concentration of aerosol (V_{conc}) was monitored using SMPS.

^b The initial [H⁺] of the internally mixed aerosol before reactions is predicted using Eq. (10).

^c The Y_{diOS} is the dialkylsulfates yield of sulfuric acid in the aerosol calculated using the aerosol acidity at the end of the reaction (Fig. 4).





Fig. 1. The experimental set up for the FTIR studies using a flow chamber.











Fig. 3. The organosulfate concentrations ([OS]) formed via the esterification of 1-heptanol and sulfuric acid particle measured by FTIR vs. the [OS] semiempirically predicted using Eq. (7) at given experimental conditions.









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