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

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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 H_2SO_4 aerosol internally mixed with multialcohols was studied by measuring the proton 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 ($M_{\text{H}_2\text{O}}$) in the multialcohol- H_2SO_4 particle was monitored using the FTIR spectrometer. A large reduction of $M_{\text{H}_2\text{O}}$ 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.

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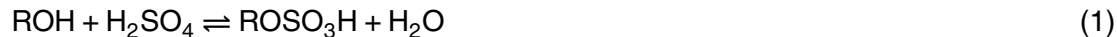
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1 Introduction

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).



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; Iinuma 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, Iinuma et al. (2009)

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identified organosulfates from the reactive uptake of monoterpene oxides on acidic sulfate particles. Surratt et al. (2010) showed organosulfates formation through the acid-catalyzed reactive uptake of isoprene epoxydiols (IEPOX). Lal et al. (2012) detected organosulfate produced from the reaction of α -pinene oxide with sulfuric acid solution 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 Liggió et al. (2005). Nozière et al. (2010) also suggested that radical reactions would be a plausible origin for the atmospheric organosulfates.

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 forward reaction rate constant for esterification of alcohols in high concentration of sulfuric acid solution (65 wt %) is slow (e.g., $5.7 \times 10^{-6} \text{ L mol}^{-1} \text{ min}^{-1}$ 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 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).

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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 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 organosulfate 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-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

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



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 MgSO_4 particles as a control. No C-H stretching band has appeared in the MgSO_4 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.

10 Stearic acid [$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$] 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 1 shows the mass of organosulfate at the end of reaction after reaching to a plateau (assuming that organosulfate forms as $\text{CH}_3(\text{CH}_2)_6\text{OSO}_3\text{H}$, 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 ($[\text{CH}_3(\text{CH}_2)_6\text{OH}]_p$, Eq. 3) is necessary. $[\text{CH}_3(\text{CH}_2)_6\text{OH}]_p$ is estimated from the gas phase concentration ($[\text{CH}_3(\text{CH}_2)_6\text{OH}]_g$) and the partitioning coefficient (K_{in}) of an organic compound onto an inorganic particle medium (in) at a given experimental condition.

20
$$[\text{CH}_3(\text{CH}_2)_6\text{OH}]_p = K_{in} \times [\text{CH}_3(\text{CH}_2)_6\text{OH}]_g \times M_{in} \quad (5)$$

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M_{in} ($\mu\text{g m}^{-3}$) is the mass concentration of inorganic aerosol, which is calculated from the sulfuric acid aerosol mass normalized by the volume of the flow chamber ($1.33 \times 10^{-5} \text{ m}^3$).

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:

$$\frac{d[\text{OS}]_p}{dt} = k_1[\text{CH}_3(\text{CH}_2)_6\text{OH}]_p[\text{H}_2\text{SO}_4]_p - k_{-1}[\text{OS}]_p[\text{H}_2\text{O}]_p \quad (6)$$

where $[\text{OS}]_p$, $[\text{H}_2\text{SO}_4]_p$, and $[\text{H}_2\text{O}]_p$ 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 $[\text{OS}]_p$ has the form of:

$$[\text{OS}]_p = \frac{k_1[\text{CH}_3(\text{CH}_2)_6\text{OH}]_g K_{in} M_{in} [\text{H}_2\text{SO}_4]_p}{k_{-1}[\text{H}_2\text{O}]_p} \left(1 - e^{-k_{-1}[\text{H}_2\text{O}]_p t}\right) \quad (7)$$

The $[\text{H}_2\text{SO}_4]_p$ and $[\text{H}_2\text{O}]_p$ 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).

$$K_{in} = \frac{f_{in} 760 RT}{MW_{in} \gamma \rho_{l,i}^0 10^6} \quad (8)$$

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, $\rho_{l,i}^0$ 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 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 $[\text{OS}]_p$ using six experimental data, which were obtained from two different reaction time (less than 5 min) with three different $\text{CH}_3(\text{CH}_2)_6\text{OH}(\text{g})$ levels at given RH (20%, 40% and 60%, Table 1). The $[\text{OS}]_p$ measured by FTIR is plotted vs. the $[\text{OS}]_p$ 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 $\pm 40\%$ due to the uncertainties in the K_{in} estimation and experimental measurements.

Both k_1 and k_{-1} increase as RH increases: from $3.10 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$ at RH = 20% to $5.25 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$ at RH = 60% for k_1 and from $5.53 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$ at RH = 20% to $8.26 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$ 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 diffusion 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.

$\text{CH}_3(\text{CH}_2)_6\text{OSO}_2\text{O}(\text{CH}_2)_6\text{CH}_3$ may form through further equilibrium reactions of $\text{CH}_3(\text{CH}_2)_6\text{OSO}_3\text{H}$ with gaseous 1-heptanol as $\text{CH}_3(\text{CH}_2)_6\text{OSO}_3\text{H}$ produces. It is expected that $\text{CH}_3(\text{CH}_2)_6\text{OSO}_2\text{O}(\text{CH}_2)_6\text{CH}_3$ is hydrophobic due to the long aliphatic carbon chain. For example, diethyl sulfate ($\text{CH}_3\text{CH}_2\text{OSO}_2\text{OCH}_2\text{CH}_3$), 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, $\text{CH}_3(\text{CH}_2)_6\text{OSO}_2\text{O}(\text{CH}_2)_6\text{CH}_3$ will have much lower solubility in water than diethyl sulfate and may build up a separated organic layer. The backward reaction of $\text{CH}_3(\text{CH}_2)_6\text{OSO}_2\text{O}(\text{CH}_2)_6\text{CH}_3$ (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-

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ric acid should be $\text{CH}_3(\text{CH}_2)_6\text{OSO}_3\text{H}$ (Eq. 4), which is reversible. The predicted boiling point of $\text{CH}_3(\text{CH}_2)_6\text{OSO}_3\text{H}$ is 306°C , which is estimated using group contribution (e.g., $-\text{SO}_3\text{H}$: 131°C from the comparison between ethanol and ethyl bisulfate). Thus, $\text{CH}_3(\text{CH}_2)_6\text{OSO}_3\text{H}$ 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 $3.2 \times 10^{-5} \text{ L mol}^{-1} \text{ min}^{-1}$, respectively (equivalent $\text{RH} = 10\%$). In this study, the observed k_1 and k_{-1} values from 1-heptanol-sulfuric acid particle are 3.10×10^{-3} and $5.53 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$ ($\text{RH} = 20\%$), 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

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- H_2SO_4 aerosols is measured by the change of acidity via esterification of H_2SO_4 using the C-RUV technique (Jang et al., 2008, 2010; Li and Jang, 2012). C-RUV measures the proton concentration ($[\text{H}^+]$, 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.

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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 (CH_3OSO_3H), 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- H_2SO_4 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:

$$Y_{diOS} = \frac{[H^+]_0 - [H^+]_t}{[H^+]_0} \quad (9)$$

$[H^+]_0$ 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:

$$[H^+]_0 = \frac{n_0(H^+)}{V_{\text{conc}} V_{\text{chamber}}} \quad (10)$$

where $n_0(H^+)$ is the number of moles of proton introduced into the chamber (from dissociation of H_2SO_4 , 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 m^3).

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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 H_2SO_4 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- H_2SO_4 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- H_2SO_4 aerosol ranges from 72 ± 7.2 to 79 ± 7.9 % under different RH levels. Y_{diOS} in glyceol- H_2SO_4 aerosol ranges from 80 ± 8.0 to 88 ± 8.8 %. For the sucrose- H_2SO_4 aerosols, Y_{diOS} slightly increases as the sucrose fraction increases (Table 3) but Y_{diOS} is less than those in in glyoxal- H_2SO_4 aerosols or in glycerol- H_2SO_4 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, resulting in low Y_{diOS} values in sucrose- H_2SO_4 aerosols (Fig. 5).

3.2.2 Kinetics of dialkylsulfate formation

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:

$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = -k_2[\text{MOH}]_t[\text{H}_2\text{SO}_4]_t + k_{-2}[\text{cy-diOS}][\text{H}_2\text{O}] \quad (11)$$

where $[\text{MOH}]_t$, $[\text{H}_2\text{SO}_4]_t$, and $[\text{cy-diOS}]$ 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 $[\text{MOH}]_t$ is estimated using K_{in} , M_{in} , the total mass concentration of MOH ($M_{\text{MOH},t}$) at reaction time t in the chamber, and V_{conc} .

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

The K_{in} of glycerol partitioning onto sulfuric acid aerosol is estimated using Eq. (8). 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 $[\text{H}_2\text{SO}_4]_t$ can be derived as: Eq. (13)

$$[\text{H}_2\text{SO}_4]_t = -\frac{M_{\text{MOH},0}}{2V_{\text{conc}} \text{MW}_{\text{MOH}}} + \frac{[\text{H}_2\text{SO}_4]_0}{2} - \frac{k_{-2}[\text{H}_2\text{O}]}{2k_2\alpha} + \frac{\beta(1 + \epsilon)}{2k_2\alpha(\epsilon - 1)} \quad (13)$$

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. $M_{\text{MOH},0}$ is the initial total mass concentration of MOH in the chamber, MW_{MOH} is the molecular weight of MOH, and $[\text{H}_2\text{SO}_4]_0$ is the initial concentration of sulfuric acid in aerosol. $[\text{H}_2\text{SO}_4]_0$ and $[\text{H}_2\text{O}]$ 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 $[\text{H}_2\text{SO}_4]_t$ (Eq. 13) to experimentally measured $[\text{H}_2\text{SO}_4]_t$ (C-RUV data) using the initial data point for each set of experiment (Table 3).

k_2 of glycerol- H_2SO_4 at RH = 54.2% is $2.26 \times 10^{-2} \text{L mol}^{-1} \text{min}^{-1}$. 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- H_2SO_4 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 $4.19 \times 10^5 \text{ Matm}^{-1}$ (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- H_2SO_4 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- H_2SO_4 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- H_2SO_4 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 $^1\text{H-NMR}$, Minerath et al. (2008) have recently reported that the yields of organosulfate from ethylene glycol were 2.8% in 65 wt% D_2SO_4 - D_2O solution (D_2SO_4 excess condition at ethylene glycol : D_2SO_4 = 1 : 82 with equivalent RH = 10% at 298 K) and 17.5% in 75 wt% D_2SO_4 - D_2O solution (ethylene glycol : D_2SO_4 = 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- H_2SO_4 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. High yields and the rapid formation of organosulfate in aerosol bulk phase comprising of sulfuric acid and a multialcohol (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 ($M_{\text{H}_2\text{O}}$, 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. $M_{\text{H}_2\text{O}}$ in NaCl particle was theoretically estimated using E-AIM (Clegg et al., 1998). The correlation between the theoretical $M_{\text{H}_2\text{O}}$ of the NaCl particles and the measured FTIR intensity at 1652 cm^{-1} (A_{1652}) permits the calculation of the water content in particle samples.

$$M_{\text{H}_2\text{O}} = \zeta \times A_{1652} \quad (14)$$

where ζ is the correlation coefficient ($\zeta = 1.7 \times 10^3 \mu\text{g}$). In this way, FTIR spectra of H_2SO_4 particle, glyoxal particle, glycerol particle, and sucrose particle were monitored at a given RH to estimate $M_{\text{H}_2\text{O}}$ of these particles. The resulting data are shown in Table 2. All three multialcohol- H_2SO_4 particle systems showed a considerable reduction of $M_{\text{H}_2\text{O}}$ by organosulfate formation (Fig. S3). For example, the water loss fraction of the total $M_{\text{H}_2\text{O}}$ was 67.9 % for sucrose- H_2SO_4 aerosol, 59.1 % for glyoxal- H_2SO_4 aerosol, and 73.4 % for glycerol- H_2SO_4 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

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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:

$$\tau = \frac{dp^2}{4\pi^2 D_l} \quad (15)$$

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 $8.3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (Lees and Sarram, 1971). When the particle diameter is $0.1 \mu\text{m}$, the estimated diffusion characteristic time of a water molecule in glycerol is $3.1 \times 10^{-5} \text{ s}$, 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). $M_{\text{H}_2\text{O}}$ 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 products (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 ($M_{\text{H}_2\text{O}}$) in multialcohol- H_2SO_4 aerosol accords with the observation in Sects. 3.1 (Kinetic study of esterification of sulfuric acid with an aliphatic alcohol) and 3.2 (Formation of dialkylsulfates in multialcohol-sulfuric acid aerosol), supporting our hypothesis that organosulfate formation is more efficient in the aerosol phase. The similar result has been reported in the study by Nguyen et al.

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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).

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.

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](http://www.atmos-chem-phys-discuss.net/13/23217/2013/acpd-13-23217-2013-supplement.pdf)**

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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.

Set	Particle	M_p^a μg	[1-heptanol] $_g^b$ mol m ⁻³	RH %	[H ₂ SO ₄] $_p^c$ mol L ⁻¹	[H ₂ O] $_p^d$ mol L ⁻¹	γ^e × 10 ⁻⁵	M_{OS}^f μg	$k_1 \times 10^{-3}$ L mol ⁻¹ min ⁻¹	$k_{-1} \times 10^{-3}$ L mol ⁻¹ min ⁻¹
1	H ₂ SO 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	H ₂ SO ₄	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	H ₂ SO ₄	56	0.72	40	6.7	39.7	7.22	38	4.37	6.75
6	H ₂ SO ₄	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.

^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] $_p$) 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.

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

Particle composition	$M_{\text{Total}}^{\text{a}}$ μg	RH %	$M_{\text{H}_2\text{O}}^{\text{b}}$ μg	M_{OC}^{c} μg	$M_{\text{H}_2\text{SO}_4}^{\text{d}}$ μg	$\delta f_{\text{H}_2\text{O}}^{\text{e}}$ %
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_2SO_4	123	50	27.9	44.3	50.8	67.9
Glyoxal- H_2SO_4	88	50	28.5	16.2	43.3	59.1
Glycerol- H_2SO_4	169	50	37.2	46.9	84.9	73.4

^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 ($M_{\text{H}_2\text{O}}$) 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 ($M_{\text{H}_2\text{SO}_4}$) before reaction.

^e The water loss fraction ($\delta f_{\text{H}_2\text{O}}$) of the total aerosol water before reaction.

^f not applicable.

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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 by mole	RH %	$V_{\text{conc}}^{\text{a}}$ $\text{cm}^3 \text{m}^{-3}$	$[\text{H}^+]_0^{\text{b}}$ mol L^{-1}	$Y_{\text{diOS}}^{\text{c}}$ %	$k_2 \times 10^{-2}$ $\text{L mol}^{-1} \text{min}^{-1}$	k_{-2} $\text{L mol}^{-1} \text{min}^{-1}$
Sucrose- H_2SO_4 (1 : 2)	26.1	1.51×10^{-4}	5.26	86 ± 8.6	0.96	~0
Sucrose- H_2SO_4 (1 : 4)	25.8	1.58×10^{-4}	6.72	79 ± 7.9	0.89	~0
Sucrose- H_2SO_4 (1 : 6)	25.4	1.53×10^{-4}	7.41	74 ± 7.4	0.96	~0
Sucrose- H_2SO_4 (1 : 9)	24.8	1.56×10^{-4}	7.95	56 ± 5.6	0.82	~0
Glyoxal- H_2SO_4	70.0	1.60×10^{-4}	4.47	72 ± 7.2	6.03	~0
Glyoxal- H_2SO_4	41.8	1.53×10^{-4}	6.08	77 ± 7.7	3.62	~0
Glyoxal- H_2SO_4	22.5	1.51×10^{-4}	7.20	79 ± 7.9	2.58	~0
Glycerol- H_2SO_4	60.3	1.52×10^{-4}	4.38	80 ± 8.0	5.30	~0
Glycerol- H_2SO_4	54.2	1.81×10^{-4}	4.68	84 ± 8.4	2.26	~0
Glycerol- H_2SO_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 $[\text{H}^+]$ 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).

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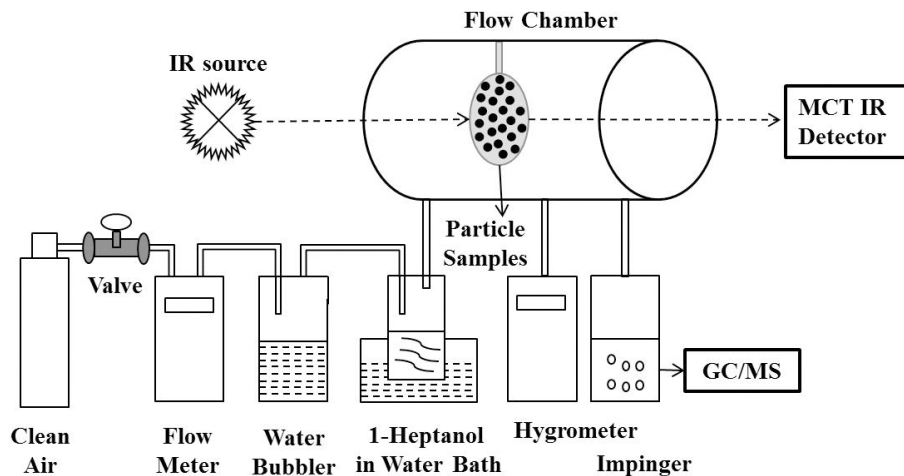


Fig. 1. The experimental set up for the FTIR studies using a flow chamber.

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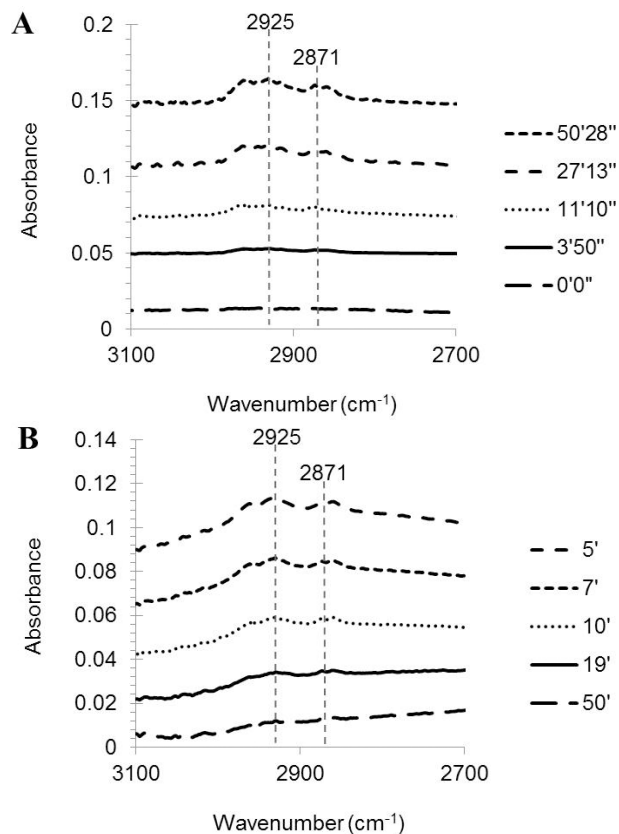


Fig. 2. (A) The FTIR spectra H₂SO₄ particle after introducing gaseous 1-heptanol into the FTIR flow chamber. The experimental conditions were shown in Table 1 experiment Set 1. **(B)** The change of FTIR spectra for 1-heptanol-H₂SO₄ particle (esterification is done) after purging clean air in to the FTIR flow chamber.

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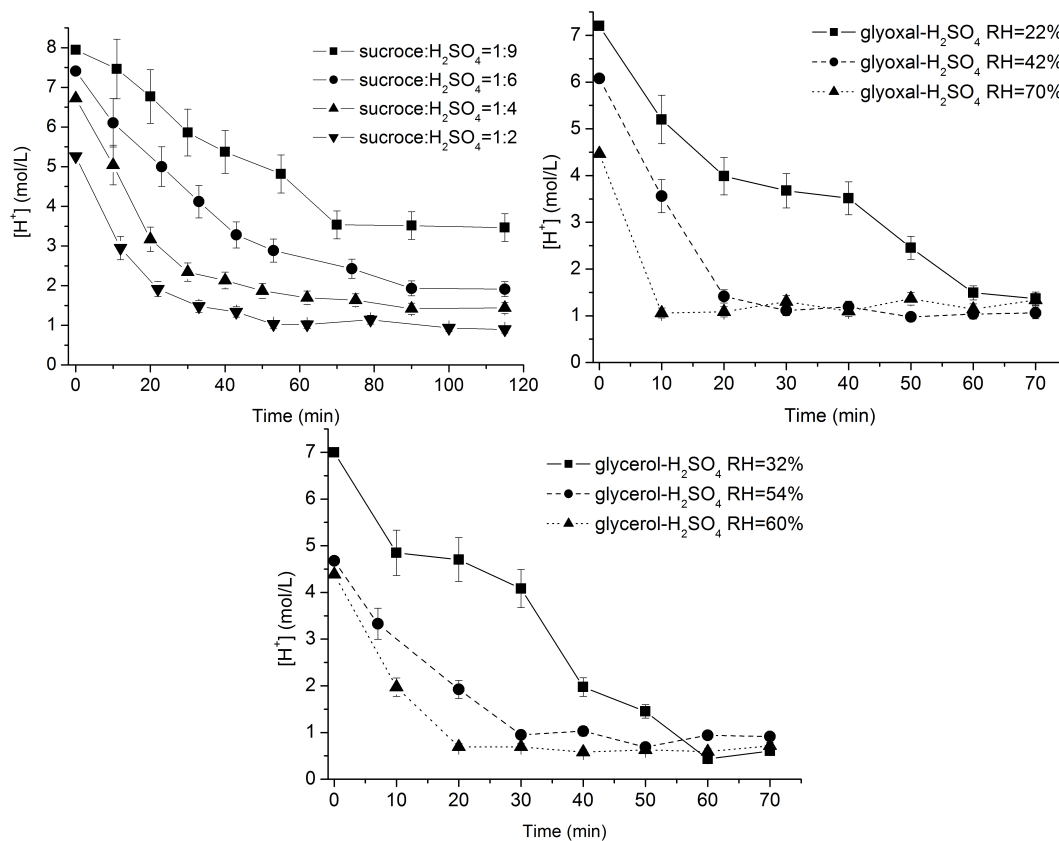


Fig. 4. The dynamics of aerosol acidity ($[H^+]$, mol L⁻¹) over the aerosol-phase reaction of H_2SO_4 internally mixed with sucrose, glyoxal or glycerol. The experimental conditions for the acidity measurement are listed in Table 3.

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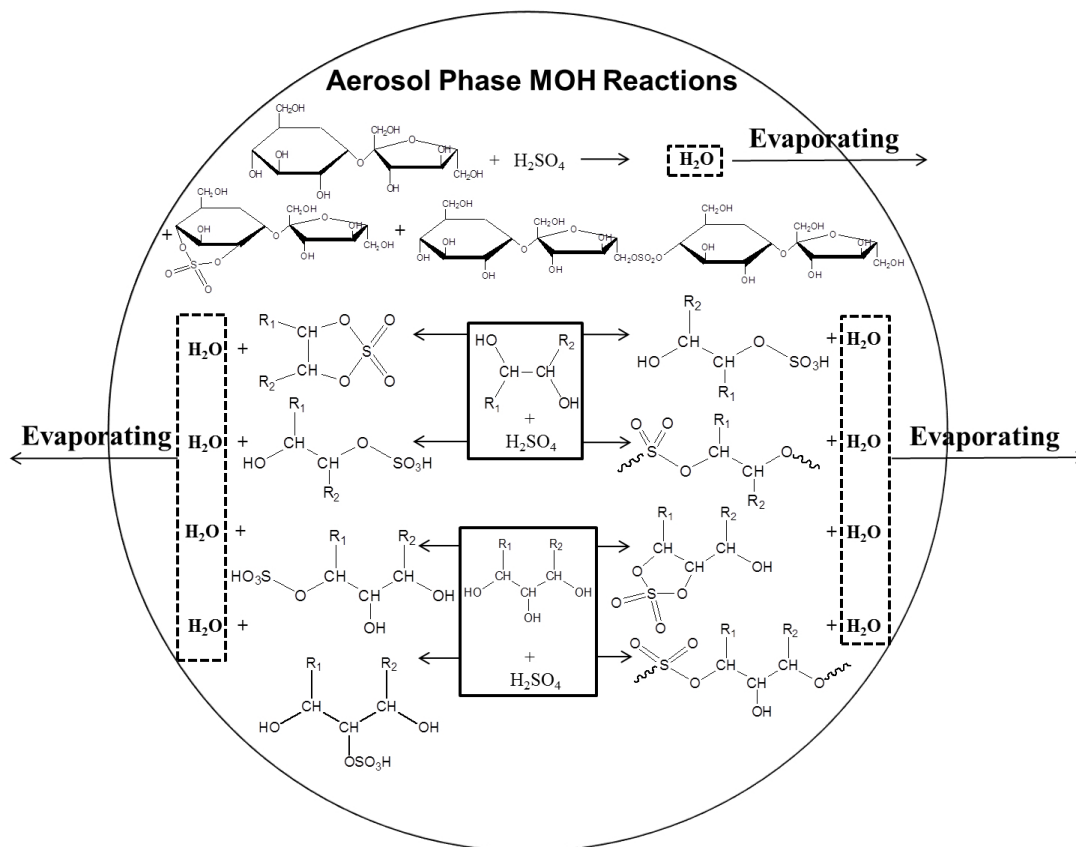
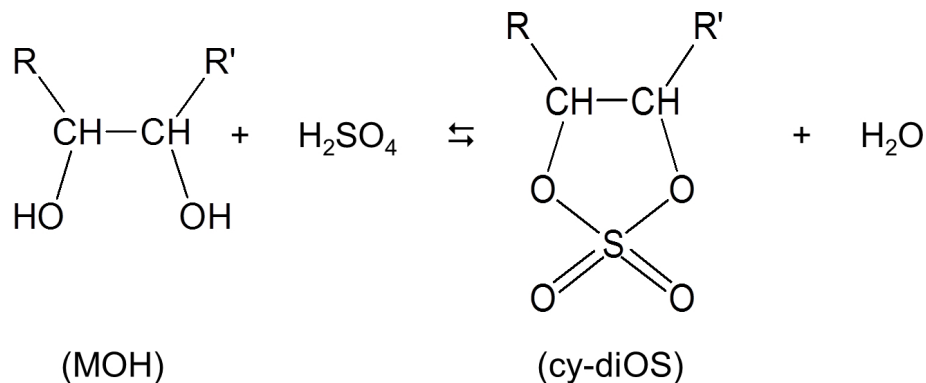


Fig. 5. Tentative mechanisms of esterification between sulfuric acid and alcohols in the aerosol bulk phase. Some of the products were shown in the $^1\text{H-NMR}$ data of this study (Fig. S1). The product shown in this figure via the sucrose- H_2SO_4 reaction was an example for the linear dialkylsulfate.

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**Fig. 6.** Formation of cyclic dialkylsulfate (cy-diOS) in the multialcohol-sulfuric acid aerosol.

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