Kinetic Study of Esterification of Sulfuric Acid with Alcohols in Aerosol Bulk Phase

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Supplementary Materials

Number of Sections: 4

Number of Figures: 4

Section 1: Description of indoor chamber experiment

All chamber experiments shown in table 3 were conducted in a 2-m^3 indoor Teflon film chamber described previously (Czoschke and Jang 2006). The chamber was flushed with air purified by a clean air generator (Aadco Model 737) before each experiment. The particle number concentration and population were measured using a scanning mobility particle sizer (TSI, SMPS Model 3080) associated with a condensation nuclei counter (TSI, Model 3025A). The humidity of the chamber air was controlled by passing the clean dry air through a water bubbler. The temperatures for chamber experiments were 295 to 298 K.

Section 2: Organosulfate formation from the reaction between glyoxal or glycerol with D_2SO_4-D_2O solution

To identify organosulfate products, glyoxal or glycerol was mixed with excess amounts of the D_2SO_4-D_2O solution and monitored using ^{1}H-NMR. The fraction of D_2SO_4 in the solution is 50 wt% which is equivalent to RH of 35.5% at 298 K. Compared to the ^{1}H-NMR spectrum of the glyoxal in D_2O, the ^{1}H-NMR spectrum of the glyoxal-D_2SO_4 solution shows the formation of organosulfate appearing at 6.13 ppm (Figure S1B). The peak intensity at 6.13 ppm kept increasing over 36 hours after glyoxal was mixed with the D_2SO_4-D_2O solution, indicating that the formation of organosulfate products progresses slowly in the solution. Figure S1D shows the ^{1}H-NMR spectrum of glycerol in the D_2SO_4-D_2O solution three days after mixing. Peaks d-g in Figure S1D which appeared 2 hours after glycerol is mixed with D_2SO_4-D_2O indicate organosulfates formation though the reaction of glycerol and sulfuric acid in the highly concentrated sulfuric acid solution. The structures of oranosulfate products were proposed based on the chemical shifts of those compounds in the NMR spectra and shown in Figure S1.
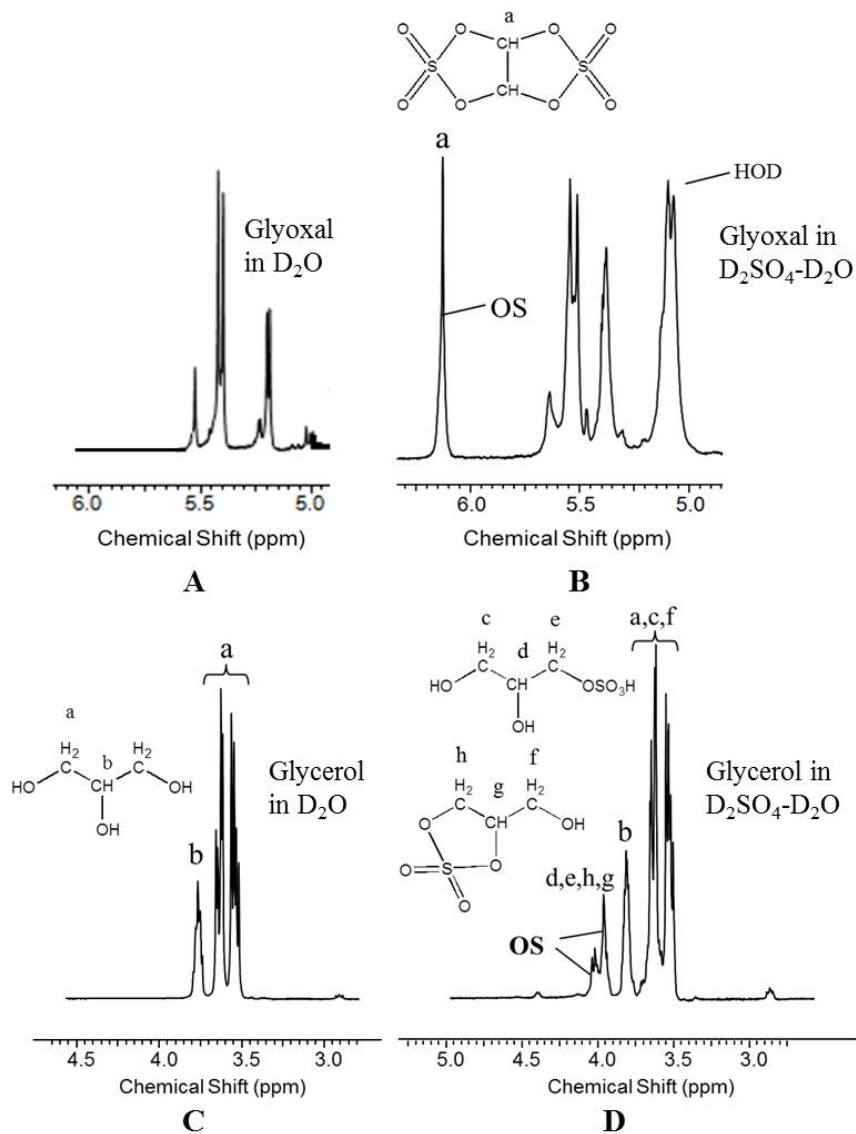
FIGURE S1. NMR spectra of glyoxal in D_2O, glyoxal in D_2SO_4-D_2O solution, glycerol in D_2O, and glycerol in D_2SO_4-D_2O solution (glyoxal:D_2SO_4 = 1:5.67 and glycerol:D_2SO_4 = 1:8.92 in mole ratio). The D_2SO_4-D_2O solution solution was made by 1:1 mass ratio, which is equivalent to the D_2SO_4 aerosol composition at relative humidity = 35.5% at 298 K.

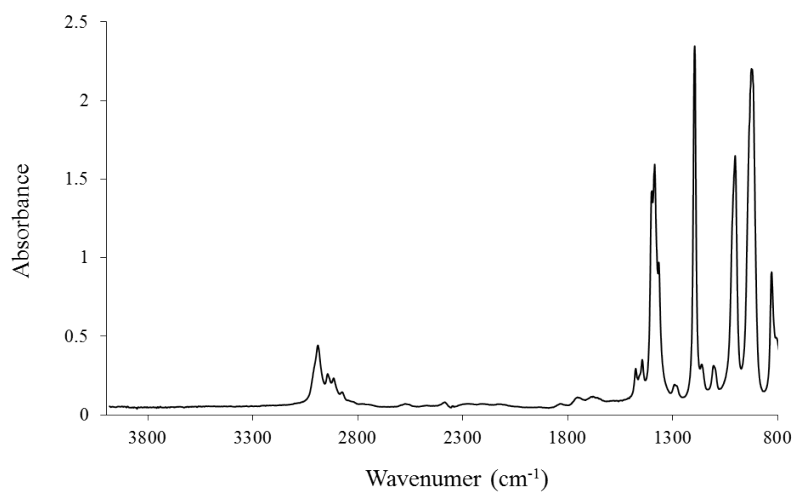## Section 3: Measurements of aerosol water content using FTIR

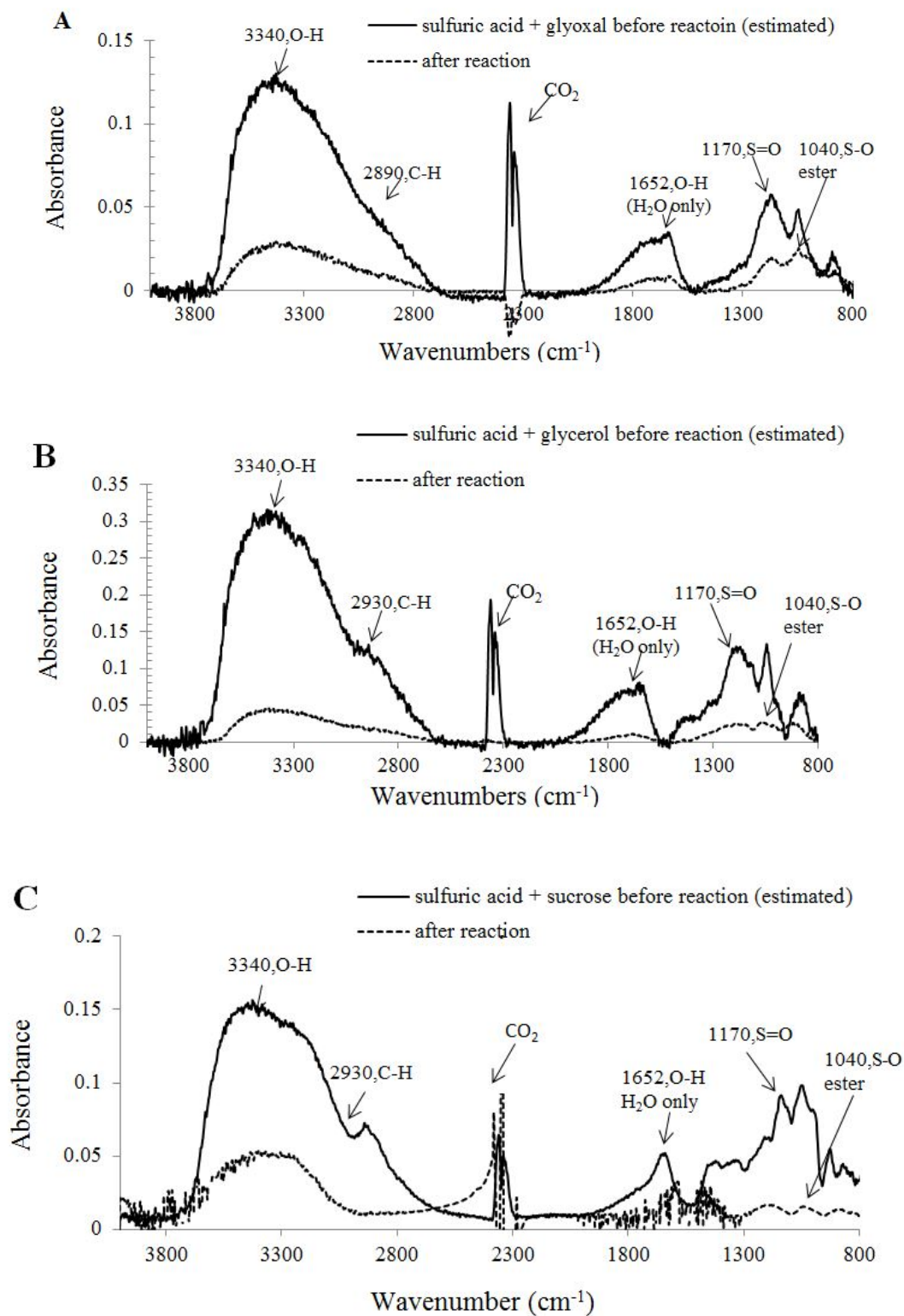FIGURE S2. The FTIR spectrum of diethyl sulfate at RH=60% under room temperature.

FIGURE S3. FTIR spectra as a sum of the contribution from H_2SO_4 and glyoxal aerosol (A), H_2SO_4 and glycerol aerosol (B), and H_2SO_4 and sucrose aerosol (C), assuming no reaction in aerosol (before reaction), and FTIR spectra of the internally mixed multialcohol-H_2SO_4 aerosol (after reaction). The experimental conditions for FTIR studies are listed in Table 2.
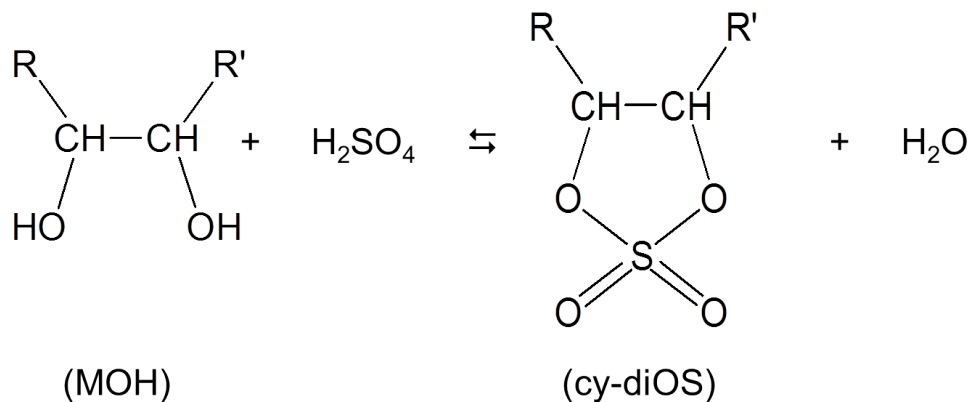
FIGURE S4. Formation of cyclic dialkylsulfate (cy-diOS) in the multialcohol-sulfuric acid aerosol.

Section 4: Derivation of Equation 13 in manuscript

Nomenclature

k_2: forward and backward reaction rate constant for multiacohol-H_2SO_4 reaction (L mol^{-1} min^{-1})
k_{-2}: backward reaction rate constant for multiacohol-H_2SO_4 reaction (L mol^{-1} min^{-1})
[cy-diOS]: concentration of cyclic dialkylsulfate in aerosol (mol L^{-1})
[H_2O]: water concentration in aerosol (mol L^{-1})
[H_2SO_4]$_0$: initial concentration of sulfuric acid in aerosol (mol L^{-1})
[H_2SO_4]$_t$: concentration of sulfuric acid in aerosol at reaction time t (mol L^{-1})
$M_{MOH,0}$: initial total mass concentration of a multiacohol in the chamber (g m^{-3})
$M_{MOH,t}$: total mass concentration of a multiacohol in the chamber at reaction time t (g m^{-3})
[MOH]$_t$: concentration of a multiacohol in aerosol at reaction time t (mol L^{-1})
MW_{MOH}: molecular weight of a multiacohol (g mol^{-1})
K_{in}: partitioning coefficient of an organic compound onto inorganic particles (m^3 μg^{-1})
M_{in}: mass concentration of inorganic aerosol in the chamber (μg m^{-3})
V_{conc}: volume concentration of the aerosol in the chamber (L m^{-3})

Derivation of analytical solution

The cyclic dialkylsulfate (cy-diOS) formation in multiacohol-H_2SO_4 aerosol can be expressed as Figure S4 (Fig. 6 in manuscript). MOH is a multialcohol, and both R and R are H, alkyls or OH groups. Similar to 1-heptanol, MOH is distributed between both gas phase and aerosol phase depending on the volatility. The aerosol phase concentration ([MOH]$_t$) of a multiacohol (MOH) at reaction time t was estimated using the partitioning coefficient of a MOH onto inorganic particles (K_{in}), the mass concentration of inorganic aerosol in the chamber (M_{in}), the total mass concentration of the MOH ($M_{MOH,t}$) in the chamber at reaction time t, and the aerosol volume concentration (V_{conc}).

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

$M_{MOH,t}$ can be estimated using the difference between initial total mass concentration of a multiacohol in the chamber ($M_{MOH,0}$), and the consumed MOH during the reaction. Since the consumption of MOH equals that of sulfuric acid, and term $\frac{K_i n M_i n}{1 + K_i n M_i n}$ is defined as α, then,

$$(2) \qquad M_{MOH,t} = M_{MOH,0} - ([H_2SO_4]_0 - [H_2SO_4]_t)V_{conc}MW_{MOH}$$

As shown in Figuire S4, 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 is described as below:

$$(3) \qquad \frac{d[H_2SO_4]}{dt} = -k_2[MOH]_t[H_2SO_4]_t + k_{-2}[cy - diOS][H_2O]$$

Since

$$(4) \qquad [cy - diOS] = [H_2SO_4]_0 - [H_2SO_4]_t$$

Combine Eqs. (S1) – (S4),

$$(5)$$
$$\frac{d[H_2SO_4]}{dt} = -k_2\frac{\alpha\{M_{MOH,0} - ([H_2SO_4]_0 - [H_2SO_4]_t)V_{conc}MW_{MOH}\}}{V_{conc}MW_{MOH}}[H_2SO_4]_t + k_{-2}([H_2SO_4]_0 - [H_2SO_4]_t)[H_2O]$$

Term

$$\sqrt{(\frac{k_2\alpha M_{MOH,0}}{V_{conc}MW_{MOH}} - k_2\alpha[H_2SO_4]_0 + k_{-2}[H_2O])^2 + 4k_2k_{-2}\alpha[H_2SO_4]_0[H_2O]}$$

is defined as β, then, Eq. (S5) was reformed into

$$(6) \qquad \frac{d[H_2SO_4]}{dt} = -k_2\alpha \times ([H_2SO_4] - \frac{\frac{k_2\alpha M_{MOH,0}}{V_{conc}MW_{MOH}} - k_2\alpha[H_2SO_4]_0 + k_{-2}[H_2O] + \beta}{-2k_2\alpha})$$
$$\times ([H_2SO_4] - \frac{\frac{k_2\alpha M_{MOH,0}}{V_{conc}MW_{MOH}} - k_2\alpha[H_2SO_4]_0 + k_{-2}[H_2O] - \beta}{-2k_2\alpha})$$

$$(7) \qquad \int_{[H_2SO_4]_0}^{[H_2SO_4]_t} \frac{d[H_2SO_4]}{([H_2SO_4] - \frac{\frac{k_2\alpha M_{MOH,0}}{V_{conc}MW_{MOH}} - k_2\alpha[H_2SO_4]_0 + k_{-2}[H_2O] + \beta}{-2k_2\alpha})([H_2SO_4] - \frac{\frac{k_2\alpha M_{MOH,0}}{V_{conc}MW_{MOH}} - k_2\alpha[H_2SO_4]_0 + k_{-2}[H_2O] - \beta}{-2k_2\alpha})}$$

$$= \int_0^t -k_2\alpha \, dt$$

After integration,

(8)

$$ln\{\frac{2k_2\alpha[H_2SO_4]_t + \frac{k_2\alpha M_{MOH,0}}{V_{conc}MW_{MOH}} - k_2\alpha[H_2SO_4]_0 + k_{-2}[H_2O] + \beta}{2k_2\alpha[H_2SO_4]_t + \frac{k_2\alpha M_{MOH,0}}{V_{conc}MW_{MOH}} - k_2\alpha[H_2SO_4]_0 + k_{-2}[H_2O] - \beta}\} - ln\{\frac{\frac{k_2\alpha M_{MOH,0}}{V_{conc}MW_{MOH}} + k_2\alpha[H_2SO_4]_0 + k_{-2}[H_2O] + \beta}{\frac{k_2\alpha M_{MOH,0}}{V_{conc}MW_{MOH}} + k_2\alpha[H_2SO_4]_0 + k_{-2}[H_2O] - \beta}\}$$

$$= -\beta t$$

Term

$$exp\{ln(\frac{\frac{k_2\alpha M_{MOH,0}}{V_{conc}MW_{MOH}} + k_2\alpha[H_2SO_4]_0 + k_{-2}[H_2O] + \beta}{\frac{k_2\alpha M_{MOH,0}}{V_{conc}MW_{MOH}} + k_2\alpha[H_2SO_4]_0 + k_{-2}[H_2O] - \beta}) + \beta t\}$$

is defined as ϵ, thus,

(9)
$$[H_2SO_4]_t = -\frac{M_{MOH,0}}{2V_{conc}MW_{MOH}} + \frac{[H_2SO_4]_0}{2} - \frac{k_{-2}[H_2O]}{2k_2\alpha} + \frac{\beta(1 + \epsilon)}{2k_2\alpha(\epsilon - 1)}$$

References

Czoschke, N. and Jang, M. (2006). Acidity effects on the formation of alpha-pinene ozone SOA in the presence of inorganic seed. Atmospheric Environment 40:4370-4380.