Aqueous Chemistry; Chemistry of S-Species

✓ **Oxidized sulfur compounds** – mostly anthropogenic: SO$_2$, H$_2$SO$_4$, sulfates, ...

✓ **Reduced sulfur compounds** – mostly biogenic: CH$_3$SCH$_3$ (DMS), CH$_3$SH, H$_2$S, CS$_2$, COS, ...

✓ All of them are eventually oxidized to sulfuric acid by various gas-phase and heterogeneous processes

---

**TABLE 2.3 Observed Mixing Ratios of Atmospheric Sulfur Gases**

<table>
<thead>
<tr>
<th>Compound and Location</th>
<th>Average Mixing Ratio (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S</td>
<td></td>
</tr>
<tr>
<td>Marine surface layer</td>
<td>3.6–7.5</td>
</tr>
<tr>
<td>Coastal regions</td>
<td>65</td>
</tr>
<tr>
<td>Forests</td>
<td>35–60</td>
</tr>
<tr>
<td>Wetlands</td>
<td>450–840</td>
</tr>
<tr>
<td>Urban areas</td>
<td>365</td>
</tr>
<tr>
<td>Free troposphere (2–5 km)</td>
<td>6–8.5</td>
</tr>
<tr>
<td>CH$_3$SCH$_3$</td>
<td></td>
</tr>
<tr>
<td>Marine surface layer</td>
<td>80–110</td>
</tr>
<tr>
<td>Continental surface layer</td>
<td>8–60</td>
</tr>
<tr>
<td>Free troposphere (2–5 km)</td>
<td>1.5–15</td>
</tr>
<tr>
<td>CS$_2$</td>
<td></td>
</tr>
<tr>
<td>Marine surface layer</td>
<td>2–18</td>
</tr>
<tr>
<td>Continental surface layer</td>
<td>35–120</td>
</tr>
<tr>
<td>Free troposphere (2–5 km)</td>
<td>5–7</td>
</tr>
<tr>
<td>OCS</td>
<td></td>
</tr>
<tr>
<td>Total troposphere</td>
<td>500</td>
</tr>
<tr>
<td>Marine surface layer</td>
<td>500</td>
</tr>
<tr>
<td>Continental surface layer</td>
<td>545</td>
</tr>
<tr>
<td>SO$_2$</td>
<td></td>
</tr>
<tr>
<td>Marine surface layer</td>
<td>20</td>
</tr>
<tr>
<td>Free troposphere (&gt;5 km)</td>
<td></td>
</tr>
<tr>
<td>Europe/North Sea/Arctic</td>
<td>50</td>
</tr>
<tr>
<td>North America clean continental</td>
<td>160</td>
</tr>
<tr>
<td>Coastal Europe</td>
<td>260</td>
</tr>
<tr>
<td>Polluted continental air</td>
<td>1500</td>
</tr>
</tbody>
</table>

*Source: Berresheim et al. (1995) (detailed references given by the authors).*
Volcanic Eruptions and Sulfur Compounds

- **Volcanoes** can inject vast quantities of H$_2$S and SO$_2$ in the air over a short period of time.
- **Result**: significant perturbation of the atmosphere for 1-3 years after each major eruption by sulfuric acid aerosols.

\[ \text{H}_2\text{S}, \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 \rightarrow \text{aerosol} \leftrightarrow \text{clouds} \]

Source: NOAA Mauna Loa Observatory website
Sulfuric Acid (H$_2$SO$_4$)

Sulfuric acid (and its salts) are the terminal products of oxidation of all S-containing compounds.

**Production:**

Gas phase oxidation of SO$_2$:

\[
\text{OH} + \text{SO}_2 (+ \text{M}) \rightarrow \text{HOSO}_2
\]

\[
\text{HOSO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2
\]

\[
\text{SO}_3 + \text{H}_2\text{O} (+ \text{H}_2\text{O}) \rightarrow \text{H}_2\text{SO}_4 (+ \text{H}_2\text{O})
\]

Liquid phase oxidation of SO$_2$:

\[
\text{SO}_2(\text{dissolved}) + \text{oxidant} \rightarrow \text{H}_2\text{SO}_4
\]

Oxidant = O$_3$, H$_2$O$_2$, O$_2$/Fe, NO$_2$, etc.

**Measurements:**

Very challenging (!) due to the very small concentration of H$_2$SO$_4$ ($\sim 10^6$ cm$^{-3}$)

CHEMICAL IONIZATION MASS SPECTROMETRY DETECTION

\[
\text{NO}_3^- + \text{H}_2\text{SO}_4 \rightarrow \text{HNO}_3 + \text{HSO}_4^-
\]

A closely-related technique can be used to detect OH by converting it to isotopically-labeled H$_2^{34}$SO$_4$ first and then detecting H$_2^{34}$SO$_4$:

\[
\text{OH} + {^{34}}\text{SO}_2 (+ \text{M}) \rightarrow {^{34}}\text{HOSO}_3
\]

\[
{^{34}}\text{HOSO}_3 + \text{O}_2 \rightarrow {^{34}}\text{SO}_3 + \text{HO}_2
\]

\[
{^{34}}\text{SO}_3 + \text{H}_2\text{O} ( + \text{M}) \rightarrow \text{H}_2{^{34}}\text{SO}_4
\]

**Measurement of the Gas Phase Concentration of H$_2$SO$_4$ and Methane Sulfonic Acid and Estimates of H$_2$SO$_4$ Production and Loss in the Atmosphere**

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 98, NO. D5, PAGES 9001-9010, MAY 20, 1993
Deposition of $\text{H}_2\text{SO}_4$ (and Other Compounds)

**Dry Deposition**
Direct transport of gas-phase compounds and small particles to the surface (soil, canopy, grass, ocean)

**Wet Deposition**
Uptake of gases and particles by air-borne aqueous droplets followed by transport to the surface inside the droplets (= acid rain in case of deposition of $\text{H}_2\text{SO}_4$ and other acids)

**Important Species in Controlling Acidity of Droplets:**
- $\text{H}_2\text{SO}_4$ – sulfuric acid (produced from $\text{SO}_2$
- $\text{HNO}_3$ – nitric acid (produced from $\text{NO}_2$, $\text{N}_2\text{O}_5$)
- $\text{RCOOH}$ – organic acids (produced via VOC oxidation)
- $\text{H}_2\text{CO}_3$ – carbonic acid (dissolved $\text{CO}_2$); provides buffering capacity
- $\text{NH}_3$ and $\text{R-NH}_2$ – ammonia and amines neutralize the acids
According to "IPCC Climate change 2001 - Synthesis report" there has been a significant increase in the amount of deposited sulfates (from aerosols) in the last century.
Sulfur Dioxide (SO$_2$) – Criteria Pollutant

- 90% of anthropogenic sulfur emissions are in the form of SO$_2$ from the fossil fuel consumption

- There is a strong correlation between SO$_2$ emissions and fuel consumption (implying that it is the major source of SO$_2$)

**FIGURE 2.8** SO$_2$ emissions in many different regions as a function of rate of fuel consumption. Data for Europe and the United States are for 1980, and those for Asia are for 1987 (from Kato and Akimoto, 1992).

**FIGURE 2.9** Contribution of various sources to total anthropogenic SO$_2$ emission United States in 1996 (from EPA, 1997).
Measurements of SO$_2$

Most instruments rely on SO$_2$ fluorescence to sensitively measure its concentration:

$$\text{SO}_2 + h\nu \rightarrow \text{SO}_2^*$$
$$\text{SO}_2^* \rightarrow \text{SO}_2 + h\nu' \quad (h\nu' \text{ is detected})$$

DOAS is also suitable because the SO$_2$ absorption spectrum has a lot of structure.

This image comes from a very useful database "MPI-Mainz-UV-VIS Spectral Atlas of Gaseous Molecules" that compiled absorption cross sections of various molecules recorded at different pressures and temperatures.

http link
Gas-Phase Oxidation of SO₂ by OH

The most significant pathway:

1. \( \text{OH} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2 \)
   \[ k_\infty = 2 \times 10^{-12} \text{ cm}^3/\text{#}/\text{s} \]
   \[ k_0 = 4 \times 10^{-31} \text{ cm}^6/\text{#}^2/\text{s} \]
   at atmospheric pressure:
   \[ \frac{k_0 \cdot [M]}{k_\infty} = 4.9 \Rightarrow \text{fall off regime} \]
   Remember: \( \left( \frac{k_0 \cdot [M]}{k_\infty} \ll 1 \Rightarrow \text{low } P \text{ limit} \right) \)
   \( \left( \frac{k_0 \cdot [M]}{k_\infty} \gg 1 \Rightarrow \text{high } P \text{ limit} \right) \)

2. \( \text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3 \)
   \[ k \approx 4 \times 10^{-13} \text{ cm}^3/\text{#}/\text{s} \]

3. \( \text{SO}_3 + \text{"H}_2\text{O}" \rightarrow \text{H}_2\text{SO}_4 \)
   requires at least two \( \text{H}_2\text{O} \) molecules

Solve in class: calculate the rate of SO₂ oxidation by OH in %/hour at \( P = 1 \text{ atm}, T = 300 \text{ K}, [\text{OH}] = 10^6 \text{ #/cm}^3 \)
(Note: reaction 1 is the rate limiting step). Answer: 0.14%/hour

FIGURE 8.4 Predicted energetics for various mechanisms for the \( \text{SO}_3-\text{H}_2\text{O} \) reaction transition states are marked with a ♦ symbol (adapted from Morokuma and Muguruma, 1994).
Gas-Phase Oxidation of SO$_2$ by "Criegees"

Reminder:

\[ O_3 + \implies \text{Criegee biradical} \]

Reaction with SO$_2$:

\[ \text{HC} = \text{NOO}^+ + \text{SO}_2 \implies [\text{Adduct}]^* \implies \text{HCl} + \text{OH} + \text{SO}_2 \]

\[ \text{H}_2\text{CO} + \text{SO}_2 + \text{SO}_2 \implies \text{HC} = \text{C} - \text{O} - \text{O} \implies \text{S} = \text{O} \]

However, this mechanism of SO$_2$ oxidation is less important than reaction \( \text{OH} + \text{SO}_2 \) and even less important than liquid phase chemistry.

- Strong evidence from field observations for the importance of the stabilized Criegee intermediate reactions
- Criegee we linked to biogenic VOCs
Solve in class: Calculate equilibrium concentrations of \([\text{H}_2\text{O}_2]_{\text{aq}}\), \([\text{O}_2]_{\text{aq}}\) and \([\text{O}_3]_{\text{aq}}\) for 1 ppb of \(\text{H}_2\text{O}_2\) and 10 ppb of \(\text{O}_3\) in the gas-phase at STP. Henry's constants for \(\text{H}_2\text{O}_2\), \(\text{O}_2\), and \(\text{O}_3\) are \(10^5\) M/atm, 0.001 M/atm, and 0.01 M/atm, respectively.
Effective Henry's Constant: Henry's Law Modified by Chemical Reactivity

\[ [X]_g \]

\[ \downarrow \]

\[ [X]_{aq} \]

\[ K_{eq} = \frac{[X]_{aq}}{[X]_g} \]

Equilibrium constant

\[ H = \frac{[X]_{aq}}{P_x} \]

\( H \equiv \) Henry's constant

\( P_x \equiv \) Pressure of \( X \)

\[ [X]_g \]

\[ \downarrow \]

\[ [X]_{aq} \leftrightarrow [XA]_{aq} \leftrightarrow \ldots \]

In this case it is convenient to define effective Henry's constant:

\[ H^* = \frac{\sum [X \text{ derivative}]_{aq}}{P_x} \]

\( H^* \) can be \( \gg H \)
Related Problem: Solubility of CO$_2$

1. $\text{CO}_2 \quad H_1 = 0.034 \text{ M/atm} = \frac{[\text{CO}_2 \cdot \text{H}_2\text{O}]}{P_{\text{CO}_2}}$
   
   (true Henry's constant)

2. $\text{CO}_2 \cdot \text{H}_2\text{O}(\text{aq}) \quad \iff \quad \text{HCO}_3^- + \text{H}^+ \quad K_2 = 4.3 \cdot 10^{-7} \text{ M}$

3. $\text{HCO}_3^- \quad \iff \quad \text{CO}_3^{2-} + \text{H}^+ \quad K_3 = 4.7 \cdot 10^{-11} \text{ M}$

\[ H^* = \frac{[\text{CO}_2 \cdot \text{H}_2\text{O}(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]}{P_{\text{CO}_2}} \quad \text{(effective Henry's constant)} \]

\[ H^* = H_1 \cdot \left\{ 1 + \frac{K_2}{[\text{H}^+]} + \frac{K_2 K_3}{[\text{H}^+]^2} \right\} \]

(derive in class!)

Conclusion: $H^*$ is pH dependent

- low pH $\iff$ smaller $H^*$
- high pH $\iff$ larger $H^*$
Solubility of SO₂

Similar to CO₂:

\[
SO₂ + H₂O \rightleftharpoons SO₂ \cdot H₂O(aq) \quad H_1 = 1.24 \text{ M/atm}
\]

\[
SO₂ \cdot H₂O \rightleftharpoons HSO₃⁻ + H⁺ \quad K_2 = 0.0132 \text{ M}
\]

\[
HSO₃⁻ \rightleftharpoons H⁺ + SO₃²⁻ \quad K_3 = 6.42 \times 10^{-8} \text{ M}
\]

Define \( H^* \) for all S(IV) as:

\[
H^* = \frac{[SO₂ \cdot H₂O] + [HSO₃⁻] + [SO₃²⁻]}{P_{SO₂}}
\]

\( HSO₃⁻ \) = bisulfate; has two isomeric forms:

\( HSO₃⁻ \) and \( HOSO₂⁻ \)

\( HSO₃⁻ \) is the dominant form of S(IV) at typical atmospheric pH values.

\[ H^* \gg H_1 \]

8.7 Mole fraction of sulfur species in solution at different acidities (adapted from Martin and Damschen, 1981).
Further Complications
SO$_2$ is not the only game in town!

$H^*$ for S(IV) can be affected by other dissolved chemicals such as aldehydes:

$H_2CO + HSO_3^- \rightleftharpoons H-C=\overset{\text{OH}}{\text{S}}\overset{\text{O}^-}{\text{O}}$

$H_2CO + SO_3^{2-} \rightleftharpoons H-C=\overset{\text{O}^-}{\text{S}}\overset{\text{O}^-}{\text{O}}$

As a result: $H^* = \frac{[SO_2\cdot H_2O] + [CHSO_3^-] + [SO_3^{2-}] + \ldots}{P_{SO_2}}$

Conversely, $HSO_3^-$ increases solubility of aldehydes:

$H^*$ for RCHO = $\frac{[RCHO] + RCH(OH)_2 + RCHO\cdot HSO_3^-}{P_{(RCHO)}}$

Conclusion: different equilibria are strongly mixed with each other.
Metal-Catalyzed Oxidation of SO$_2$ by O$_2$

- Oxidation by O$_2$ in pure water does occur but it is VERY slow.
- However, the reactions can be catalyzed by metals.
- Enough metals are present in aerosols, fogs, and clouds to make the catalytic oxidation of SO$_2$ by O$_2$ important. The mechanism is complicated.

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O} & \quad \rightarrow \quad \text{FeOH}^{2+} - \text{H}^+ \\
\text{SO}_3^- + \text{H}_2\text{O}_2 & \quad \rightarrow \quad \text{HOFeSO}_3^- \\
\text{HOFeSO}_3^- & \quad \rightarrow \quad \text{O}_2 + \text{HOFeSO}_3^- (\text{adduct})
\end{align*}
\]

- Reaction is self-inhibiting
  \[
  k \approx 10^4 \text{s}^{-1}
  \]
Oxidation of SO$_2$ by H$_2$O$_2$

- H$_2$O$_2$ is very soluble (H = 10$^5$ M/atm). In addition, H$_2$O$_2$ can be produced directly in the aqueous phase via photo-oxidation of organics.
- Oxidation of SO$_2$ by H$_2$O$_2$ is known to be quite fast:

\[
\begin{align*}
\text{HSO}_3^- + \text{H}_2\text{O}_2 & \rightleftharpoons \text{S}-\text{OOH} + \text{H}_2\text{O} \\
\text{S}-\text{OOH} + \text{HA} & \rightarrow \text{H}_2\text{SO}_4 + \text{A}^- \\
(\text{HA} & \equiv \text{acid}) \\
\text{H}_2\text{O}_2 + \text{H}_2\text{O} \cdot \text{SO}_2 & \rightarrow \text{S}-\text{OOH} + \text{H}^+ \\
\text{HSO}_4^- & \\
\end{align*}
\]

**FIGURE 8.16** \(k_0\) in expression \(d[S(\text{VI})]/dt = k_0[H_2O_2][S(\text{IV})]\); effect of buffer removed and results converted to 25°C (adapted from Martin and Damschen, 1981).
Oxidation of SO\textsubscript{2} by O\textsubscript{3}

Oxidation of SO\textsubscript{2} by O\textsubscript{3} is very fast. The rate of oxidation increases in the order H\textsubscript{2}O\cdot SO\textsubscript{2} → HSO\textsubscript{3}\textsuperscript{-} → SO\textsubscript{3}\textsuperscript{2-}, which makes O\textsubscript{3} important at higher pH relative to other mechanisms.

**TABLE 8.8** Rate Constants for Reactions of \textit{SO}_{2} \cdot H_{2}O_{(aq)}, HSO_{3}^{-}, and SO_{3}^{2-} with O_{3} in Aqueous Solution at Room Temperature\textsuperscript{a}

<table>
<thead>
<tr>
<th>Reacting species</th>
<th>$k$ (L mol\textsuperscript{-1} s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO\textsubscript{2} \cdot H\textsubscript{2}O\textsubscript{(aq)}</td>
<td>$k_{0} = (2.4 \pm 1.1) \times 10^{4}$</td>
</tr>
<tr>
<td>HSO\textsubscript{3}\textsuperscript{-}</td>
<td>$k_{1} = (3.7 \pm 0.7) \times 10^{5}$</td>
</tr>
<tr>
<td>SO\textsubscript{3}\textsuperscript{2-}</td>
<td>$k_{2} = (1.5 \pm 0.6) \times 10^{9}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} From Hoffmann (1986).

**FIGURE 8.15** Rate of S(IV) oxidation by O\textsubscript{3} in the aqueous phase under conditions typical of a Los Angeles atmosphere, with SO\textsubscript{2} = 20 ppb and O\textsubscript{3} = 50 ppb (adapted from Hoffmann, 1986).
Photo / Free Radical Oxidation of SO$_2$

Production of radicals:

(a) $O_3 \xrightarrow{h\nu} H_2O_2 + O_2$

$H_2O_2 \xrightarrow{h\nu} OH + OH$

(b) $A(S_0) + h\nu \rightarrow A(T_1)$

$A(T_1) + O_2 \rightarrow \sqrt{O_2^-} + A^+$

$A \equiv$ organic chromophore

$\uparrow$ superoxide

$O_2^- + H^+ \rightleftharpoons NO_2$

$O_2^- + HNO_2 \xrightarrow{H^+} O_2 + H_2O_2 \xrightarrow{h\nu} 2OH$

$O_2^- + NO \rightarrow ONOO^-$

ONOO$^- \xrightarrow{H^+} NO_2NO \rightarrow OH + NO_2$

(c) $NO_2^- \xrightarrow{h\nu} NO + OH + OH^-$

and many other ways...
Mechanism of Free Radical Oxidation of SO$_2$

(Will be on the Final … Ha Ha Ha…)

Note: this is not a complete mechanism. I am including it here to illustrate the complexity of atmospheric sulfur chemistry.
Relative Importance of SO₂ Oxidation Channels

- Under typical pH conditions (4-7), liquid-phase oxidation of SO₂ is dominated by H₂O₂ and O₃.
- At daytime, gas-phase oxidation of SO₂ becomes more important than aqueous-phase chemistry of dissolved SO₂.

**FIGURE 8.21** Estimated rates of oxidation of S(IV) in a hypothetical cloud with liquid water content of 1 mL m⁻³ (i.e., LWC of 1 g m⁻³) based on 5 ppb gaseous SO₂ as a function of pH (adapted from Martin, 1984; Martin et al., 1991).

**FIGURE 8.22** Calculated contributions to S(IV) oxidation in a cloud of the iron-catalyzed oxidation by O₂/Fe(III), by H₂O₂ and OH in solution, and by OH in the gas phase, OH(g), expressed in terms of rate of production of column S(IV) (adapted from Jacob et al., 1989).
Oxidation of Reduced Sulfur Species
(Chapter 8E of the FP² book)

There are two competing channels for OH + DMS reactions:

\[
\begin{align*}
\text{CH}_3\text{SCH}_3 (\text{DMS}) + \text{OH} & \rightarrow \text{CH}_3\text{SCH}_2 + \text{H}_2\text{O} & k_1 = 4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\
\text{DMS} + \text{OH} (+\text{M}) & \rightarrow \text{CH}_3\text{S(OH)}\text{CH}_3 & k_2 = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 1 atm}
\end{align*}
\]

The DMS+OH rate constant given in table 8.17 is the sum of \( k_1 \) and \( k_2 \):

\[
\text{CH}_3\text{S(OH)}\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{S(O)CH}_3 (\text{DMSO}) + \text{HO}_2 \quad (\text{and other products})
\]

\[
\text{CH}_3\text{SCH}_2 + \text{O}_2 (+\text{M}) \rightarrow \text{CH}_3\text{SCH}_2\text{O}_2 \rightarrow \text{chemistry is similar to that of RO}_2 \text{ radicals}
\]

### Solve in class:
Predict possible products of oxidation of \( \text{CH}_3\text{SCH}_2\text{O}_2 \) in low-NOx and high-NOx environments
Fate of CH$_3$SCH$_2$O$_2$

Methyl thioformate has been detected amongst products of low-NOx oxidation of DMS
Fate of \(\text{CH}_3\text{S}\)

\[
\text{CH}_3\text{S} + \text{O}_2 \text{ (}+ \text{M)} \rightarrow \text{CH}_3\text{SOO} \quad \tau \sim 0.15
\]

\[
\text{CH}_3\text{S} + \text{O}_3 \rightarrow \text{CH}_3\text{SO} \quad \tau \sim 0.2 \text{ s at 40 ppb O}_3
\]

\[
\text{CH}_3\text{SOO} + \text{NO} \rightarrow \text{CH}_3\text{SO} + \text{NO}_2
\]

\[
+ \text{NO}_2 \rightarrow \text{CH}_3\text{SO} + \text{NO}_3
\]

\[
\text{CH}_3\cdots\text{S}=\text{O} + \text{O}_2 \rightarrow \text{CH}_3\cdots\text{S}=\text{O} \quad \text{NO} \rightarrow \text{CH}_3\cdots\text{S}=\text{O}
\]

\[
\text{CH}_3\cdots\text{S}=\text{O} \\ \downarrow \text{M} \quad \text{CH}_3 + \text{SO}_2
\]

\[
\text{CH}_3\cdots\text{S}=\text{O} \quad \text{NO}_2 \rightarrow \text{CH}_3\cdots\text{S}=\text{O} \quad \text{NO}_2 \rightarrow \text{CH}_3\cdots\text{S}=\text{O}
\]

\[
\text{CH}_3\cdots\text{S}=\text{O} \quad \text{CH}_3\cdots\text{S}=\text{O}
\]

methane sulfonic acid
Summary of DMS Oxidation

FIGURE 8.25 Overview of oxidation of DMS by OH in the troposphere (note that many of the reactions after the first step are the same in DMS reactions with SO₃, Cl, etc.).
Sulfuric and Methane Sulfonic Acids

Both $\text{H}_2\text{SO}_4$ and $\text{CH}_3\text{S(O)}_2\text{OH}$ are very strong acids. They acidify aerosols and catalyze aldol condensation, esterification hemiacetal formation, isomerization, etc. in organic aerosols effectively increasing the organic aerosol mass.

**Heterogeneous Atmospheric Aerosol Production by Acid-Catalyzed Particle-Phase Reactions**

Myoseon Jang,* Nadine M. Czoschke, Sangdon Lee, Richard M. Kamens

Science 298 (2002) 814
Esters of sulfuric acid have now been observed in multiple field studies as well as aerosol chamber studies. In chamber studies, they tend to form whenever sulfuric acid is present. The Surrat's paper is the most comprehensive paper to date on this topic.
Organosulfates (and Organonitrates)

CAVEATS:
- Epoxide pathway is much more efficient that ester formation (kinetically constrained) in forming organosulfates
- Only primary organonitrates and organosulfates are stable – the rest appear to quickly hydrolyze