Sulfur radical formation from the tropospheric irradiation of aqueous sulfate aerosols

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Atmospheric sulfur chemistry doesn’t end at sulfate!

\[
\text{SO}_4^{2-} + \text{HO-CH(OH)-CH(OH)-O-} \rightarrow \text{HO-CH(OH)-CH(OH)-O-SO}_3^-
\]

\[
\text{OH}, \quad \text{NO}_3^- \quad \text{S(IV)} \rightarrow \text{S(VI)} \rightarrow \text{SO}_4^{2-} \rightarrow ...
\]

… but the sulfate anion radical (SO\textsubscript{4}^\textsubscript{-}) is considered scarce, and only thought to be formed by more reactive radicals (e.g. OH, NO\textsubscript{3})
Atmospheric sulfur chemistry doesn’t end at sulfate!

... but the sulfate anion radical (SO$_4^{-}$) is considered scarce, and only thought to be formed by more reactive radicals (e.g. OH, NO$_3$)
Previous findings cast doubt on the need for another radical source

\[ \text{(NH}_4\text{)}_2\text{SO}_4 + \text{H}_2\text{O} \xrightarrow{hv} \text{glyoxal sulphate} \]

\[ \text{glyoxal + (NH}_4\text{)}_2\text{SO}_4 \text{ seed + lights} \]

\[ \text{RT} = 0.85 \text{ min} \]

\[ \text{Measured Mass: m/z 154.9642} \]

\[ \text{TOFMS Suggested Ion Formula: C}_2\text{H}_2\text{O}_3\text{S}^- \]

\[ \text{Error Between Measured and Theoretical Mass: } 0.8 \text{ mDa} \]

\[ \text{glyoxal + (NH}_4\text{)}_2\text{SO}_4 \text{ seed + no lights} \]

\[ \text{glyoxal + MgSO}_4 + \text{H}_2\text{SO}_4 \text{ seed + no lights} \]

\[ \text{glycolic acid sulphate standard} \]

\[ \text{RT} = 0.85 \text{ min} \]

\[ \text{Measured Mass: m/z 154.9654} \]

\[ \text{TOFMS Suggested Ion Formula: C}_3\text{H}_4\text{O}_4\text{S}^- \]

\[ \text{Error Between Measured and Theoretical Mass: } 0.4 \text{ mDa} \]

\[ \text{(NH}_4\text{)}_2\text{SO}_4 \text{ or } \text{Na}_2\text{SO}_4 \xrightarrow{hv} \text{organosulfates} \]
Can we initiate sulfate radical chemistry from only tropospheric radiation?

erythritol (E) | K$_2$S$_2$O$_8$ | H$_2$O

photolysis only: X
with (NH$_4$)$_2$SO$_4$, dark: X
with hv + H$_2$O$_2$: ✓
with hv + 4M (NH$_4$)$_2$SO$_4$: ✓
with hv + H$_2$O$_2$ + (NH$_4$)$_2$SO$_4$: ✓ ✓

Lines: kinetic model with SO$_4^{2-}$ + hv → e$^-$ + SO$_4^{•-}$. 

\[
\ln\left(\frac{\text{[Erythritol]}}{\text{[Erythritol]}_0}\right) = k t
\]

E + hv + H$_2$O$_2$ + AS (dark)
E + AS + hv
E + H$_2$O$_2$ + AS + hv

So, yes, we can photochemically generate $SO_4^{2-}$, but what if…

it’s just erythritol?

- Erythritol
- 1,2-DHI (dihydroxy-isoprene)
- DHDN (dihydroxy-dinitrooxy-isoprene)
- PA (pinonic acid)
- p-NP (para-nitrophenol)
- THB (trihydroxy benzene)
So, yes, we can photochemically generate $\text{SO}_4^{2-}$, but what if…

it's just erythritol?

it's just our lamp?

![Graph showing ln([A]/[A_0]) vs. reaction time (h) with data points and trend lines for p-NP + hv and p-NP + AS + hv.]

![Graphs showing photon flux vs. wavelength for A) UVA lamps used for chamber experiments, B) UVB lamps used for bulk aqueous experiments, and C) Solar Radiation at noon.]

So, yes, we can photochemically generate SO$_4^{\cdot-}$, but what if…

- it’s just erythritol?
- it’s just our lamp?
- it’s actually OH?

| Scavenger     | tert-butanol | methanol |
|---------------|--------------|----------|
| k(OH)         | fast         | fast     |
| k(SO$_4^{\cdot-}$) | slow        | fast     |

![Graph](image1.png)

![Graph](image2.png)
So, yes, we can photochemically generate $SO_4^{2-}$, but what if...

it’s just erythritol?

it’s just our lamp?

it’s actually $OH$?

it’s the ammonium?

![Chart showing first order loss rate (h⁻¹) minus direct photolysis for different compounds.](image)
So, yes, we can photochemically generate $SO_4^{2-}$, but what if…

- it’s just erythritol?
- it’s just our lamp?
- it’s actually -OH?
- it’s the ammonium?
- it’s a metal impurity?

\[
\ln\left(\frac{[A]}{[A_0]}\right) 
\]

![Graph showing ln([A]/[A_0]) vs. reaction time (h)]
So, yes, we can photochemically generate $\text{SO}_4^{2-}$, but what if…

- it’s just erythritol?
- it’s just our lamp?
- it’s actually OH?
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- it’s an absorbing impurity?
So, yes, we can photochemically generate $\text{SO}_4^{2-}$, but what if...

- it's just erythritol?
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- it's an absorbing impurity?
So, yes, we can photochemically generate $\text{SO}_4^{2-}$, but what if…

- it’s just erythritol?
- it’s just our lamp?
- it’s actually OH?
- it’s the ammonium?
- it’s a metal impurity?
- it’s another impurity?
- it’s oxygen?
So, yes, we can photochemically generate \( \text{SO}_4^{2-} \), but what if...

- It’s just erythritol?
- It’s just our lamp?
- It’s actually OH?
- It’s the ammonium?
- It’s a metal impurity?
- It’s another impurity?
- It’s oxygen?
- It’s pH dependent?
So, yes, we can photochemically generate $\text{SO}_4^{\cdot-}$, but what if... 

it’s just erythritol?

it’s just our lamp?

it’s actually OH?

it’s the ammonium?

it’s a metal impurity?

it’s another impurity?

it’s oxygen?

it’s pH-dependent? (…?)

it’s only in bulk solution?
So, *yes*, we can photochemically generate $\text{SO}_4^{2-}$, but what if…

- it’s just erythritol?
- it’s just our lamp?
- it’s actually OH?
- it’s the ammonium?
- it’s a metal impurity?
- it’s another impurity?
- it’s oxygen?
- it’s pH-dependent?
- it’s only in bulk?

**gas phase:**
fragmentation products

**particle phase:**
organo-sulfates

**ESI signal : noise**

**1,2-DHI**
hydroxy-acetone

**formic acid**

**product formation (ppb)**

**1,2-DHI loss (ppb)**

**Reaction Time (h)**

**Mass to charge ratio (m/z)**
Limitations & implications

What’s the mechanism? (direct e\textsuperscript{-} ejection?)

Estimated aerosol \([\text{SO}_4 \cdot]_{ss}\) of \(10^{-14}=10^{-12}\) M, potentially exceeding OH

\(\text{SO}_4 \cdot\) oxidation of S(IV) could catalyze more sulfate formation

Fragmentation of organics by \(\text{SO}_4 \cdot\) could lead to particle mass loss and production of gas-phase acids & oxygenates

Functionalization of organics by \(\text{SO}_4 \cdot\) could lead to particle mass gain and changes in surface properties

Chamber experimental results may be complicated (and to some extent explained) by \(\text{SO}_4 \cdot\) chemistry
