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Supplement of

A potential source of atmospheric sulfate from $\text{O}_2^-$-induced $\text{SO}_2$ oxidation by ozone

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S1 Determination of unimolecular rate constants and atmospheric lifetimes

The unimolecular rate constants of $\text{O}_2\cdots\text{O}_2\cdots\text{O}_3\cdots(\text{H}_2\text{O})_{0.1}$ reaction (in reaction (R3)) are determined as:

$$k_{\text{uni}} = \frac{k_B T}{h} \times \exp\left(\frac{-\Delta G^0}{RT}\right) \tag{S1}$$

where $\Delta G^0$ is the Gibbs free energy barrier separating $\text{O}_2\cdots\text{O}_2\cdots\text{O}_3\cdots(\text{H}_2\text{O})_{0.1}$ and the products, $h$ is the Planck’s constant, $k_B$ is the Boltzmann constant and $R$ is the molar gas constant. Based on these rate constants, the atmospheric lifetimes of $\text{O}_2\cdots\text{O}_2\cdots\text{O}_3\cdots(\text{H}_2\text{O})_{0.1}$ are determined as

$$\tau = \frac{1}{k_{\text{uni}}} \tag{S2}$$

S2 Details on the determination of $K_{eq}$ and $p_{H_2O}$

For the $\text{O}_2\text{SOO}^\cdots\text{H}_2\text{O}$ formation according to the equation

$$\text{O}_2\text{SOO}^\cdots + \text{H}_2\text{O} \leftrightarrow \text{O}_2\text{SOO}^\cdots\text{H}_2\text{O}, \tag{S3}$$

the equilibrium constant at different temperatures is calculated as

$$K_{eq} = \left(\frac{k_B T}{p^0}\right) \times \exp(-\Delta G/RT) \tag{S4}$$

where $\Delta G$ is the Gibbs free energy change for the $\text{O}_2\text{SOO}^\cdots\text{H}_2\text{O}$ formation, $k_B$ is the Boltzmann’s constant, $R$ is the molar gas constants and $p^0$ is the atmospheric pressure.

The water vapor pressure is determined as $p_{H2O} = RH/100 \times p_{H2O}^{eq}$, where RH is the relative humidity and $p_{H2O}^{eq}$ is the equilibrium water vapor pressure calculated using the parametrization of Wagner and Prus (Wagner and Pruss, 1993), revised by Murphy and Koop (Murphy and Koop, 2005) as given below:

$$\ln p_{H2O}^{eq} = 54.842763 - \frac{6763.322}{T} - 4.210 \times \ln T + 0.000367 T + \tanh(0.0415(T - 218.8)) \left(53.878 - \frac{1331.22}{T} - 9.44523 \times \ln T + 0.014025 T\right) \tag{S5}$$

This parametrization fits suitably to all temperatures encountered in the atmosphere ($123 < T < 332$ K).
S3 Units of constants and variables used in Eqs. (4), (5)

| Constants and variables | CGS units                  | SI units                  |
|-------------------------|----------------------------|---------------------------|
| $T$                     | 298 K                      | 298 K                     |
| $k_B$                   | $1.38 \times 10^{-16}$ erg K$^{-1}$ | $1.38 \times 10^{-23}$ J K$^{-1}$ |
| $\hbar$                 | $6.63 \times 10^{-27}$ erg s               | $6.63 \times 10^{-34}$ J s               |
| $q$                     | $4.80 \times 10^{-10}$ statC                  | $1.60 \times 10^{-19}$ C                  |
| $\varepsilon_0$        | $(1/(4\pi))$                      | $8.85 \times 10^{-12}$ F m$^{-1}$          |
| $\mu$ (unhydrated)     | $5.32 \times 10^{-23}$ g                  | $5.32 \times 10^{-26}$ kg                  |
| $\mu$ (monohydrated)   | $5.61 \times 10^{-23}$ g                  | $5.61 \times 10^{-26}$ kg                  |
| $\alpha$               | $2.60 \times 10^{-24}$ cm$^3$                  | $2.34 \times 10^{-8}$ F m$^2$                  |
| $\alpha_D$             | $5.30 \times 10^{-19}$ StatC cm                   | $1.77 \times 10^{-30}$ C.m                  |

**Table S1:** Outer rate constants ($k_{\text{out}}$) and inner rate constants ($k_{\text{in}}$) of the O$_2$SOO$^+$ + O$_3$ reaction both in the absence and in the presence of water, calculated at 298.15 K using Equations (4) and (5), respectively, given in the main manuscript. Units are cm$^3$ molecule$^{-1}$s$^{-1}$.

|                      | $k_{\text{out}}$ | $k_{\text{in}}$ |
|----------------------|------------------|------------------|
| Unhydrated reaction  | $8.25 \times 10^{-10}$ | $1.27 \times 10^{-14}$ |
| Monohydrated reaction| $8.03 \times 10^{-10}$ | -                |

**Figure S1** Optimized structures of the different reactants species in reaction (R1), calculated with the M06-2X/aug-cc-pVTZ method.
Figure S2 Formation of the O₃···O₂SOO⁻···H₂O from O₃ and O₂SOO⁻···H₂O collision. The spin density indicates the migration of the extra charge from O₂SOO in the reactant state to O₃ in the product state.

Cartesian coordinates and actual values of the expectation value of the $\hat{S}^2$ operator ($\langle \hat{S}^2 \rangle$) for all species in Fig. 1 and Fig.2 in the main manuscript

RC1 = O₃···O₂SOO⁻, $\langle \hat{S}^2 \rangle = 0.7586$

| Atom | $x$   | $y$   | $z$   |
|------|-------|-------|-------|
| O    | -0.88915 | 1.20794 |  0.62611 |
| O    | -0.11707 | 1.94739 | -0.0965  |
| S    | -1.55912 | -0.27516 | -0.42147 |
| O    | -0.3465 | -1.10626 | -0.47054 |
| O    | -2.55494 | -0.75015 |  0.54717 |
| O    |  2.00879 | -0.01164 |  0.19102 |
| O    |  2.49143 | -0.84249 |  0.96308 |
| O    |  2.52567 |  0.10552 | -0.91741 |

RC2 = O₂···O₂S–O₃⁻, $\langle \hat{S}^2 \rangle = 1.7622$

| Atom | $x$   | $y$   | $z$   |
|------|-------|-------|-------|
| O    |  3.21447 |  0.04233 | -0.3778 |
| O    |  3.52629 | -1.03545 |  0.01499 |
| S    | -0.04943 |  0.35018 | -0.20367 |
| O    |  0.40973 | -0.55845 |  0.85324 |
| O    |  0.36378 |  1.744  | -0.00485 |
| O    | -2.50542 | -0.60536 |  0.3645 |
| O    | -1.86328 |  0.6353 |  0.30245 |
| O    | -3.04672 | -0.92273 | -0.74518 |

TS2, $\langle \hat{S}^2 \rangle = 2.2166$

| Atom | $x$   | $y$   | $z$   |
|------|-------|-------|-------|
| O    |  2.92464 | -1.00425 | -0.18039 |
| O    |  1.98318 | -1.54671 |  0.30002 |
| S    | -0.07317 |  1.21684 | -0.12087 |
| O    |  0.38207 |  0.52086 | -1.34299 |
| O    |  0.98952 |  1.35384 |  0.9071  |
| O    | -2.10061 | -0.71917 | -0.38046 |
| O    | -0.90411 | -0.05163 |  0.7495  |
| O    | -3.12835 | -0.98662 |  0.18897 |
\[ PC_2 = SO_3 + 2O_2, \quad \langle \hat{S}^2 \rangle = 2.7874 \]

|    |       |       |       |
|----|-------|-------|-------|
| O  | 0.40581 | -2.56797 | 0.18275 |
| O  | 0.95455 | -1.66405 | -0.36104 |
| S  | -1.52768 | 0.72525 | 0.17335 |
| O  | -0.85736 | 0.17204 | 1.37341 |
| O  | -1.88873 | -0.43834 | -0.8086 |
| O  | 2.15538 | 0.85125 | 0.58195 |
| O  | -0.45143 | 1.15446 | -0.87683 |
| O  | 2.73713 | 1.04211 | -0.43834 |

\[ RCW_1 = O_3\cdots SOO\cdots H_2O, \quad \langle \hat{S}^2 \rangle = 0.7581 \]

|    |       |       |       |
|----|-------|-------|-------|
| O  | -0.64085 | -1.68754 | -0.80368 |
| O  | 0.61579 | -1.9498 | -0.9284 |
| S  | -0.92016 | -0.53559 | 0.67699 |
| O  | -0.25762 | 0.68486 | 0.17685 |
| O  | -2.38924 | -0.47173 | 0.57476 |
| O  | -2.6674 | 2.19035 | -0.60188 |
| H  | -2.9713 | 1.33186 | -0.27703 |
| H  | -1.71279 | 2.06043 | -0.52979 |
| O  | 2.41812 | 0.35228 | -0.16394 |
| O  | 2.65848 | 0.02323 | 0.99512 |
| O  | 2.68856 | 1.50551 | -0.50195 |

\[ RCW_2 = O_2\cdots O_2S\cdots O_3\cdots H_2O, \quad \langle \hat{S}^2 \rangle = 1.7622 \]

|    |       |       |       |
|----|-------|-------|-------|
| O  | -1.2241 | 1.9624 | -0.55509 |
| O  | -0.47401 | 2.47577 | 0.21045 |
| S  | 0.14657 | -1.23777 | 0.06723 |
| O  | -0.42759 | -0.50464 | 1.20878 |
| O  | -0.79176 | -1.36644 | -1.06126 |
| O  | -3.22024 | -0.45534 | 0.3167 |
| H  | -2.71162 | -0.77756 | -0.43962 |
| H  | -2.49605 | -0.27271 | 0.93019 |
| O  | 2.11674 | 0.55001 | 0.21218 |
| O  | 3.18673 | -0.13675 | 0.20954 |
| O  | 1.19206 | 0.08181 | -0.73709 |

\[ TSW_2, \quad \langle \hat{S}^2 \rangle = 2.1889 \]

|    |       |       |       |
|----|-------|-------|-------|
| O  | -0.28481 | 2.14309 | -0.55001 |
| O  | 0.70281 | 2.27976 | 0.09662 |
| S  | -0.4068 | -1.35567 | 0.14863 |
| O  | -0.65781 | -0.35796 | 1.21852 |
| O  | -1.37621 | -1.24222 | -0.97505 |
| O  | -3.14476 | 0.75693 | 0.21226 |
| H  | -2.83508 | 0.15707 | -0.48105 |
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