Supplement for

A potential source of atmospheric sulfate from O_2^--induced SO_2 oxidation by ozone

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S1 Determination of unimolecular rate constants and atmospheric lifetimes

The unimolecular rate constants of $O_2\cdots O_2S\text{-}O_3^-\cdots(H_2O)_{0\text{-}1}$ reaction (in reaction (R3)) are determined as:

$$k_{\mathrm{uni}} = \frac{k_{\mathrm{B}}T}{h} \times \exp\left(-\frac{\Delta G^{\#}}{RT}\right) \tag{S1}$$

where $\Delta G^{\#}$ is the Gibbs free energy barrier separating $O_2\cdots O_2S\text{-}O_3^-\cdots(H_2O)_{0\text{-}1}$ 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 $O_2\cdots O_2S\text{-}O_3^-\cdots(H_2O)_{0\text{-}1}$ are determined as

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

S2 Details on the determination of K_{eq} and p_{H2O}

For the $O_2SOO^-\cdots H_2O$ formation according to the equation

$$O_2SOO^- + H_2O \leftrightarrow O_2SOO^-\cdots H_2O, \tag{S3}$$

the equilibrium constant at different temperatures is calculated as

$$K_{\mathrm{eq}} = (k_{\mathrm{B}}T/p^0) \times \exp(-\Delta G/RT) \tag{S4}$$

where ΔG is the Gibbs free energy change for the $O_2SOO^-\cdots H_2O$ 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 $p_{\mathrm{H2O}} = RH/100 \times p_{\mathrm{H2O}}^{eq}$, where RH is the relative humidity and p_{H2O}^{eq} is the equilibrium water vapor pressure calculated using the parametrization of Wagner and Prus[1], revised by Murphy and Koop[2] as given below:

$$\ln p_{\mathrm{H2O}}^{\mathrm{eq}} = 54.842763 - \frac{6763.22}{T} - 4.210 \times \ln T + 0.000367T + \tanh\{0.0415(T - 218.8)\}\left(53.878 - \frac{1331.22}{T} - 9.44523 \times \ln T + 0.014025T\right) \tag{S5}$$

This parametrization fits suitably to all temperatures encountered in the atmosphere ($123 < T < 332$ K).

Table S1: Outer rate constants (k_{out}) and inner rate constants (k_{in}) of the $O_2SOO^- + O_3$ 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_{out}	k_{in}
Unhydrated reaction	8.25×10^{-10}	1.27×10^{-14}
Monohydrated reaction	8.03×10^{-10}	2.67×10^{-4}

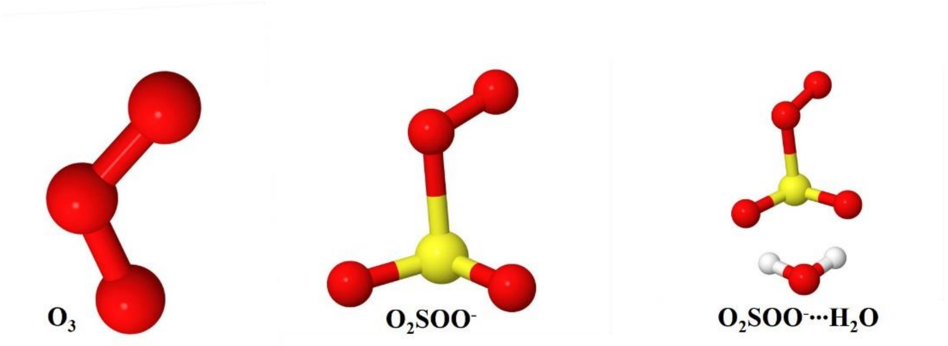

Figure S1 Optimized structures of the different reactants species in reaction (R1), calculated with the M06-2X/aug-cc-pVTZ method.

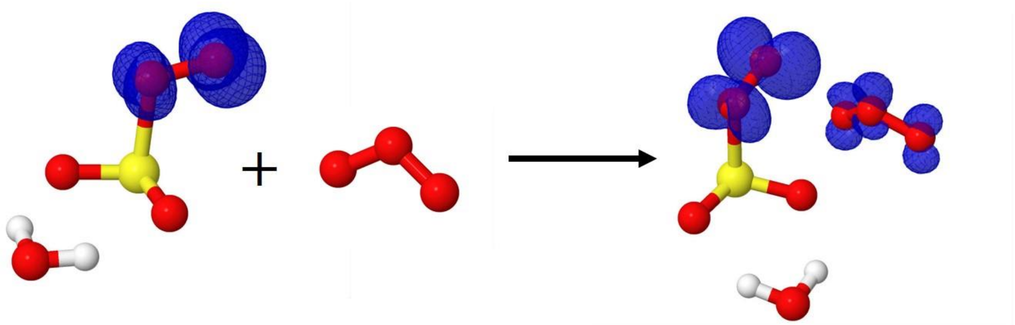

Figure S2 Formation of the $O_3 \cdots O_2SOO^- \cdots H_2O$ from O_3 and $O_2SOO^- \cdots H_2O$ collision. The spin density indicates the migration of the extra charge from O_2SOO in the reactant state to O_3 in the product state.

References

1. Wagner, W., Pruss, A. International Equations for the Saturation Properties of Ordinary Water Substance. Revised According to the International Temperature Scale of 1990. Addendum to J. Phys. Chem. Ref. Data 16, 893 (1987). *J. Phys. Chem. Ref. Data* **1993**, *22*, 783-787.
2. Murphy, D. M., Koop, T. Review of the Vapour Pressures of Ice and Supercooled Water for Atmospheric Applications. *Q. J. R. Meteorol. Soc.* **2005**, *131*, 1539-1565.