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Supplement of

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

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

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 (Wagner and Pruss, 1993), revised by Murphy and Koop (Murphy and Koop, 2005) 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).

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	1.38×10^{-16} erg K^{-1}	1.38×10^{-23} J K^{-1}
h	6.63×10^{-27} erg s	6.63×10^{-34} J s
q	4.80×10^{-10} statC	1.60×10^{-19} C
ε_0	$1/(4\pi)$	8.85×10^{-12} F m^{-1}
μ (unhydrated)	5.32×10^{-23} g	5.32×10^{-26} kg
μ (monohydrated)	5.61×10^{-23} g	5.61×10^{-26} kg
α	2.60×10^{-24} cm^3	2.34×10^{-8} F m^2
α_D	5.30×10^{-19} StatC cm	1.77×10^{-30} C.m

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}	-

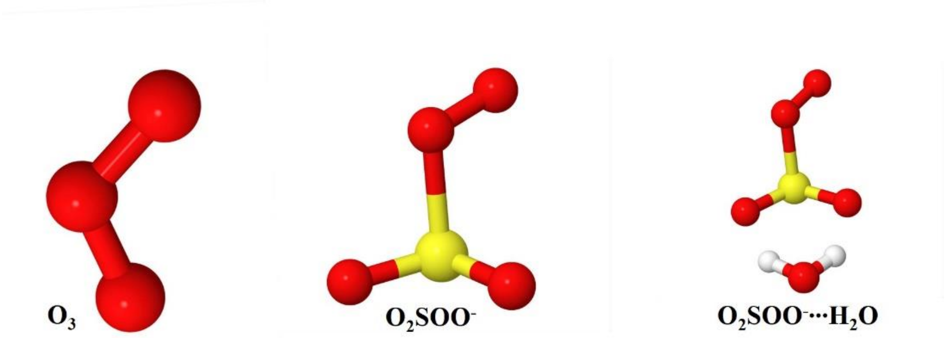

Figure S1 Optimized structures of the different reactants species in reaction (R1), calculated with the M06-2X/aug-cc-pVTZ method.

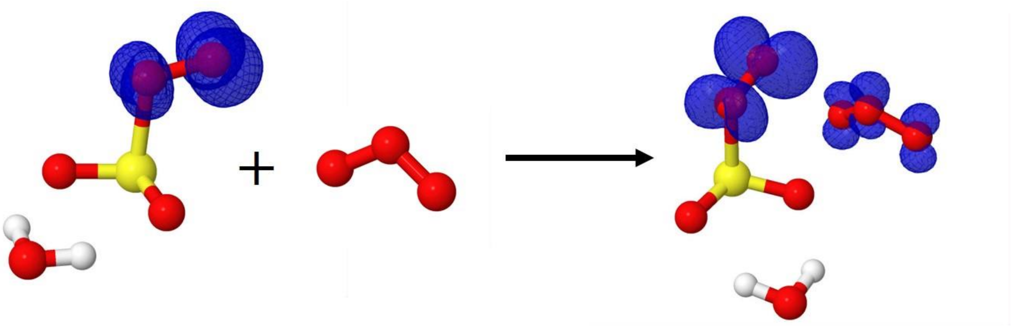

Figure S2 Formation of the $O_3 \cdots O_2SOO^- \cdots H_2O$ from O_3 and $O_2SOO^- \cdots H_2O$ collision. The spin density indicates the migration of the extra charge from O_2SOO in the reactant state to O_3 in the product state.

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 = $O_3 \cdots O_2SOO^-$, $\langle \hat{S}^2 \rangle = 0.7586$

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 = $O_2 \cdots O_2S{-}O_3^-$, $\langle \hat{S}^2 \rangle = 1.7622$

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

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

PC2 = $SO_3^- + 2O_2$, $\langle \hat{S}^2 \rangle = 2.7874$

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

RCW1 = $O_3 \cdots O_2SOO^- \cdots H_2O$, $\langle \hat{S}^2 \rangle = 0.7581$

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

RCW2 = $O_2 \cdots O_2S{-}O_3^- \cdots H_2O$, $\langle \hat{S}^2 \rangle = 1.7622$

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

TSW2, $\langle \hat{S}^2 \rangle = 2.1889$

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

H	-2.40609	0.66567	0.831
O	2.13054	-0.23102	0.46007
O	3.20304	-0.10766	-0.06821
O	0.89594	-0.63242	-0.7352

PCW2 = $SO_3^{-}\cdots H_2O + 2O_2$, $\langle \hat{S}^2 \rangle = 2.7774$

O	0.56126	2.16447	-1.35127
O	1.19219	1.19843	-1.06603
S	-1.72749	-0.66833	-0.04558
O	-1.15768	-0.69161	-1.40703
O	-1.69501	0.79785	0.51526
O	0.73561	1.43542	2.04176
H	-0.0826	1.65884	1.57847
H	0.74348	0.48435	1.87441
O	1.93378	-1.70038	-0.51204
O	-0.60124	-0.97709	1.0023
O	2.40348	-1.15834	0.43658

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