Exploring the atmospheric chemistry of $O_2SO_3^-$ and assessing the maximum turnover number of ion catalysed H_2SO_4 formation

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Supplementary information:

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Table SI-1: Entropies and Gibbs free energies of all species. Transition states energies are given in Table SI-2.

Species	ΔS (cal mol^{-1}K^{-1})	ΔG $_{298.15\ K}$(Hartree)
SO_3	64.911	-623.867143
SO_3^-	66.639	-623.962534
$SO_3^-(H_2O)$	83.571	-700.403577
O_3	56.738	-225.447418
O_3^-	58.879	-225.549824
$O_3^-(H_2O)$	78.503	-301.998782
$O_2SO_3^-$	78.261	-774.337657
$O_2SO_3^-(H_2O)$	95.869	-850.775256
$O_2SO_3^-$ O_3	114.465	-999.780495
$O_2SO_3^-(H_2O)(O_3)$	132.813	-1076.217975
$O_3SO_3^-$	87.203	-849.495301
$O_3SO_3^-(H_2O)$	108.671	-925.933002
O_2	48.948	-150.355933
H_2O	46.449	-76.434954 height

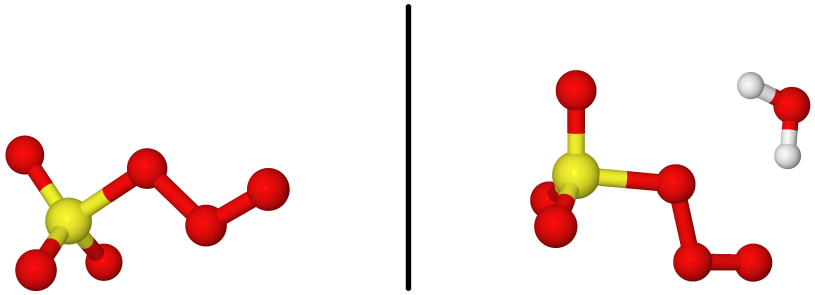

Figure SI-1: Structure of the most stable $O_3SO_3^-$ and $O_3SO_3^-(H_2O)$ clusters. Sulfur (yellow), oxygen (red), hydrogen (white).

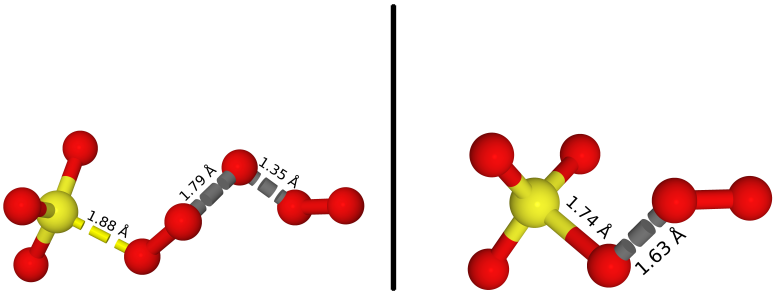

Figure SI-2: Structures of the dehydrated transition states of reaction (R12) and (R13) in the main article. Sulfur (yellow), oxygen (red).

Determining the inherent limitations of ion catalysed SO_2 oxidation.

We here determine the overall probability of reaction (R3a) vs. (R3b). The rates of these reactions are given as

$$\begin{aligned} \mathrm{r}_{3a\ dehyd} &= \mathrm{k}_{3a\ dehyd} * [O_3][O_2SO_3^-] && (1)\\ \mathrm{r}_{3a\ monohyd} &= \mathrm{k}_{3a\ monohyd} * [O_3][O_2SO_3^-(H_2O)] && (2)\\ \mathrm{r}_{3b\ dehyd} &= \mathrm{k}_{3b\ dehyd} * [O_3][O_2SO_3^-] && (3)\\ \mathrm{r}_{3b\ monohyd} &= \mathrm{k}_{3b\ monohyd} * [O_3][O_2SO_3^-(H_2O)] && (4) \end{aligned}$$

The rate constants, k, are determined via transition state theory,

$$\mathrm{k(T)} = \mathrm{A} \times \exp\left(\frac{-\mathrm{E}_A}{\mathrm{RT}}\right). \quad (5)$$

The barrier heights, E_A, and prefactors, A, are given in Table SI-2.

The fraction of hydrated clusters is given by the law of mass action i.e.

$$\frac{[O_2SO_3^-(H_2O)]}{[O_2SO_3^-]} = [H_2O] \times \exp\left(\frac{-\Delta\mathrm{G}}{\mathrm{RT}}\right) \quad (6)$$

where ΔG = ΔH - TΔS, ΔH = -12.3 kJ mol^{-1}, and ΔS = -82.8 J mol^{-1} K^{-1}.

The total rate of reaction (R3a) vs. (R3b) is hereby readily obtained as

$$F = \frac{r_{3a\ dehyd} + r_{3a\ monohyd}}{r_{3b\ dehyd} + r_{3b\ monohyd}} \quad (7)$$

Table SI-2: Enthalpy and entropy changes of the de- and monohydrated reactions (R3a) and (R3b).

Parameter	Reaction	
E_a	(R3a) dehyd.	ΔG = 27.1 kJ mol^{-1}, ΔS = -57.0 J mol^{-1} K^{-1}
A	(R3a) dehyd.	3.12×10^{10} s^{-1}
E_a	(R3a) monohyd.	ΔG = 39.6 mol^{-1}, ΔS = -158.5 J mol^{-1} K^{-1}
A	(R3a) monohyd.	1.90×10^{9} s^{-1}
E_a	(R3b) dehyd.	ΔG = 31.9 kJ mol^{-1}, ΔS = 157.9 J mol^{-1} K^{-1}
A	(R3b) dehyd.	540 cm^{-1} = 1.62×10^{13} s^{-1}
E_a	(R3b) monohyd.	ΔG = 12.3 kJ mol^{-1}, ΔS = -82.8 J mol^{-1} K^{-1}
A	(R3b) monohyd.	540 cm^{-1} = 1.62×10^{13} s^{-1}