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, Gibbs free energies and basis set superposition errors of all stable species calculated with CAM-B3LYP/aug-cc-pVTZ.

Species	ΔS (cal mol^{-1}K^{-1})	ΔG $_{298.15\ K}$(Hartree)	BSSE (kJ mol^{-1})
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	0.52
$O_2SO_3^-$	78.261	-774.337657	1.46
$O_2SO_3^-(H_2O)$	95.869	-850.775256	2.08
$O_2SO_3^-$ O_3	114.465	-999.780495	2.10
$O_2SO_3^-(H_2O)(O_3)$	132.813	-1076.217975	2.68
$O_3SO_3^-$	87.203	-849.495301	1.67
$O_3SO_3^-(H_2O)$	108.671	-925.933002	2.22
O_2	48.948	-150.355933	
H_2O	46.449	-76.434954	

Table SI-2: Relative entropies and gibbs free energies of species corresponding to the potential energy surface shown in Figure 3 in the main article calculated with CAM-B3LYP/aug-cc-pVTZ. Values are corrected for basis set superposition error.

Dehydrated reaction	ΔS(J mol^{-1}K^{-1})	ΔG(kJ(mol)
$O_2SO_3^-$ + O_3	0.0	0.0
$O_2SO_3^-O_3$	-85.9	12.66
O_3^-+O_2+SO_3	157.9	30.50
TS	-147.0	28.8
SO_6^-+O_2	4.8	-173.45
TS	-12.1	-160.0
SO_4^-+2 O_2	140.6	251.4
Monohydrated reaction	**ΔS(J mol^{-1}K^{-1})**	**ΔG(kJ(mol)**
$O_2SO_3^-(H_2O)$ + O_3	0.0	0.0
$O_2SO_3^-(H_2O)O_3$	-82.8	12.9
$O_3^-(H_2O)$+O_2+SO_3	166.3	-0.6
TS	-147.0	35.1
$SO_6^-(H_2O)$+O_2	21.0	-173.8
TS	-5.8	-160.6
$SO_4^-(H_2O)$+2 O_2	158.3	-250.8

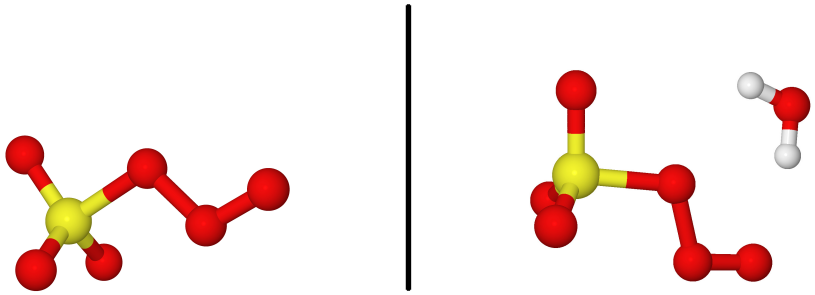

Figure SI-1: Structure of the most stable $O_3SO_3^-$ and $O_3SO_3^-(H_2O)$ clusters. Sulfur (yellow), oxygen (red), hydrogen (white).

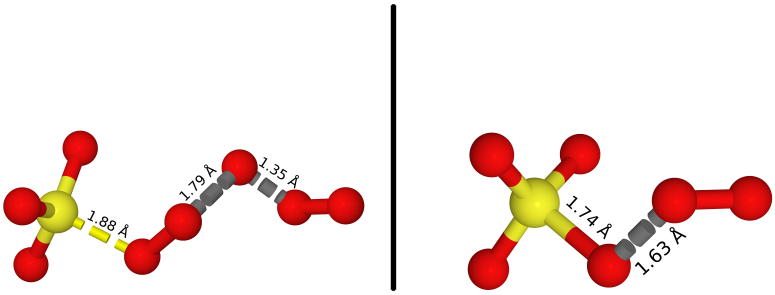

Figure SI-2: Structures of the dehydrated transition states of reaction (R12) and (R13) in the main article. Sulfur (yellow), oxygen (red).

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-3: XYZ coordinates of stable species in Ångstroms.

SO_3			
S	-1.242506	-0.434132	0.000000
O	-1.956959	0.803271	0.000000
O	-1.956959	-1.671534	0.000000
O	0.186364	-0.434132	0.000000
SO_3^-			
S	-1.242745	-0.434132	0.092698
O	-1.961210	0.810919	0.469678
O	-1.961210	-1.679182	0.469678
O	0.195104	-0.434132	0.467946
$SO_3^-(H_2O)$			
S	-0.703534	0.000006	-0.259332
O	0.092226	1.240999	-0.042272
O	-2.019035	-0.000133	0.417778
O	0.092441	-1.240868	-0.042324
O	2.718435	-0.000047	0.157072
H	2.091764	-0.737547	0.113619
H	2.092244	0.737841	0.113655
O_3			
O	0.000000	0.000000	0.425791
O	0.000000	1.063717	-0.212896
O	0.000000	-1.063717	-0.212896
O_3^-			
O	0.000000	0.000000	0.476637
O	0.000000	1.125087	-0.238318
O	0.000000	-1.125087	-0.238318
$O_3^-(H_2O)$			
O	-1.275980	-0.057099	0.000684
O	-0.467785	-1.127033	-0.000454
O	-0.662584	1.118989	-0.000426
O	2.044935	0.031793	0.000168
H	1.271401	-0.574163	-0.000145
H	1.544198	0.857661	-0.000005
$O_2SO_3^-$			
S	-0.492653	-0.065117	-0.000013
O	-1.306145	1.136269	-0.000648
O	-0.468266	-0.830694	-1.230756
O	-0.469002	-0.829851	1.231237
O	2.110299	-0.090974	0.000057
O	1.118420	0.745485	0.000136
$O_2SO_3^-(H_2O)$			
O	-3.107206	-0.619335	0.009221
O	2.121796	-1.272023	0.076638
O	1.190567	-0.822729	-0.707968
S	0.191065	0.445857	0.059139
O	1.148923	1.479429	0.378413
O	-0.411609	-0.247833	1.185531
O	-0.695810	0.699832	-1.065948
H	-2.441360	-0.728296	0.701183
H	-2.588981	-0.144131	-0.654511
$O_2SO_3^-(O_3)$			
S	-0.941890	-0.502628	0.013875
O	-2.008578	-1.329772	-0.509094
O	-0.006465	0.029744	-0.961180
O	-0.373735	-0.895532	1.289856
O	-2.449162	1.575548	-0.368280
O	-1.807324	0.966491	0.581011
O	3.150675	-0.730735	-0.432775
O	2.503989	0.103756	0.216660
O	2.874381	1.285755	0.156051

Table SI-4: XYZ coordinates of stable species in Ångstroms.

$O_2SO_3^-(O_3)(H_2O)$			
O	-3.760072	0.845435	1.267732
O	-1.998277	-1.612739	0.453825
O	-1.160407	-1.430704	-0.518880
S	-0.473203	0.229681	-0.562206
O	0.242046	0.312481	0.694844
O	-1.656949	1.065162	-0.675851
O	0.327432	0.083791	-1.758298
H	-3.445841	-0.044842	1.452713
H	-3.112644	1.137387	0.606168
O	3.457309	1.109474	0.470342
O	2.978681	0.013691	0.143801
O	3.336453	-0.982521	0.789537
$O_3SO_3^-$			
S	-0.881747	-0.043815	0.000050
O	-0.894092	-0.820496	-1.225816
O	-0.893672	-0.819846	1.226330
O	-1.664295	1.176823	-0.000140
O	2.837890	0.178407	0.000151
O	1.696542	-0.339901	-0.000201
O	0.681122	0.712643	-0.000423
$O_3SO_3^-(H_2O)$			
O	0.438866	-0.031188	0.359284
O	0.820146	-1.398481	0.067309
O	2.071259	-1.474456	-0.047398
O	3.091579	1.468017	-0.022802
H	2.952349	0.512252	-0.042573
H	2.190549	1.799306	0.067766
S	-1.253405	0.196675	-0.037066
O	-1.322779	-0.131673	-1.446403
O	-1.296406	1.603537	0.307628
O	-1.938720	-0.718050	0.853365
O_2			
O	0.000000	0.034895	0.021469
O	0.000000	1.053605	0.648231
H_2O			
H	0.764176	-0.465239	0.000000
O	0.000000	0.116284	0.000000
H	-0.764176	-0.465030	0.000000

Table SI-5: Cartesian coordinates (Å) and harmonic frequencies (cm^{-1}) of transition states of Reaction (R3a)

Dehydrated			
S	1.696799	0.089378	-0.031464
O	2.411514	0.193075	1.222670
O	2.085038	-0.985014	-0.919485
O	1.273404	1.323424	-0.654194
O	-0.756669	-0.810417	-0.231269
O	0.130948	-0.550602	0.671802
O	-1.868110	0.599211	-0.445934
O	-2.866908	0.399614	0.435032
O	-3.802815	-0.348046	-0.015694
Frequencies	-321.9394	28.9034	35.6838
	67.1859	119.7483	208.6322
	252.9011	321.4741	365.5565
	434.6550	500.0760	543.4828
	584.2074	609.1592	663.4043
	848.1631	1062.1889	1167.9925
	1192.1632	1323.6536	1327.8310

Monohydrated			
O	-4.139019	-0.723724	0.506573
O	1.027279	-1.222804	-0.290461
O	-0.013047	-0.784810	-0.934377
S	-0.918027	0.483048	-0.027922
O	0.051019	1.544037	0.098670
O	-1.287300	-0.208777	1.193324
O	-1.982726	0.666216	-0.997164
H	-3.359208	-0.785292	1.073296
H	-3.772300	-0.248234	-0.250170
O	3.692386	-0.199709	0.991694
O	2.892432	0.420986	0.213331
O	2.486467	-0.328321	-0.828638
Frequencies	-398.3860	18.7961	24.7694
	44.5390	74.3038	96.3138
	120.3842	150.6197	220.4618
	261.9621	287.3842	318.3708
	337.9176	365.1388	436.2471
	504.9036	549.6088	579.0489
	604.1542	628.7218	673.4874
	846.0554	1058.9886	1145.5589
	1193.9943	1299.3217	1331.9861
	1686.6462	3772.8979	3811.0335

Table SI-6: Cartesian coordinates (Å) and harmonic frequencies (cm^{-1}) of transition states of Reaction (11)

Dehydrated			
S	-0.852454	0.081842	0.047629
O	-0.534869	1.530032	-0.002265
O	-1.854504	-0.406808	-0.934389
O	-0.935267	-0.496415	1.411700
O	2.731013	0.276631	-0.185921
O	1.780503	-0.367126	0.296526
O	0.518033	-0.699998	-0.680909
Frequencies	-422.1284	100.4235	113.9359
	181.0144	323.581	346.5348
	472.8692	507.5197	530.5524
	560.7382	706.7543	994.0551
	1223.0578	1223.683	1308.5782

Monohydrated			
O	-2.039858	2.123877	-0.060867
O	0.450184	1.094480	-0.895909
S	1.079592	0.086975	-0.044124
O	1.687418	-1.010922	-0.769579
O	-0.209700	-0.603318	0.805920
O	-1.141454	-1.382531	-0.266024
O	-2.293259	-1.411597	0.151230
O	1.808043	0.600521	1.100293
H	-1.159032	1.885708	-0.405576
H	-2.205438	1.438608	0.591047
Frequencies	-166.2702	34.2897	49.0112
	55.3997	131.4588	163.2900
	193.2041	207.3905	363.6081
	378.1218	386.2142	446.2851
	549.6016	556.6035	608.8597
	663.4326	784.4685	1056.4784
	1266.7248	1309.2055	1388.5282
	1684.7588	3600.2298	3885.8532

Table SI-7: Thermodynamic data of the transition states of the de- and monohydrated reactions (R3a) and (R3b). Values are corrected for basis set superposition error.

Parameter	Reaction	
E_a	(R3a) dehyd.	ΔG = 28.8 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 = 35.1 mol^{-1}, ΔS = -147.0 J mol^{-1} K^{-1}
A	(R3a) monohyd.	7.40×10^{9} s^{-1}
E_a	(R3b) dehyd.	ΔG = 30.5 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 = 12.9 kJ mol^{-1}, ΔS = -82.8 J mol^{-1} K^{-1}
A	(R3b) monohyd.	540 cm^{-1} = 1.62×10^{13} s^{-1}