Structures and reaction rates of the gaseous oxidation of SO₂ by an O₃⁻(H₂O)₀₋₅ cluster - an ab initio study

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Supplementary information:

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Figure SI-1: Structures of the most stable $\text{SO}_3^-(\text{H}_2\text{O})_n$ clusters. Structurally, these are similar to the $\text{O}_2\text{SO}_3^-(\text{H}_2\text{O})_n$ complexes shown in Fig. 7 in the main article. Sulfur (yellow), oxygen (red), hydrogen (white).

Table SI-1: Gibbs free energies of the most important configurations, relative to the sum of the $\text{O}_3^-(\text{H}_2\text{O})_n$ and SO_2 energies at $T = 298.15$ K. Units are kJ/mol. See also Fig. 3 in the main article.

n	$\text{O}_3^-\text{SO}_2\text{W}_n$	$\text{TS}_{\min}$	$\text{SO}_3^-\text{O}_2\text{W}_n$	$\text{SO}_3^-\text{W}_n+\text{O}_2$
0	-87	-59	-242	-217
1	-60	-38	-212	-196
2	-50	-34	-200	-194
3	-42	-26	-192	-191
4	-41	-19	-184	-178
5	-34	-9	-175	-174

Table SI-2: Harmonic prefactors, entropy and Gibbs free energies of the "loose" and "tight" transition states at standard conditions. There seems to be no apparent reason for the large prefactor for the "loose" $n=4$ complex. Units are cm^{-1} and kJ/mol.

n	Loose TS			Tight TS		
	$\log_{10}(A)$	$\Delta S \cdot T$	ΔG	$\log_{10}(A)$	$\Delta S \cdot T$	ΔG
0	13.6	1.3	27.6	13.6	1.3	27.6
1	13.4	-1.5	28.9	13.4	0.5	22.1
2	13.5	1.9	20.1	13.8	2.6	16.6
3	13.9	20.9	16.5	13.7	1.7	24.5
4	15.0	29.3	21.7	14.0	3.0	26.3
5	13.8	25.2	26.3	13.9	2.9	25.6

Table SI-3: Frequencies (cm^{-1}) for the most stable $\text{SO}_2\text{O}_3^-(\text{H}_2\text{O})_n$ clusters, shown in Fig. 2 in the main article.

n=0	n=1	n=2	n=3	n=4	n=5
50	29	11	43	40	30
64	48	41	55	58	32
171	61	55	63	65	48
235	105	73	75	71	56
336	161	94	86	81	62
463	190	128	121	87	72
525	266	169	150	101	79
622	322	185	155	136	86
843	353	194	181	159	104
1083	383	259	185	167	136
1182	489	344	202	188	141
1236	540	364	207	197	171
	620	412	265	228	181
	664	434	360	236	194
	828	459	451	247	202
	1070	524	454	255	229
	1152	538	478	339	240
	1246	629	511	438	253
	1694	688	543	460	279
	3740	746	578	488	340
	3767	829	596	496	345
		1072	635	521	395
		1164	661	561	437
		1269	722	593	457
		1678	742	618	475
		1696	839	629	501
		3621	965	651	517
		3696	1075	721	547
		3750	1159	743	597
		3824	1266	811	616
			1650	823	628
			1678	842	637
			1697	1022	692
			3559	1083	734
			3614	1169	775
			3631	1258	820
			3675	1687	824
			3677	1694	840
			3775	1699	1021
				1705	1082
				3407	1165
				3509	1260
				3522	1671
				3579	1683
				3657	1692
				3677	1699
				3774	1707
				3790	3434
					3507
					3526
					3560
					3606
					3648
					3698
					3769
					3782
					3853

Table SI-4: Frequencies (cm^{-1}) for the most stable "tight" transition states, shown in Fig. 4 in the main article.

n=0	n=1	n=2	n=3	n=4	n=5
i831	i776	i753	i569	i555	i557
23	25	12	26	29	26
79	34	23	46	42	32
123	72	40	54	53	39
308	106	63	78	65	43
390	136	83	86	81	51
448	181	139	118	85	62
509	320	144	149	90	80
663	338	181	160	122	85
1035	401	200	164	158	89
1123	412	235	199	173	125
1411	459	326	203	182	138
	520	409	211	195	164
	658	419	280	220	187
	701	448	365	237	193
	1022	493	445	273	208
	1094	526	474	273	225
	1434	578	488	349	267
	1699	646	490	367	272
	3719	701	552	428	275
	3736	845	562	445	333
		1020	582	490	350
		1097	598	522	369
		1441	667	557	400
		1663	767	569	432
		1699	782	593	444
		3363	950	630	489
		3659	1045	667	513
		3729	1108	763	542
		3897	1508	774	570
			1679	820	593
			1683	838	638
			1705	1025	672
			3534	1046	697
			3563	1111	775
			3594	1511	805
			3670	1681	832
			3702	1693	849
			3743	1702	1022
				1704	1046
				3344	1107
				3434	1511
				3532	1674
				3579	1681
				3607	1691
				3654	1697
				3727	1705
				3878	3356
					3475
					3494
					3574
					3577
					3600
					3688
					3716
					3855
					3879

Table SI-5: Frequencies (cm^{-1}) for the most stable "loose" transition states, shown in Fig. 6 in the main article.

n=0	n=1	n=2	n=3	n=4	n=5
i831	i816	i765	i731	i713	i705
23	45	22	16	9	14
79	57	37	24	20	18
123	74	54	34	26	24
308	81	68	43	36	28
390	131	72	52	44	35
448	189	97	67	51	40
509	275	139	70	64	50
663	314	172	91	75	62
1035	411	183	132	78	69
1123	424	246	159	113	82
1411	463	315	165	137	91
	525	326	191	155	95
	635	378	235	178	137
	722	394	268	184	156
	1021	430	290	191	168
	1121	470	319	210	181
	1410	532	359	218	197
	1685	638	365	284	228
	3530	670	386	307	250
	3874	703	427	343	264
		1009	475	363	283
		1093	532	373	317
		1433	622	428	336
		1677	636	438	349
		1693	664	474	363
		3565	693	528	402
		3713	1009	536	432
		3790	1074	621	461
		3882	1461	632	474
			1673	655	480
			1675	687	528
			1690	786	551
			3582	1009	609
			3617	1076	615
			3735	1453	632
			3810	1655	677
			3881	1667	808
			3882	1673	879
				1691	1009
				3498	1084
				3633	1456
				3670	1665
				3703	1666
				3765	1668
				3878	1676
				3889	1683
				3898	3371
					3448
					3650
					3664
					3767
					3808
					3818
					3869
					3888
					3899

Table SI-6: Frequencies (cm^{-1}) for the configurations into which the "loose" transition states relax on the reactant side.

n=0	n=1	n=2	n=3	n=4	n=5
50	39	27	27	28	20
64	60	38	31	35	22
171	70	57	39	39	30
235	104	69	44	44	31
336	152	87	66	53	39
463	174	101	72	74	40
525	267	154	88	77	54
622	338	169	99	84	65
843	375	182	142	99	77
1083	398	279	151	121	85
1182	439	303	170	138	96
1236	542	346	184	162	122
	621	354	266	176	141
	661	366	285	180	143
	828	380	309	199	173
	1074	455	326	274	178
	1170	554	339	292	185
	1254	611	350	297	209
	1690	640	356	310	249
	3666	649	376	334	275
	3819	806	457	354	284
		1059	551	357	292
		1136	599	382	321
		1268	610	439	328
		1680	621	456	356
		1690	632	504	382
		3676	794	545	402
		3734	1060	575	458
		3809	1129	597	466
		3840	1271	622	482
			1671	668	551
			1674	730	551
			1687	809	574
			3697	1063	589
			3720	1138	616
			3762	1260	680
			3819	1656	746
			3850	1667	797
			3853	1678	857
				1690	1062
				3590	1134
				3701	1271
				3736	1662
				3754	1665
				3780	1673
				3849	1676
				3853	1684
				3877	3400
					3591
					3668
					3713
					3780
					3804
					3817
					3832
					3879
					3901