Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary deposit.

The Gas-Phase Reaction of Methane Sulfonic Acid with Hydroxyl Radical without and with Water Vapor

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Formation of H_2SO_4

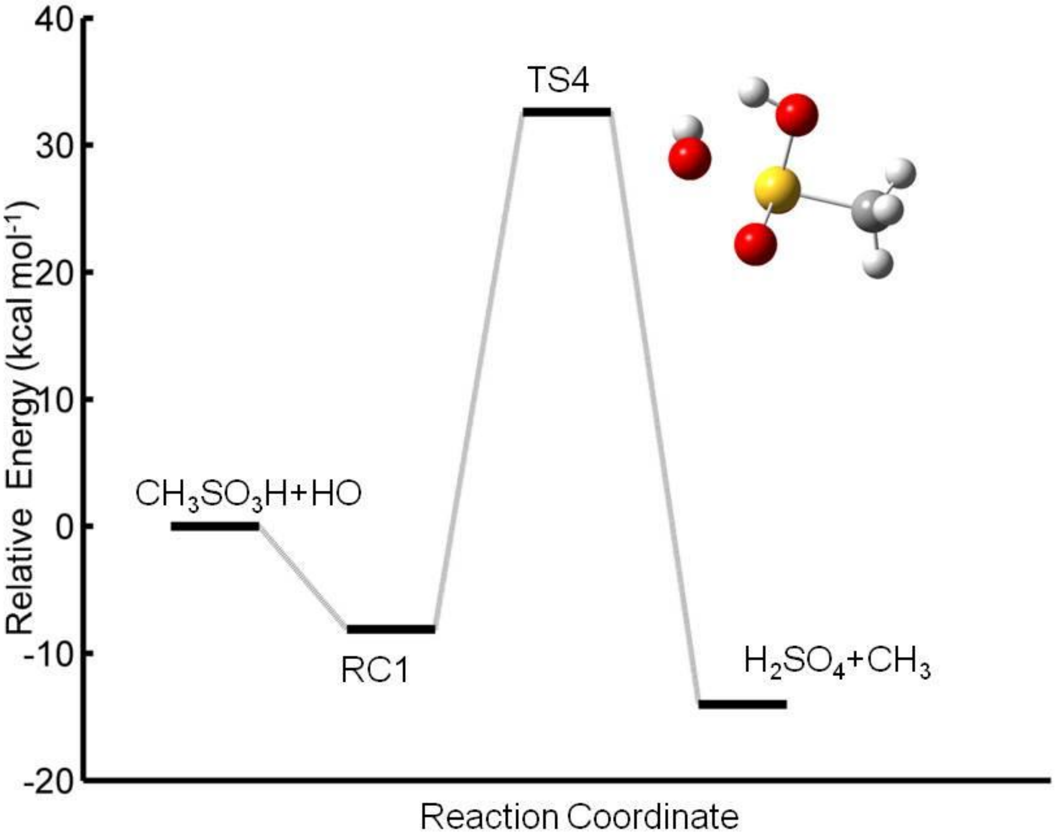
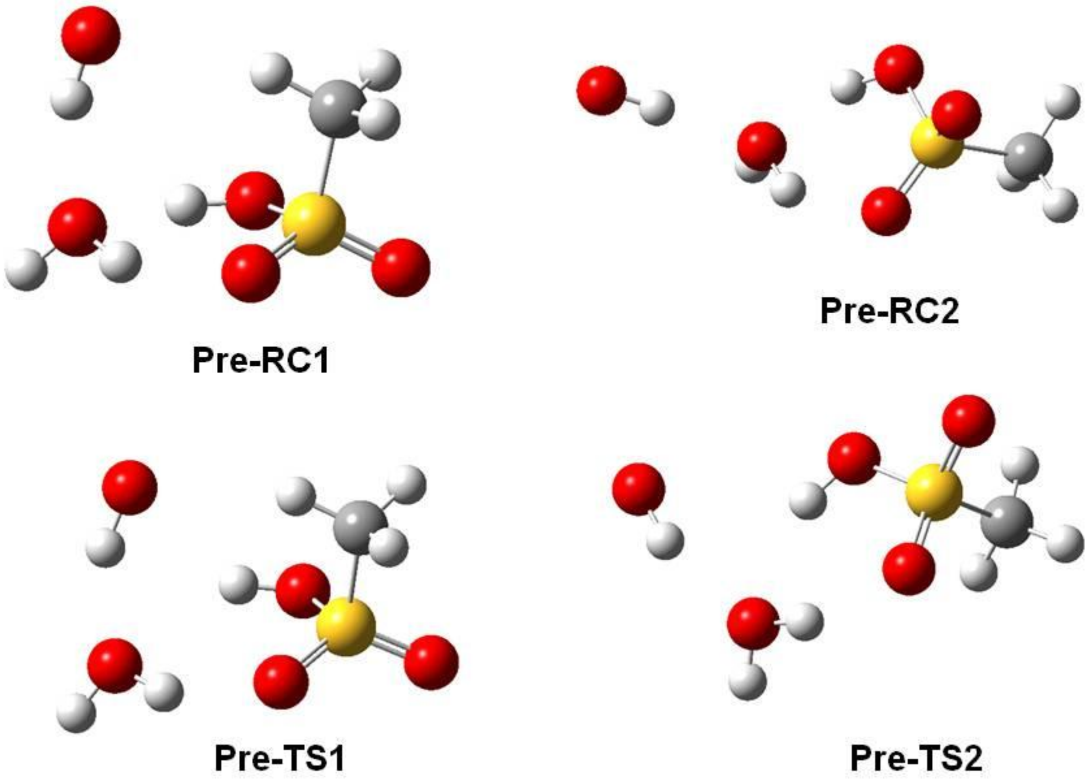


Figure S1. Energy profile for the reaction CH_3SO_3H + HO → H_2SO_4 + CH_3 obtained at CCSD(T)-F12a/VDZ-F12//B3LYP/aug-cc-pV(T+d)Z level of theory. The energy includes zero point vibrational energy obtained at B3LYP/aug-cc-pV(T+d)Z level of theory. The reaction coordinate of the transition state TS4 is 607i cm^{-1}.

Formation of pre-pre reactive complex and transition states.



Pre-RC1

Pre-RC2

Pre-TS1

Pre-TS2

Figure S2. Geometries of the pre-pre-reactive complexes and pre-transition states for the formation of the RC1 and RC2 complexes for the M1 and M2 complexes optimized at B3LYP/aug-cc-pV(T+d)Z level of theory.

Rate constants for the reaction between $CH_3SO_3H{\bullet}H_2O$ and HO

The rate constant for reaction channel like M1+HO → pre-RC1→RC1w→PC1w is given by

$$k_i = K_{eq}\left(\frac{k_2 + k_3}{k_2 k_3}\right)k_2$$

Where the K_{eq} is the equilibrium constant for the formation pre-RC1 from M1+HO, k_2 is the rate constant for the formation of RC1w from pre-RC1 through pre-TS1, and k_3 is the rate constant for the formation of PC1w from RC1w through the TS1aw. In Tables S1 and S2 we have collected the corresponding equilibrium and kinetic constants computed at 298 K.

The rate constants for M1 + HO and M2 + OH leading to the products CH_3SO_3 + $(H_2O)_2$ are 2.43×10^{-18} and 1.39×10^{-16} cm^3 s^{-1} $molecule^{-1}$, respectively. The branching ratio of CH_3SO_3 + $(H_2O)_2$ is 0.01 and 3 % for M1+HO and M2+HO, respectively. Taking into account that relative abundance of M1 and M2 is 44.2 and 19.0 % we can estimate an effective rate constant of $0.0001*0.442*2.43\times10^{-18}+0.03*0.19*1.39\times10^{-16}=5.31\times10^{-19}$ cm^3 s^{-1} $molecule^{-1}$ which is four orders of magnitude lower than the bare reaction (8.31×10^{-15} cm^3 s^{-1} $molecule^{-1}$).

Table S1: Equilibrium constant K_{eq} (in cm^3 molecule^{-1}); tunneling parameters Γ; rate coefficients k_3, k_2 (in s^{-1}) and the rate constant k_i (in cm^3 s^{-1} molecule^{-1}) for the different reaction pathways at 298.15 K for the reaction between M1 + HO. The overall rate constant (k_{TOT}) and branching ratios δ (in %) are also included.

Reaction path	K_{eq}	Γ_2	k_2[a]	Γ_3	k_3[a]	k_i	δ
M1→RC1w→TS1aw	8.73×10^{-24}	1.03	3.96×10^{12}	330.8	1.43×10^{-3}	4.14×10^{-24}	0.0
M1→RC1w→TS2aw	8.73×10^{-24}	1.03	3.96×10^{12}	6.8	4.08×10^{4}	2.43×10^{-18}	0.0
M1→RC1w→TS3w	8.73×10^{-24}	1.03	3.96×10^{12}	1.8	5.72×10^{6}	8.99×10^{-17}	0.2
M1→RC1w→pre-TS1	8.73×10^{-24}	1.03	3.96×10^{12}	1.03	4.99×10^{9}	4.48×10^{-14}	99.8
k_{TOT}						4.49×10^{-14}	

[a] The rate constant is without tunneling coefficient.

Table S2: Equilibrium constant K_{eq} (in cm^3 molecule^{-1}); tunneling parameters Γ; rate coefficients k_3, k_2 (in s^{-1}) and the rate constant k_i (in cm^3 s^{-1} molecule^{-1}) for the different reaction pathways at 298.15 K for the reaction between M2 + HO. The overall rate constant (k_{TOT}) and branching ratios δ (in %) are also included.

Reaction path	K_{eq}	Γ_2	k_2[a]	Γ_3	k_3[a]	k_i	δ
M2→RC2w→TS1bw	3.37×10^{-23}	1.0	1.84×10^{10}	9.3	2.10×10^{-4}	6.59×10^{-26}	0.0
M2→RC2w→TS2bw	3.37×10^{-23}	1.0	1.84×10^{10}	6.4	5.07×10^{5}	1.10×10^{-16}	2.4
M2→RC2w→TS2cw	3.37×10^{-23}	1.0	1.84×10^{10}	2.3	3.73×10^{5}	2.89×10^{-17}	0.6
M2→RC2w→TS3w	3.37×10^{-23}	1.0	1.84×10^{10}	1.8	5.72×10^{6}	3.47×10^{-16}	7.5
M2→RC2w→pre-TS2	3.37×10^{-23}	1.0	1.84×10^{10}	1.0	1.22×10^{8}	4.13×10^{-15}	89.5
k_{TOT}						4.61×10^{-15}	

[a] The rate constant is without tunneling coefficient.

Anharmonic and Harmonic Frequencies

In order to help for a possible experimental identification of these complexes we have collected in Table S3 the most important calculated stretching frequencies (anharmonic values) and their intensities for M1 to M5 along with the corresponding values for MSA and H_2O, respectively. The full set of the computed harmonic and anharmonic values can be found in the supplementary material. The M1 and M2 complex differ only in the orientation of the dangling hydrogen atom and consequently both complexes present very similar IR spectra. Our calculations predict a very intense band close to to 2950 cm^{-1}, that corresponds to the (S)O-H stretching, and that can be considered as fingerprints for identifying the M1 and M2. Our results also predict that this band is red-shifted, with respect the (S)O-H stretching band of MSA, by as much as 653 (635) cm^{-1} for M1 (M2) complexes, and their relative intensity is enhanced from 126 up to 1190 $km \cdot mol^{-1}$. These large red-shifts are in agreement with the very short (S)O-H···OH_2 bond lengths (1.699 Å) in both complexes and with their great stability. In addition, our calculations predict red-shifts of 144 and 134 cm^{-1} for the O-H stretching mode of water forming an hydrogen bond with MSA. In the M3 to M5 complexes the the O-H stretching vibration of the water moiety is moderately red-shifted (up to 94 cm^{-1}). All the harmonic and anharmonic frequencies are given Tables S4-S6.

Table S3: The most relevant anharmonic stretching frequencies (in cm^{-1}) and the corresponding intensities (in km mol^{-1}) for CH_3SO_3H, H_2O and the $CH_3SO_3H•H_2O$ complexes, computed at B3LYP/aug-cc-pV(T+d)Z level

Mode	CH_3SO_3H	H_2O	M1	M2	M3	M4	M5
asym-(H)O-H	--	3723(63)	3677 (117)	3681 (110)	3674(107)	3705(108)	3694(111)
sym-(H)O-H	--	3634 (5)	3490 (176)	3500(163)	3540 (170)	3564 (166)	3628 (32)
(S)O-H	3596(126)	--	2943(1176)	2961(1190)	3570 (129)	3560 (124)	3567 (138)
C-H	3020 (0.2)	--	3019 (0.5)	3017 (0.3)	3027 (0.2)	3029 (0.2)	3021 (6)
C-H	3012(0.2)	--	3012 (4)	3012 (2)	3019 (6)	3022 (5)	3006 (6)
C-H	2948 (0.2)	--	2947 (0.3)	2946 (0.5)	2952(6)	2956 (4)	2939 (8)
S=O	1371(277)	--	1364 (236)	1358 (268)	1366 (307)	1363 (295)	1364 (265)
S=O	1177 (201)	--	1147 (154)	1145 (141)	1166 (213)	1187 (224)	1176 (204)
S-O(H)	787 (211)	--	843 (184)	842(183)	799 (210)	821 (209)	783 (194)

Table S4: Computed Harmonic (H) and anharmonic (AH) frequencies (in cm^{-1}) for the $CH_3SO_3H{\bullet}H_2O$ complexes, obtained at B3LYP/aug-cc-pv(T+d)Z level of theory.

	M1		M2		M3		M4		M5	
mode	H	AH	H	AH	H	AH	H	AH	H	AH
1	3859	3677	3865	3681	3876	3674	3874	3705	3880	3694
2	3678	3491	3686	3500	3766	3570	3766	3560	3772	3628
3	3179	2943	3193	2961	3724	3540	3723	3564	3767	3567
4	3164	3019	3164	3017	3167	3027	3168	3029	3161	3021
5	3157	3012	3156	3012	3155	3019	3157	3022	3154	3006
6	3064	2947	3065	2946	3061	2952	3063	2956	3057	2939
7	1624	1579	1624	1574	1638	1587	1636	1590	1629	1630
8	1462	1415	1461	1415	1461	1418	1460	1409	1468	1446
9	1459	1420	1459	1421	1455	1418	1455	1416	1460	1418
10	1413	1364	1406	1358	1388	1366	1393	1363	1407	1364
11	1359	1328	1359	1327	1366	1342	1365	1342	1365	1322
12	1325	1284	1322	1275	1189	1166	1187	1166	1198	1176
13	1166	1147	1166	1146	1130	1086	1123	1067	1130	1097
14	994	977	994	973	1003	981	1001	971	1000	976
15	983	963	982	962	986	966	987	966	992	986
16	864	843	864	842	819	799	821	791	797	783
17	805	721	785	658	727	712	727	710	716	701
18	739	723	740	720	519	511	518	509	516	507
19	583	494	562	413	499	464	502	461	490	489
20	522	514	520	511	462	340	461	399	449	435
21	505	496	502	493	439	434	442	386	391	313
22	463	448	469	447	335	319	339	299	336	293
23	350	237	333	294	318	286	311	305	312	301
24	330	322	324	240	304	294	291	372	250	178

25	301	295.414	300	292	222	150	231	--	218	62
26	266	235.387	246	268	203	--	207	89	198	219
27	224	198.479	222	202	137	--	139	--	137	581
28	208	183.216	203	190	123	--	125	--	101	176
29	153	110.264	150	101	86	13	79	14	81	88
30	39	0.362	40	8	24	17	21	--	17	90

Table S5: Computed Harmonic (H) and anharmonic (AH) frequencies (in cm^{-1}) for CH_3SO_3H.

Mode	H	A
1	3766	3596
2	3166.	3020
3	3157	3012
4	3065	2948
5	1461	1421
6	1459	1418
7	1405	1372
8	1358	1330
9	1197	1177
10	1127	1086
11	991	973
12	981	961
13	812	787
14	725	708
15	516	508
16	490	487
17	437	368
18	331	313
19	310	328
20	224	201
21	201	203

Table S6: Computed Harmonic (H) and anharmonic (AH) frequencies (in cm^{-1}) for H_2O

Mode	H	AH
1	1627	1575
2	3900	3723
3	3797	3634