Supplementary Information for ***Acta Phys. -Chim. Sin.*** **2013**, *29* (6): 1161-1167
doi: 10.3866/PKU.WHXB201304021

CH_3SO_3 裂解反应的机理和热力学性质

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Mechanism and Thermodynamic Properties of CH_3SO_3 Decomposition

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Table S1 Zero point energies (ZPE, Hartrees), electronic energies (*E*, Hartrees), relative energies (E_R, kJ•mol^{-1}) of the reactant, intermediates, transition states, products for the decomposition of CH_3SO_3

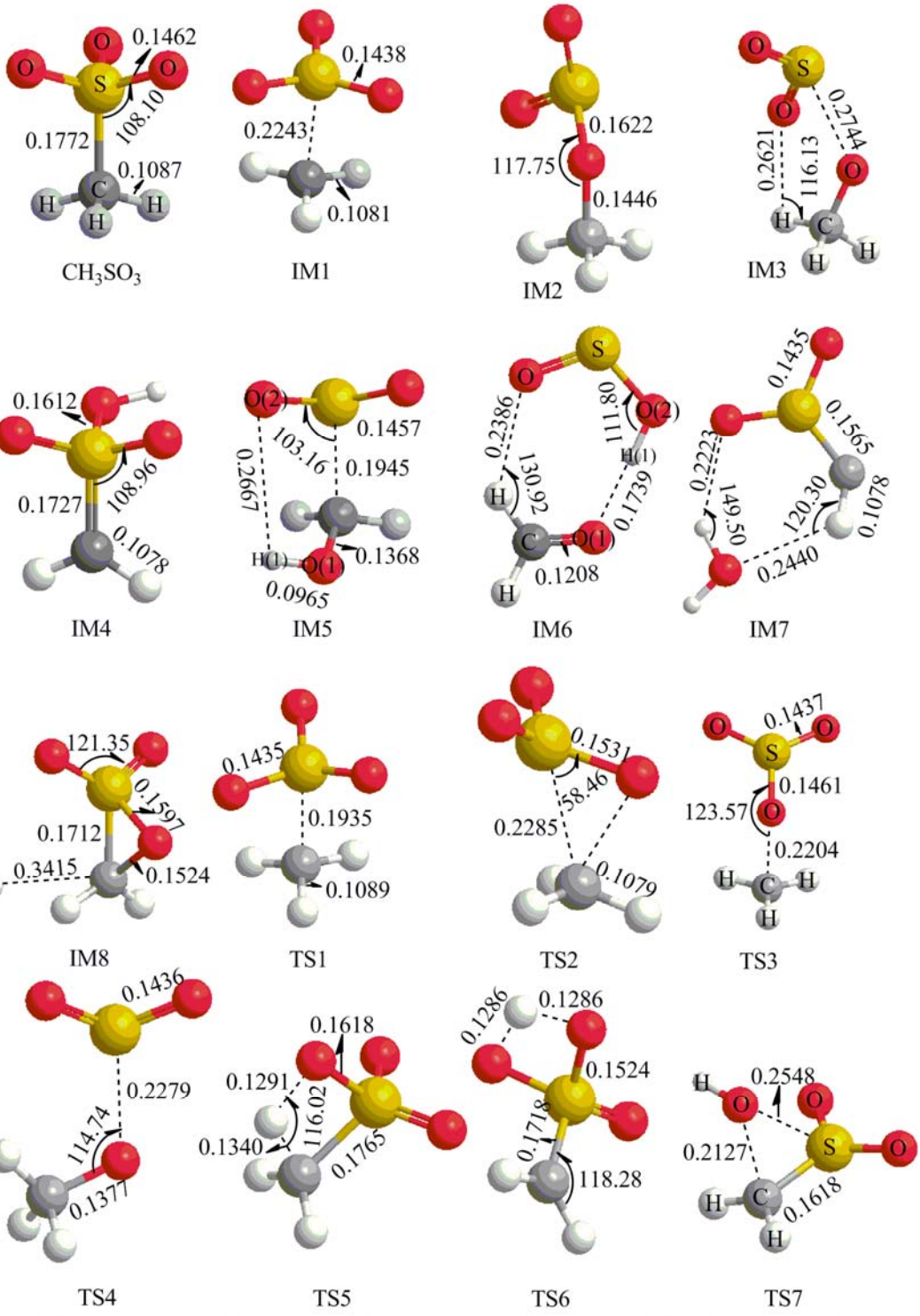
Species	ZPE[a]	E[b]	E_R[b]
CH_3SO_3	0.048072	-662.953550	0.00
IM1	0.046720	-662.934059	51.17
IM2	0.050328	-662.967974	-37.87
IM3	0.045005	-662.937810	41.33
IM4	0.047562	-662.960908	-19.32
IM5	0.050143	-662.968629	-39.58
IM6	0.046280	-662.983849	-79.55
IM7	0.044302	-662.888840	169.90
IM8	0.040396	-662.867206	226.70
TS1	0.047387	-662.928966	64.55
TS2	0.047265	-662.894501	155.03
TS3	0.044627	-662.908052	119.46
TS4	0.045991	-662.938207	40.28
TS5	0.043718	-662.902877	133.04
TS6	0.043363	-662.911694	109.89
TS7	0.045855	-662.880819	190.96
TS8	0.043174	-662.948420	13.47
TS9	0.042199	-662.836900	306.27
TS10	0.042442	-662.854946	258.89
TS11	0.040541	-662.848040	277.02
TS12	0.041424	-662.855712	256.87
TS13	0.038407	-662.809969	376.97
P1(CH_3+SO_3)	0.042028	-662.929351	63.53
P2(CH_3O+SO_2)	0.043106	-662.940592	34.02
P3(HCHO+HOSO)	0.043026	-662.971094	-46.06
P4($CHSO_2$+H_2O)	0.047958	-662.881980	187.91
P5(CH_2SO_3+H)	0.040110	-662.864484	233.84
P6($CHSO_3$+H_2)	0.036663	-662.865509	231.15

[a] at the B3LYP/6-311+G(3df,2p) level.
[b] at the G3XMP2//B3LYP/6-311+G(3df,2p).

Table S2 Moments of inertia and vibrational frequencies for the reactant, complexes and transition states computed at the B3LYP/6-311+G(3df,2p) level of theory

Species	I_A, I_B, I_C/a.u.	Frequencies (cm^{-1})
CH_3SO_3	342.7, 387.9, 388.06	137, 141, 206, 327, 327, 523, 754, 968, 970, 997, 999, 1082, 1368, 1461, 1461, 3063, 3160, 3160
IM1	362.5, 436.4, 436.5	140, 157, 175, 175, 488, 507, 508, 587, 590, 1026, 1087, 1306, 1307, 1418, 1419, 3092, 3263, 3264
IM2	208.5, 494.6, 667.6	82, 133, 244, 406, 469, 526, 689, 993, 1101, 1174, 1183, 1296, 1468, 1489, 1502, 3050, 3132, 3155
IM3	248.4, 782.2, 912.6	36, 60, 89, 104, 161, 190, 526, 841, 1011, 1110, 1172, 1344, 1357, 1375, 1501, 2877, 2971, 3031
IM4	362.9, 375.8, 389.1	71, 274, 285, 355, 445, 482, 537, 553, 768, 827, 928, 1130, 1186, 1388, 1411, 3160, 3301, 3779
IM5	260.6, 535.7, 656.5	77, 198, 244, 347, 442, 478, 554, 888, 1068, 1126, 1168, 1261, 1275, 1394, 1487, 3048, 3161, 3796
IM6	233.7, 858.5, 1083.5	44, 69, 118, 156, 225, 242, 430, 740, 823, 1138, 1228, 1260, 1287, 1526, 1784, 2937, 3034, 3274
IM7	183.6, 841.3, 1016.5	44, 65, 96, 116, 227, 295, 365, 370, 486, 517, 701, 995, 1242, 1349, 1631, 3254, 3788, 3909
IM8	305.9, 400.8, 461.2	25, 25, 77, 295, 412, 452, 480, 635, 784, 888, 969, 1064, 1163, 1250, 1403, 1463, 3118, 3230
TS1	343.6, 396.0, 413.9	241*i*, 174, 228, 297, 464, 471, 514, 849, 863, 865, 1156, 1261, 1329, 1399, 1451, 3053, 3189, 3238
TS2	272.3, 458.1, 553.8	675*i*, 92, 145, 300, 439, 478, 532, 822, 831, 929, 1159, 1225, 1331, 1422, 1457, 3094, 3245, 3246
TS3	246.6, 645.4, 764.9	411*i*, 42, 64, 98, 417, 470, 487, 521, 524, 852, 963, 1257, 1344, 1417, 1421, 3118, 3294, 3301
TS4	222.3, 685.5, 857.8	192*i*, 63, 117, 126, 224, 242, 517, 978, 1058, 1118, 1167, 1356, 1368, 1384, 1506, 2915, 2995, 3057
TS5	323.1, 378.5, 420.5	269, 359, 422, 436, 487, 581, 733, 803, 919, 975, 1058, 1203, 1373, 1399, 1813, 3117, 3243
TS6	325.9, 369.2, 418.6	114, 281, 336, 462, 489, 558, 665, 805, 937, 959, 1019, 1067, 1351, 1390, 2130, 3164, 3306
TS7	304.4, 515.1, 594.1	129, 146, 303, 324, 390, 487, 663, 737, 778, 929, 946, 1221, 1389, 1412, 3189, 3324, 3763
TS8	211.7, 777.3, 846.0	1186*i*, 68, 121, 157, 328, 443, 479, 619, 950, 1057, 1181, 1211, 1315, 1440, 1592, 1724, 3077, 3191
TS9	274.2, 580.8, 686.4	1343*i*, 36, 114, 297, 313, 376, 440, 450, 639, 824, 959, 1077, 1137, 1272, 1420, 2238, 3128, 3784
TS10	346.4, 424.8, 440.0	1364*i*, 210, 284, 305, 315, 462, 512, 525, 677, 775, 860, 1013, 1192, 1307, 1398, 1865, 3155, 3775
TS11	287.4, 369.9, 447.6	1130*i*, 222, 317, 329, 428, 448, 496, 612, 772, 818,

		894, 925, 1028, 1236, 1409, 1418, 3155, 3288
TS12	280.8, 370.2, 453.9	874*i*, 264, 339, 359, 452, 453, 498, 582, 784, 869, 913, 1053, 1145, 1237, 1404, 1420, 3142, 3269
TS13	338.8, 382.7, 399.6	638*i*, 135, 263, 278, 406, 467, 491, 517, 563, 703, 728, 774, 1030, 1108, 1212, 1346, 3189, 3648
CH_3	6.3, 6.3, 12.6	539, 1407, 1407, 3108, 3284, 3284
SO_3	174.0, 174.1, 348.1	495, 524, 525, 1076, 1399, 1400
HOSO	51.9, 191.6, 242.6	97, 394, 759, 1066, 1178, 3748
HCHO	6.34, 45.9, 52.3	1198, 1266, 1531, 1820, 2886, 2944
$CHSO_2$	177.8, 185.2, 361.5	229, 358, 471, 492, 634, 996, 1240, 1360, 3276
H_2O	2.2, 4.2, 6.4	1626, 3825, 3929
CH_2SO_3	249.6, 343.7, 460.5	295, 412, 456, 480, 636, 784, 888, 969, 1064, 1164, 1251, 1403, 1463, 3117, 3229
SO_2	30.1, 175.5, 205.6	519, 1179, 1377
CH_3O	11.4, 64.1, 64.5	695, 960, 1109, 1355, 1365, 1512, 2883, 2962, 3006
$CHSO_3$	235.3, 336.4, 457.7	304, 391, 442, 448, 527, 713, 802, 1081, 1122, 1255, 1405, 3183
H_2	1.0, 1.0	4422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S
O
O
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0.1772
C
0.1087
H
H
H
CH_3SO_3
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0.2243
0.1081
IM1
0.1622
117.75
0.1446
IM2
O
S
O
0.2744
0.2621
116.13
O
H
C
H
H
IM3
0.1612
108.96
0.1727
0.1078
IM4
O(2)
0.1457
103.16
0.2967
0.1945
H(1)
O(1)
0.1368
0.0965
IM5
S
O
O(2)
111.80
0.2386
H(1)
130.92
0.1739
H
C
O(1)
0.1208
H
IM6
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0.1565
0.2223
149.50
120.30
0.1078
0.2440
IM7
121.35
0.1597
0.1712
0.3415
0.1524
IM8
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0.1935
0.1089
TS1
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TS2
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S
O
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123.57
O
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H
C
H
H
TS3
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C
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H
TS7

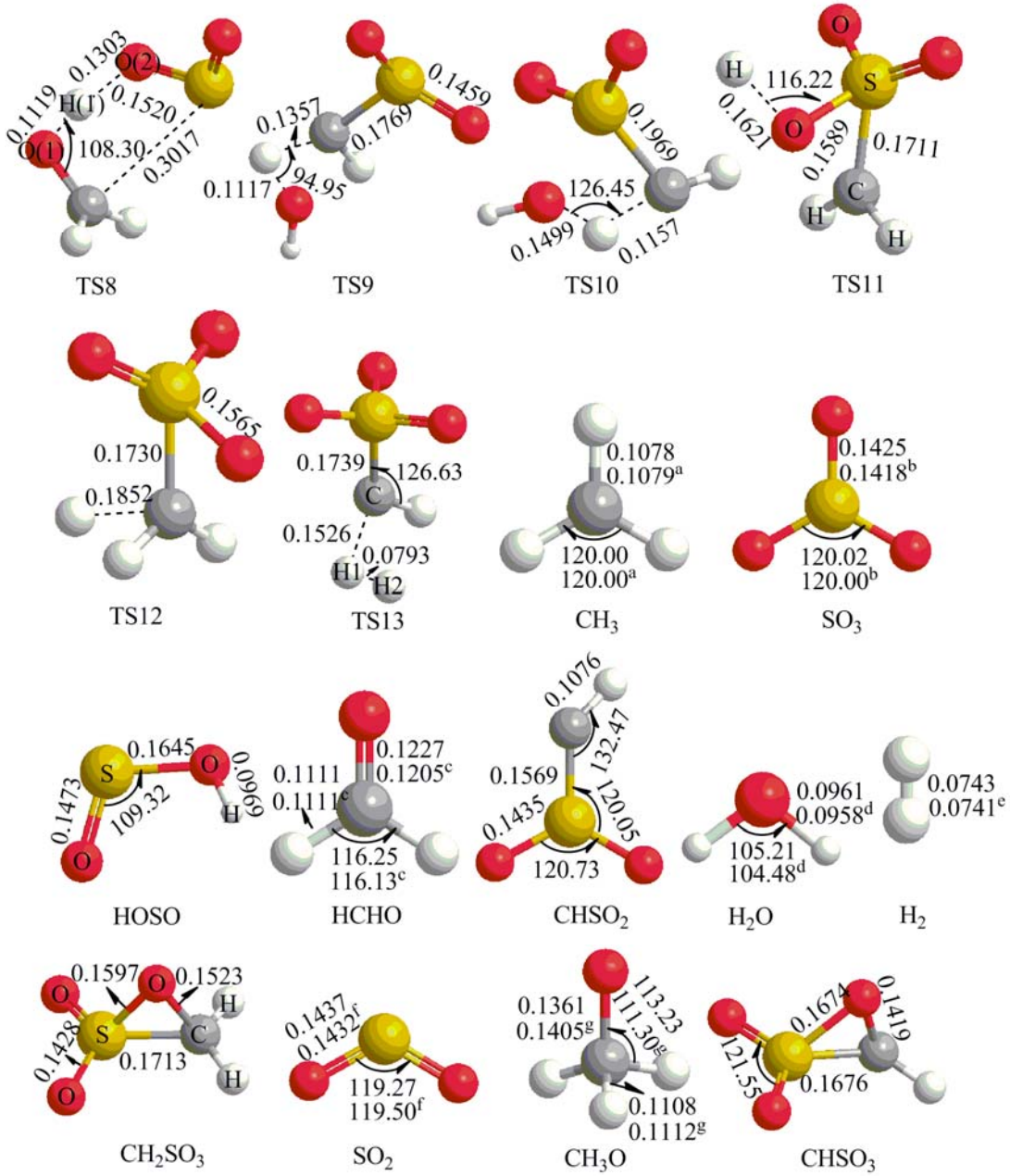

Fig.S1 Optimized geometries of all the species at the B3LYP/6-311+G(3df,2p) level of theory. Bond lengths are in nm and angles are in degrees. [a-g] are the experimental values [26-29]