Supporting Information Available

The Reaction of HO_2 and CH_3O_2: CH_3OOH Formed from The Singlet Electronic State Surface

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Geometries of various species optimized at fc-CCSD(T)/aVTZ level of theory

$CH_3OOH(C_1, {}^1A)$

CH3OOH
C
H 1 B1*
H 1 B2* 2 A1*
H 1 B3* 2 A2* 3 D1*
O 1 B4* 2 A3* 4 D2*
O 5 B5* 1 A4* 2 D3*
H 6 B6* 5 A5* 1 D4*

B1 = 1.091645197619005
B2 = 1.093522963757435
A1 = 110.132565261864912
B3 = 1.092355356550471
A2 = 110.013076468606712
D1 = -121.508894255252287
B4 = 1.420215165057833
A3 = 104.643188247094528
D2 = -118.924646619023164
B5 = 1.460965686633438
A4 = 105.263175973693833
D3 = 177.113911395724614
B6 = 0.967173702517603
A5 = 99.773803333695767
D4 = 116.580447413081416

$CH_3OO(C_s, {}^2A')$

CH3OO
O
O 1 R1*
C 2 R2* 1 A1*
H 3 R3* 2 A2* 1 T180
H 3 R4* 2 A3* 4 T2*
H 3 R4* 2 A3* 4 T3*

R1 = 1.325044184105788
R2 = 1.447180813090181
A1 = 109.899561667711836

R3 = 1.088914231377361
A2 = 105.474592243366061
T180 = 180.000000000000000
R4 = 1.089117305766924
A3 = 108.868966685897945
T2 = 119.459327100774644
T3 = -119.459327100774644

OH($C_{\infty v}$, $X^2\Pi$)

OH: Optimized at CCSD(T)/AUG-PVTZ level
O
H 1 B1*

B1 = 0.973275224901106

CH_2O (C_{2v}, X^1A_1)

CH2O
O
C 1 R1*
H 2 R2* 1 A1*
H 2 R2* 1 A1* 3 T180

R1 = 1.211515087382290
R2 = 1.103061904375071
A1 = 121.714028216910862
T180 = 180.000000000000000

H_2O (C_{2v},X^1A_1)

H2O
O
H 1 R1*
H 2 R1* 1 A1*

R1 = 0.961579640410436
A1 = 104.179636130297880

HO_2(C_s, $^2A'$)
HOO
O

O 1 R1*
H 2 R2* 1 A1*

R1 = 1.406201589137402
R2 = 0.971820663705163
A1 = 101.623458848955806

^{3}PRC(C_1, ^{3}A) optimized at fc-CCSD(T)/ANO1

PRC-1
C
H 1 B1*
H 1 B2* 2 A1*
H 1 B3* 2 A2* 3 D1*
O 1 B4* 2 A3* 3 D2*
O 5 B5* 1 A4* 2 D3*
O 1 B6* 5 A5* 6 D4*
O 7 B7* 1 A6* 5 D5*
H 8 B8* 7 A7* 1 D6*

B1 = 1.087409475690156
B2 = 1.089317097686931
A1 = 111.010088816288871
B3 = 1.088091472975338
A2 = 112.037079102666425
D1 = -124.649775170867144
B4 = 1.451179050948574
A3 = 104.983065784330321
D2 = 117.113040802826461
B5 = 1.318632841747991
A4 = 111.199811754638318
D3 = 174.158574519360116
B6 = 3.285942815787829
A5 = 101.690977689422695
D4 = 20.851100185185061
B7 = 1.335145353168462
A6 = 88.382232950781884
D5 = -44.401027359959258
B8 = 0.983333450192222
A7 = 103.741101511514074
D6 = 23.386045791970353

^{1}PRC(C_1, ^{1}A, singlet biradical) optimized at fc-CCSD(T)/ANO1

PRC-1
C
H 1 B1*
H 1 B2* 2 A1*
H 1 B3* 2 A2* 3 D1*
O 1 B4* 2 A3* 3 D2*
O 5 B5* 1 A4* 2 D3*
O 1 B6* 5 A5* 6 D4*
O 7 B7* 1 A6* 5 D5*
H 8 B8* 7 A7* 1 D6*

B1 = 1.087403697699892
B2 = 1.089309113574224
A1 = 111.007404294845685
B3 = 1.088182225057387
A2 = 112.020904042066462
D1 = -124.679537852513292
B4 = 1.451255128658495
A3 = 104.978677863370862
D2 = 117.089051490072464
B5 = 1.318626954982450
A4 = 111.207446136243576
D3 = 174.248279306103569
B6 = 3.287382297565077
A5 = 101.387635480074238
D4 = 21.878702414580815
B7 = 1.335036311766489
A6 = 87.933566163385422
D5 = -45.691395629242223
B8 = 0.983529025705268
A7 = 103.782570629372671
D6 = 24.117027786972088

MTO (C_1, ^{1}A) optimized at fc-CCSD(T)/aug-cc-pVTZ
HP1
C
H 1 B1*
H 1 B2* 2 A1*
H 1 B3* 2 A2* 3 D1*
O 1 B4* 2 A3* 4 D2*

O 5 B5* 1 A4* 2 D3*
O 6 B6* 5 A5* 1 D4*
O 7 B7* 6 A6* 5 D5*
H 8 B8* 7 A7* 6 D6*

B1 = 1.090607587203524
B2 = 1.091602254282706
A1 = 110.420368609254496
B3 = 1.091536230217569
A2 = 109.936128957077301
D1 = -122.735174590435264
B4 = 1.429904678276246
A3 = 104.332533147170295
D2 = -118.494838255635614
B5 = 1.434997229901928
A4 = 106.922815022061911
D3 = -178.699825829594772
B6 = 1.418072237437410
A5 = 107.805474592579088
D4 = -79.461507314803399
B7 = 1.437131178073441
A6 = 107.604007365687991
D5 = -78.667700486351407
B8 = 0.970145424302050
A7 = 100.849936827783608
D6 = -81.333525587515183

^{3}TS1(C_1, ^{3}A) optimized at fc-CCSD(T)/ANO1

TS1
C
H 1 B1*
H 1 B2* 2 A1*
H 1 B3* 2 A2* 3 D1*
O 1 B4* 2 A3* 3 D2*
O 5 B5* 1 A4* 2 D3*
O 5 B6* 1 A5* 6 D4*
O 7 B7* 5 A6* 1 D5*
H 8 B8* 7 A7* 5 D6*

B1 = 1.088155929600664
B2 = 1.088495526744445
A1 = 110.977389226514347

B3 = 1.089340879785024
A2 = 111.296860956388073
D1 = -124.174537729320491
B4 = 1.441608202884417
A3 = 105.227259156907792
D2 = 118.250992714733002
B5 = 1.351998473346153
A4 = 109.321641762040741
D3 = -175.510893361921376
B6 = 2.566764177982704
A5 = 94.948302362251610
D4 = 87.866184986169529
B7 = 1.289879902556786
A6 = 85.938282567330901
D5 = -112.435387258705518
B8 = 1.095001937053635
A7 = 104.767071515819481
D6 = 0.337889334635914

^{1}TS2(C_1, ^{1}A) optimized at fc-CCSD(T)/ANO1

TS2
C
H 1 B1*
H 1 B2* 2 A1*
H 1 B3* 2 A2* 3 D1*
O 1 B4* 2 A3* 3 D2*
O 5 B5* 1 A4* 2 D3*
O 5 B6* 1 A5* 6 D4*
O 7 B7* 5 A6* 1 D5*
H 8 B8* 7 A7* 5 D6*

B1 = 1.088277478688452
B2 = 1.088857131904618
A1 = 110.907562049931201
B3 = 1.089457028376928
A2 = 111.262610178100260
D1 = -124.033166264875035
B4 = 1.440069932167259
A3 = 105.183771296674252
D2 = 118.311133996585738
B5 = 1.358730536472470
A4 = 109.111985408132554
D3 = -176.173792054525791

B6 = 2.554534579795149
A5 = 95.278102118802934
D4 = 87.359773577892952
B7 = 1.283219039144297
A6 = 86.008438414806093
D5 = -111.511620496287662
B8 = 1.134400985758652
A7 = 104.590214792357415
D6 = 0.499956741524937

^{1}TS3(C_1, ^{1}A) optimized at fc-CCSD(T)/ANO1

TS3
C
H 1 B1*
H 1 B2* 2 A1*
H 1 B3* 2 A2* 3 D1*
O 1 B4* 2 A3* 4 D2*
O 5 B5* 1 A4* 2 D3*
O 6 B6* 5 A5* 1 D4*
O 7 B7* 6 A6* 5 D5*
H 8 B8* 7 A7* 6 D6*

B1 = 1.088764069734659
B2 = 1.089014359871539
A1 = 111.101882136551794
B3 = 1.088706887763198
A2 = 111.084317838082924
D1 = -123.994157509586103
B4 = 1.441996918070986
A3 = 105.475703683200592
D2 = -117.780534053605606
B5 = 1.334320521618078
A4 = 109.016016189592449
D3 = 179.248961207250744
B6 = 1.989033550897340
A5 = 103.195871453203864
D4 = -84.508520983447156
B7 = 1.351491683253663
A6 = 102.998511379817316
D5 = -15.198903912248158
B8 = 0.971566307879777
A7 = 103.584681180228117
D6 = -84.120271570665579

Ro-vibrational parameters for relevant species

CH_3O_2

Mode	Freq (cm^{-1})
vib	152.7416
vib	493.2912
vib	945.4614
vib	1143.7690
vib	1157.5899
vib	1212.2719
vib	1446.9497
vib	1480.1333
vib	1493.3817
vib	3061.2638
vib	3162.3229
vib	3170.5420
A	1.7170
B	0.3819
C	0.3323

HO_2

Mode	Freq (cm^{-1})
vib	1129.1697
vib	1433.9148
vib	3673.5880
A	20.5265
B	1.1134
C	1.0561

CH_3OOH

Har. vib. frequencies	CCSD(T)/aVTZ
Vib (1DHR)	185.2673

Vib (1DHR)	252.7168
vib	444.0688
vib	848.9585
vib	1048.3839
vib	1173.5470
vib	1206.8179
vib	1359.9221
vib	1456.3420
vib	1479.1789
vib	1520.2682
vib	3022.3930
vib	3099.9745
vib	3126.9426
vib	3769.7714
Rotational constants (cm^{-1})	
A=	1.41209
B=	0.35026
C=	0.30388

^{3}PRC

Rotationally projected vibrational frequencies

7	47.1765
8	72.8693
9	120.5581
10	145.3821
11	171.6375
12	215.3159
13	497.8588
14	593.5652
15	928.5938
16	1140.7680
17	1155.5154
18	1173.0678
19	1231.6324
20	1453.6992
21	1480.6257
22	1493.3776
23	1542.1952
24	3063.1400
25	3167.0954

26 3186.2226
27 3492.7592
Zero-point energy: 37.7021 kcal/mol =157.7459 kJ/mol = 13186.528 cm-1

Rotational constants (in cm-1):
0.0651856741 0.0798868227 0.2838477039

^{1}PRC

Rotationally projected vibrational frequencies
7 49.6007
8 75.1032
9 120.7617
10 148.2999
11 174.1507
12 215.7129
13 498.4773
14 597.0952
15 928.4713
16 1141.2384
17 1155.9339
18 1173.0655
19 1231.6676
20 1453.6935
21 1480.9750
22 1493.8893
23 1543.1351
24 3062.8403
25 3166.9262
26 3185.8583
27 3488.4377
Zero-point energy: 37.7197 kcal/mol =157.8194 kJ/mol =13192.667 cm-1
Rotational constants (in cm-1):

0.0653887793 0.0800311876 0.2836753766

MTO

Mode	Freq (cm^{-1})
vib	95.0016
vib	161.0187

vib	225.2493
vib	336.9378
vib	360.0658
vib	545.0755
vib	608.6688
vib	668.2944
vib	834.8866
vib	874.9196
vib	1024.3212
vib	1178.2199
vib	1211.3085
vib	1398.6045
vib	1447.4456
vib	1475.8510
vib	1513.0850
vib	3041.1332
vib	3129.5138
vib	3146.8148
vib	3755.5507
A	0.4373
B	0.1016
C	0.1012

^{3}TS1

Mode	Freq (cm^{-1})
IMAG	2012.0064i
vib	108.2367
vib	127.1656
vib	162.4400
vib	234.8465
vib	384.8024
vib	488.1187
vib	681.1721
vib	893.1292
vib	946.0875
vib	1149.0615

vib	1161.8779
vib	1223.4827
vib	1340.5436
vib	1444.9951
vib	1475.5016
vib	1488.6168
vib	1688.4098
vib	3059.7930
vib	3159.3982
vib	3174.7770
A	0.2828
B	0.1136
C	0.0910

^{1}TS2

Mode	Freq (cm^{-1})
IMAG	2517.9676i
vib	**108.7539**
vib	128.0817
vib	**163.6525**
vib	235.7261
vib	397.1658
vib	486.4892
vib	659.191
vib	814.8129
vib	944.6861
vib	1137.8728
vib	1151.2936
vib	1216.3409
vib	1330.3391
vib	1445.0134
vib	1475.1687
vib	1488.6503
vib	1698.0805
vib	3057.8869
vib	3156.3125

vib	3172.6067
A	0.2840
B	0.1146
C	0.0918

^{1}TS3

Mode	Freq (cm-1)
IMAG	349.9483i
vib	85.1349
vib	139.1961
vib	152.0534
vib	242.4814
vib	396.2108
vib	480.1607
vib	522.7513
vib	947.5206
vib	1041.1945
vib	1102.6471
vib	1160.7850
vib	1209.7835
vib	1430.1950
vib	1446.7382
vib	1476.9181
vib	1497.0086
vib	3059.4424
vib	3160.2798
vib	3168.5828
vib	3692.2881
A	0.2908
B	0.1174
C	0.0992

Table S1: Relative energies (ΔE, kcal mol^{-1}) and rovibrational parameters of grid points along the (variational) reaction coordinate: $HO_2 + CH_3O_2 \rightarrow {}^3PRC^*$

Mode	Rc = 3.2 A	3.4	3.6	3.8	4.2	4.5
vib	56.5299	48.9522	41.4967	36.4220	34.8631	30.3636
vib	66.2550	49.8365	50.1068	53.6113	56.8935	55.8376
vib	113.1962	95.4075	87.8184	80.9682	75.4657	68.7806
vib	147.5963	122.8202	113.6615	106.9620	101.8528	95.0797
vib	177.1380	177.1817	177.4114	177.9895	179.9092	170.4022
vib	457.8475	354.3293	305.1274	258.4917	219.5920	185.4030
vib	503.2437	494.3317	492.8265	491.6869	490.6259	489.1918
vib	903.5880	906.6240	907.4864	907.9003	908.1791	908.6522
vib	1098.2968	1093.0095	1091.0966	1089.8086	1089.0420	1088.4107
vib	1118.2657	1116.4384	1116.5131	1117.0735	1117.0388	1116.2049
vib	1127.7221	1123.7449	1122.6593	1122.9191	1124.2170	1125.5159
vib	1197.4001	1193.5533	1192.4065	1191.8791	1191.5136	1190.7021
vib	1427.9625	1426.6234	1426.2917	1426.4307	1426.7985	1427.0193
vib	1460.7659	1455.0307	1449.0069	1443.5318	1439.4512	1435.2245
vib	1469.5863	1465.7291	1464.0965	1462.7928	1461.8042	1461.0912
vib	1494.5311	1476.8149	1474.8832	1473.9507	1473.5182	1473.3698
vib	3049.1565	3048.1824	3048.0403	3048.2529	3048.7929	3049.6945
vib	3157.9937	3156.5918	3156.5270	3156.8680	3157.4900	3158.5924
vib	3175.1887	3171.2522	3170.1026	3169.8812	3170.1345	3170.2548
vib	3491.9345	3536.9127	3555.3262	3572.3655	3585.7838	3598.3108
A (cm-1)	0.2769	0.2768	0.2767	0.2759	0.2759	0.2797
B	0.0695	0.0609	0.0573	0.0541	0.0513	0.0477
C	0.0580	0.0517	0.0490	0.0466	0.0445	0.0418
Del_E (kcal/mol)	0.0000	1.6298	2.3031	2.8556	3.2921	3.7314

Table S1 (Continued):

Mode	RC = 4.7 A	5	5.2	5.5	5.7	6
vib	27.3962	23.4061	21.7600	23.6335	27.3140	24.1580
vib	55.3872	51.5755	48.2905	40.9188	39.2262	40.8896
vib	65.5395	59.9527	56.6255	50.7505	46.2628	47.8219
vib	91.0613	85.1414	80.3932	75.5683	69.0838	66.5606
vib	149.0347	120.2320	104.4872	83.8424	73.6637	67.0620
vib	181.9023	177.0048	173.3959	167.5137	162.7938	155.4677
vib	488.4832	487.7377	487.3371	487.0158	486.8912	487.8454
vib	908.9323	909.3642	909.5118	910.0198	910.4468	911.1871
vib	1088.2782	1088.4345	1088.4313	1088.9198	1089.2533	1089.5744
vib	1115.5683	1114.5915	1113.9909	1113.1879	1112.8869	1112.8916
vib	1126.0652	1126.4702	1126.2073	1125.7983	1124.6899	1122.1463
vib	1190.1756	1189.3801	1188.8424	1188.1692	1187.6073	1187.1135
vib	1426.9255	1426.5238	1425.9036	1424.7288	1423.7539	1422.8105
vib	1433.2295	1431.2032	1430.4779	1429.8584	1429.6642	1429.2985
vib	1460.7017	1459.9990	1459.3121	1458.1088	1457.1636	1456.2306
vib	1473.2105	1472.6200	1471.9590	1470.4489	1469.2028	1467.8143
vib	3050.1959	3050.8222	3051.1372	3052.0853	3052.9042	3054.4020
vib	3159.2560	3160.1192	3160.3378	3160.5610	3160.5464	3160.2588
vib	3170.2129	3170.1360	3170.2562	3171.8290	3173.5117	3177.5054
vib	3603.5177	3608.7406	3610.6340	3613.3677	3614.3825	3614.7487
A (cm-1)	0.2847	0.2958	0.3079	0.3361	0.3654	0.4574
B	0.0455	0.0426	0.0407	0.0383	0.0367	0.0345
C	0.0402	0.0382	0.0369	0.0352	0.0342	0.0327
Del_E (kcal/mol)	3.9296	4.1272	4.2149	4.3198	4.3720	4.4181

Table S2: Collisional parameters and energies are used in the E,J-resolved 2DME model.

Parameters	Values
He	Mass = 4.0 g/mol, σ = 2.55 Å, ε/k_B = 10.0 K
CH_4O_4	Mass = 80.0 g/mol, σ = 6.0 Å, ε/k_B = 350 K
E_{max}	30,000 cm^{-1} above CH_4O_4 when $T \leq 500\,K$;
ΔE_{grain}	10 cm^{-1} when $T \leq 500\,K$
$\langle \Delta E_d \rangle$	$265 \cdot \left(\frac{T}{298}\right)^1$ $(in\ cm^{-1})$, for the fixed-J ME model $250 \cdot \left(\frac{T}{298}\right)^1$ $(in\ cm^{-1})$, for the E,J-resolved ME model
J_{max}	200 with $T \leq 500\,K$
ΔJ	5