Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

for

Probing Criegee Intermediate Reactions with Methanol by FTMW Spectroscopy

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Table S1. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for PRC species.

O	0.2288	-1.1365	0.9850
O	-0.3954	-0.0624	1.5992
C	0.1079	1.0581	1.4101
H	-0.4073	1.8811	1.8874
H	0.9953	1.1557	0.7987
H	0.3310	-0.3975	-0.6978
O	0.3184	0.3443	-1.3255
C	-0.2779	-0.0921	-2.5334
H	-0.3152	0.7608	-3.2093
H	0.3067	-0.8848	-3.0080
H	-1.2971	-0.4547	-2.3740

Table S2. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for TS1 species.

O	0.1650	-1.0132	-1.2242
O	-0.5547	0.2451	-1.1504
C	0.2131	1.0870	-0.5902
H	1.2776	1.0533	-0.7827
H	-0.2631	2.0025	-0.2520
H	0.5942	-0.7103	0.2854
O	0.6296	0.0065	1.0283
C	-0.4778	-0.2038	1.9084
H	-0.3614	-1.1624	2.4161
H	-0.4799	0.5968	2.6454
H	-1.4229	-0.2089	1.3602

Table S3. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for TS2 species.

O	-1.0751	0.1703	-1.1596
O	0.3013	-0.1960	-1.4486
C	1.0252	0.3069	-0.5367
H	2.0379	-0.0791	-0.4791
H	0.7763	1.2828	-0.1358
H	-0.7259	-0.3427	0.2839
O	0.0366	-0.5301	0.9639
C	-0.1637	0.2496	2.1389
H	0.6795	0.0852	2.8073
H	-0.2436	1.3164	1.9084
H	-1.0820	-0.0670	2.6366

Table S4. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for MMHP-I conformer.

H	-1.3124	-0.3810	-1.1684
O	-0.5600	-0.2272	-1.7542
O	0.2593	0.6361	-0.9508
C	0.8790	-0.1739	0.0149
H	1.3162	-1.0503	-0.4582
H	1.6429	0.4789	0.4494
O	-0.0140	-0.6343	0.9785
C	-0.4537	0.3915	1.8577
H	-1.1377	-0.0696	2.5655
H	-0.9695	1.1865	1.3154
H	0.3936	0.8210	2.4004

Table S5. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for MMHP-II conformer.

H	-1.2887	-0.4840	1.3137
O	-0.7277	0.1887	1.7202
O	0.5668	-0.2141	1.2461
C	0.6946	0.2826	-0.0441
H	0.4478	1.3496	-0.0708
H	1.7455	0.1161	-0.3022
O	-0.1594	-0.4352	-0.8933
C	-0.2670	0.1689	-2.1668
H	-0.9485	-0.4407	-2.7543
H	0.7033	0.2070	-2.6725
H	-0.6663	1.1854	-2.0885

Table S6. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for the *a*-PRC species.

O	0.1089	-1.6010	0.0882
O	-0.2960	-0.7800	1.1371
C	0.2949	0.3131	1.2913
H	1.0974	0.5563	0.6017
C	-0.1375	1.2128	2.3775
H	-0.9584	0.7831	2.9464
H	0.7056	1.4226	3.0411
H	-0.4454	2.1706	1.9487
H	0.2787	-0.3950	-1.2328
O	0.3617	0.4875	-1.6537
C	-0.3209	0.4892	-2.8963
H	-0.2369	1.4900	-3.3197
H	0.1195	-0.2213	-3.6037
H	-1.3837	0.2509	-2.7813

Table S7. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for *a*–TS1 species.

O	0.0539	-1.8073	0.2577
O	-0.5003	-0.6412	0.9352
C	0.3656	0.2990	0.8326
H	1.4114	0.0209	0.8986
C	-0.0587	1.6757	1.1878
H	0.5400	2.3966	0.6336
H	0.1289	1.8373	2.2527
H	-1.1163	1.8316	0.9884
H	0.4784	-0.8812	-0.8003
O	0.6310	0.1294	-1.1175
C	-0.4813	0.5219	-1.9171
H	-0.3952	1.5849	-2.1396
H	-0.4719	-0.0392	-2.8536
H	-1.4285	0.3265	-1.4070

Table S8. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for *a*–TS2 species.

O	0.1251	-1.7694	0.3618
O	-0.1559	-0.6304	1.2276
C	0.3640	0.4024	0.6805
H	1.3203	0.2712	0.1825
C	-0.0330	1.7333	1.2012
H	0.0689	2.4806	0.4161
H	0.6402	2.0112	2.0167
H	-1.0562	1.7181	1.5681
H	-0.3401	-0.8970	-0.7164
O	-0.5223	0.0997	-1.0636
C	0.2427	0.3543	-2.2321
H	0.1175	1.3992	-2.5156
H	1.3073	0.1483	-2.0755
H	-0.1102	-0.2774	-3.0503

Table S9. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for *a*–MEHP-I conformer.

H	-1.3161	0.0888	-1.5246
O	-0.4670	0.0591	-1.9857
O	0.3834	-0.5146	-0.9827
C	0.5088	0.4353	0.0522
H	0.7392	1.4059	-0.3852
C	1.6313	-0.0686	0.9374
H	1.4668	-1.1039	1.2336
H	2.5716	-0.0124	0.3921
H	1.6977	0.5540	1.8289
O	-0.7222	0.6243	0.7022
C	-1.1706	-0.4796	1.4776
H	-2.2071	-0.2738	1.7339
H	-1.1164	-1.4123	0.9119
H	-0.5917	-0.5806	2.3980

Table S10. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for *a*–MEHP-II conformer.

H	-1.7152	-0.7115	-0.9848
O	-1.3677	0.1204	-1.3290
O	0.0413	-0.1484	-1.2961
C	0.5130	0.2742	-0.0383
H	0.2355	1.3229	0.1044
C	2.0112	0.0735	-0.0830
H	2.2297	-0.9853	-0.2156
H	2.4496	0.6402	-0.9031
H	2.4445	0.4071	0.8589
O	-0.0562	-0.5086	0.9772
C	-0.8795	0.2133	1.8787
H	-1.2966	-0.5123	2.5733
H	-0.2982	0.9483	2.4432
H	-1.6894	0.7248	1.3532

Table S11. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for *s*-PRC species.

O	-1.1524	-0.7270	0.5170
O	-0.8695	0.4810	1.1521
C	0.2980	0.6214	1.5757
H	0.4560	1.5876	2.0425
C	1.3354	-0.4158	1.4612
H	0.9041	-1.3740	1.7540
H	1.6179	-0.5031	0.4079
H	2.2001	-0.1560	2.0657
H	-0.1848	-0.4107	-0.9827
O	0.5240	-0.0703	-1.5557
C	-0.0186	0.2134	-2.8311
H	0.7777	0.6344	-3.4434
H	-0.3922	-0.6893	-3.3226
H	-0.8328	0.9417	-2.7726

Table S12. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for *s*–TS1 species.

O	-1.3767	-0.6384	0.5859
O	-0.8248	0.7102	0.6606
C	0.4589	0.6242	0.6239
H	0.9190	1.5687	0.3354
C	1.2654	-0.3058	1.4603
H	2.2494	-0.4504	1.0206
H	0.7616	-1.2553	1.5992
H	1.3934	0.1794	2.4339
H	-0.3530	-0.8461	-0.5208
O	0.5132	-0.4825	-1.0031
C	0.1068	0.2026	-2.1882
H	0.9820	0.6777	-2.6286
H	-0.3074	-0.5154	-2.8979
H	-0.6542	0.9549	-1.9676

Table S13. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for *s*–TS2 species.

O	-0.7524	-1.0786	-1.0352
O	0.4799	-0.3702	-1.3753
C	0.5931	0.6442	-0.5970
H	1.6177	1.0066	-0.5447
C	-0.5070	1.6112	-0.3353
H	-0.3419	2.1485	0.5984
H	-1.4757	1.1263	-0.3393
H	-0.4592	2.3520	-1.1411
H	-0.1745	-0.9902	0.3526
O	0.4739	-0.4947	1.0263
C	-0.1939	-0.1287	2.2249
H	0.4826	0.4841	2.8198
H	-1.1174	0.4224	2.0356
H	-0.4443	-1.0255	2.7963

Table S14. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for *s*–MEHP-I conformer.

H	-1.0166	1.4527	-0.6578
O	-0.4856	1.1083	-1.3872
O	0.7022	0.6840	-0.7011
C	0.4189	-0.5280	-0.0236
H	1.4076	-0.7851	0.3750
C	-0.1200	-1.6147	-0.9233
H	-1.1208	-1.3611	-1.2632
H	0.5326	-1.7321	-1.7870
H	-0.1591	-2.5515	-0.3691
O	-0.4902	-0.3204	1.0173
C	0.0505	0.4398	2.0876
H	0.3665	1.4305	1.7541
H	-0.7344	0.5387	2.8332
H	0.9077	-0.0750	2.5316

Table S15. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for *s*–MEHP-II conformer.

H	-0.8287	-1.3818	1.4021
O	-0.5153	-0.5804	1.8475
O	0.7244	-0.3386	1.1345
C	0.4442	0.3416	-0.0687
H	1.4532	0.4802	-0.4781
C	-0.2573	1.6722	0.1325
H	-1.2330	1.5160	0.5861
H	0.3396	2.3155	0.7785
H	-0.3903	2.1733	-0.8266
O	-0.2982	-0.5292	-0.9033
C	-0.0226	-0.4121	-2.2878
H	1.0394	-0.5828	-2.4969
H	-0.6102	-1.1751	-2.7936
H	-0.3091	0.5686	-2.6815

Table S16. Observed transition frequencies for MMHP-I conformer.

J′	K_a′	K_c′	J′′	K_a′′	K_c′′	Sym	$\nu_{obs.}$	$\nu_{obs.}$-$\nu_{cal.}$
2	1	2	2	0	2	E	7456.461	-0.001
2	1	2	2	0	2	A	7456.760	-0.002
1	1	1	1	0	1	E	7599.377	0.001
1	1	1	1	0	1	A	7599.708	-0.002
1	1	0	1	0	1	E	7744.687	0.001
1	1	0	1	0	1	A	7744.851	-0.002
2	1	2	1	1	1	E	12436.039	0.001
2	1	2	1	1	1	A	12436.066	-0.002
2	0	2	1	0	1	E	12578.950	-0.001
2	0	2	1	0	1	A	12579.015	-0.001
2	1	1	1	1	0	E	12726.230	-0.000
2	1	1	1	1	0	A	12726.323	-0.001
1	1	1	0	0	0	E	13889.927	-0.001
1	1	1	0	0	0	A	13890.297	0.003
1	1	0	0	0	0	E	14035.238	-0.001
1	1	0	0	0	0	A	14035.435	-0.002
3	1	3	2	1	2	E	18652.524	0.001
3	1	3	2	1	2	A	18652.630	-0.002
3	0	3	2	0	2	E	18863.051	-0.001
3	0	3	2	0	2	A	18863.148	-0.001
3	2	2	2	2	1	A	18872.115	0.003
3	2	2	2	2	1	E	18874.441	0.001
3	2	1	2	2	0	E	18877.827	-0.003
3	2	1	2	2	0	A	18880.338	-0.003
3	1	2	2	1	1	E	19087.841	0.001
3	1	2	2	1	1	A	19087.919	-0.001
2	1	2	1	0	1	E	20035.416	0.002
2	1	2	1	0	1	A	20035.781	0.002
2	1	1	1	0	1	E	20470.924	0.006
2	1	1	1	0	1	A	20471.176	-0.003
4	1	4	3	1	3	E	24867.303	0.003
4	1	4	3	1	3	A	24867.457	-0.001
4	0	4	3	0	3	E	25140.724	0.001
4	0	4	3	0	3	A	25140.855	-0.001
4	2	3	3	2	2	A	25160.782	0.002
4	2	3	3	2	2	E	25162.502	0.001
4	2	2	3	2	1	E	25179.363	-0.000
4	2	2	3	2	1	A	25181.327	-0.002
4	1	3	3	1	2	E	25447.514	-0.000
4	1	3	3	1	2	A	25447.611	0.001

Table S17. Observed transition frequencies for d-MMHP-I conformer.

J′	K_a'	K_c'	J′′	K_a''	K_c''	Sym	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	1	2	1	1	1	E	12237.951	-0.003
2	1	2	1	1	1	A	12237.911	-0.002
2	0	2	1	0	0	E	12406.468	0.002
2	0	2	1	0	1	A	12406.405	0.004
2	1	1	1	1	0	E	12581.254	0.002
2	1	1	1	1	0	A	12581.177	-0.003
3	1	3	2	1	3	E	18869.694	0.001
3	1	3	2	1	2	A	18869.623	0.001
3	0	3	2	0	3	E	18601.912	-0.001
3	0	3	2	0	3	A	18601.818	-0.001
3	1	2	2	1	1	E	18354.854	0.001
3	1	2	2	1	1	A	18354.747	-0.002

Table S18. Observed transition frequencies for *s*-MEHP-I conformer.

J′	K_a'	K_c'	J′′	K_a''	K_c''	Sym	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	0	2	1	0	1	E	10375.966	0.000
2	0	2	1	0	1	A	10376.004	-0.001
2	1	1	1	1	0	E	11416.216	0.000
2	1	1	1	1	0	A	11416.273	0.002
2	1	2	1	0	1	E	11436.966	0.000
2	1	2	1	0	1	A	11437.051	0.001
3	1	3	2	1	2	E	14573.116	0.002
3	1	3	2	1	2	A	14573.148	-0.002
3	0	3	2	0	2	E	15085.921	-0.001
3	0	3	2	0	2	A	15085.977	0.000
3	1	3	2	0	2	E	15634.114	-0.002
3	1	3	2	0	2	A	15634.197	0.002
3	2	2	2	2	1	E	15913.522	-0.003
3	2	2	2	2	1	A	15913.543	0.005
2	2	1	1	1	0	E	16321.598	0.000
2	2	1	1	1	0	A	16321.885	0.000
3	2	1	2	2	0	E	16740.916	0.001
3	2	1	2	2	0	A	16741.019	-0.004
3	1	2	2	1	1	E	16950.440	-0.002
3	1	2	2	1	1	A	16950.523	0.001
2	2	0	1	1	1	E	17361.972	-0.001
2	2	0	1	1	1	A	17362.152	0.000
4	0	4	3	1	3	E	19003.392	0.003
4	0	4	3	1	3	A	19003.432	-0.001
4	1	4	3	1	3	E	19240.537	-0.001
4	1	4	3	1	3	A	19240.579	-0.001
4	0	4	3	0	3	E	19551.581	-0.002
4	0	4	3	0	3	A	19551.653	0.001
4	2	3	3	2	2	E	21032.782	0.000
4	2	3	3	2	2	A	21032.851	-0.001
4	1	3	3	1	2	E	22220.043	-0.002
4	1	3	3	1	2	A	22220.154	0.002
4	2	2	3	2	1	E	22691.955	0.001
4	2	2	3	2	1	A	22692.054	0.000
5	1	5	4	1	4	E	23827.333	0.000
5	1	5	4	1	4	A	23827.366	0.002
5	0	5	4	0	4	E	23972.846	0.000
5	0	5	4	0	4	A	23972.938	-0.001
2	0	2	1	0	1	E	10375.966	0.000
2	0	2	1	0	1	A	10376.004	-0.001

Table S19. Observed transition frequencies for *s*-d-MEHP-I conformer.

J′	K_a'	K_c'	J′′	K_a''	K_c''	Sym	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	0	2	1	0	1	E	10260.265	0.002
2	0	2	1	0	1	A	10260.303	0.002
3	1	3	2	1	2	E	14412.077	0.000
3	1	3	2	1	2	A	14412.109	-0.003
3	0	3	2	0	2	E	14897.853	0.000
3	0	3	2	0	2	A	14897.908	0.000
3	1	2	2	1	1	E	16782.549	-0.001
3	1	2	2	1	1	A	16782.629	0.001
4	1	4	3	1	3	E	19019.908	0.000
4	1	4	3	1	3	A	19019.948	0.000
4	0	4	3	0	3	E	19301.953	-0.002
4	0	4	3	0	3	A	19302.026	0.002
4	1	3	3	1	2	E	21971.827	-0.002
4	1	3	3	1	2	A	21971.933	0.000
5	1	5	4	1	4	E	23548.062	-0.001
5	1	5	4	1	4	A	23548.089	0.002
5	0	5	4	0	4	E	23674.240	0.001
5	0	5	4	0	4	A	23674.334	-0.001

Table S20. Observed transition frequencies for *a*-MEHP-I conformer.

J′	K_a'	K_c'	J′′	K_a''	K_c''	Sym	$\nu_{obs.}$	$\nu_{obs.}$-$\nu_{cal.}$
2	0	2	1	0	1	E	10350.457	-0.002
2	0	2	1	0	1	A	10350.477	0.004
3	1	3	2	1	2	E	14460.990	-0.003
3	1	3	2	1	2	A	14461.012	-0.001
3	0	3	2	0	2	E	14942.486	0.000
3	0	3	2	0	2	A	14942.511	0.002
3	2	1	2	2	0	E	17014.618	-0.002
3	2	1	2	2	0	A	17014.642	0.001
3	1	2	2	1	1	E	17097.473	0.000
3	1	2	2	1	1	A	17097.495	0.000
4	1	4	3	1	3	E	19048.202	-0.003
4	1	4	3	1	3	A	19048.229	-0.001
4	0	4	3	0	3	E	19302.345	0.002
4	0	4	3	0	3	A	19302.377	0.003
4	2	3	3	2	2	E	21063.160	0.001
4	2	3	3	2	2	A	21063.186	0.000
4	1	3	3	1	2	E	22282.149	-0.001
4	1	3	3	1	2	A	22282.177	-0.004
4	2	2	3	2	1	E	23052.834	0.003
4	2	2	3	2	1	A	23052.859	0.001
5	1	5	4	1	4	E	23549.362	-0.004
5	1	5	4	1	4	A	23549.388	0.000
5	0	5	4	0	4	E	23652.739	0.002
5	0	5	4	0	4	A	23652.785	0.002