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Electronic Supplementary Information

for

Observation of Hydroperoxyethyl Formate from the Reaction between the Methyl Criegee Intermediate and Formic Acid

*Carlos Cabezas† and Yasuki Endo**

Department of Applied Chemistry, Science Building II, National Chiao Tung University, 1001 Ta-Hsueh Rd., Hsinchu 30010, Taiwan

AUTHOR INFORMATION

Corresponding Author

* endo@nctu.edu.tw

† Present Address: Instituto de Física Fundamental (IFF-CSIC), Group of Molecular Astrophysics, C/ Serrano 121, 28006 Madrid, Spain

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Table S1. Comparison of between the theoretical and experimental rotational constants for the HPEF conformers.

***anti*-HPEF-I**

	Th. parent[a]	Exp. parent[b]	Corr. Factor[c]	Rel.Error[d]	Th. d-iso[e]	Exp.d-iso[f]	Corrected[g]	Rel. Error[d]
***A*/MHz**	3590	**3557.66914**	1.0091	0.909	3507	**3475.24529**	3475.4166	0.914
***B*/MHz**	2616	**2592.9501**	1.0089	0.889	2557	**2534.29754**	2534.469	0.896
***C*/MHz**	1617	**1601.9461**	1.0094	0.940	1580	**1564.7546**	1565.290	0.974

***syn*-HPEF-II**

	Th. parent[a]	Exp. parent[b]	Corr. Factor[c]	Rel.Error[d]	Th. d-iso[e]	Exp.d-iso[f]	Corrected[g]	Rel. Error[d]
***A*/MHz**	3581	3557.66914	1.0007	0.656	3579	3475.24529	355.6822	2.986
***B*/MHz**	2618	2592.9501	1.0097	0.966	2520	2534.29754	2495.8878	-0.564
***C*/MHz**	2036	1601.9461	1.2710	27.095	1976	1564.7546	1554.7375	26.281

***syn*-HPEF-I**

	Th. parent[a]	Exp. parent[b]	Corr. Factor[c]	Rel.Error[d]	Th. d-iso[e]	Exp.d-iso[f]	Corrected[g]	Rel. Error[d]
***A*/MHz**	4444	**4422.36894**	1.0049	0.489	4366	**4343.7883**	4344.7486	0.511
***B*/MHz**	1908	**1889.58465**	1.0097	0.975	1855	**1836.7038**	1837.0962	0.996
***C*/MHz**	1634	**1619.18028**	1.0091	0.915	1605	**1590.5154**	1590.4433	0.910

***anti*-HPEF-II**

	Th. parent[a]	Exp. parent[b]	Corr. Factor[c]	Rel.Error[d]	Th. d-iso[e]	Exp.d-iso[f]	Corrected[g]	Rel. Error[d]
***A*/MHz**	4254	4422.36894	0.9599	-4.010	4146	4343.7883	4319.2324	-4.553
***B*/MHz**	1953	1889.58465	1.0335	3.356	1911	1836.7038	1848.9484	4.045
***C*/MHz**	1529	1619.18028	0.9443	-5.570	1501	1590.5154	1589.5288	-5.628

[a] Theoretical values for the parent species calculated at CCSD/aug-cc-pVTZ level of theory.
[b] Experimental values for the parent species. Green color means color that the values are well assigned to the predicted values. Red color means a hypothetical assignment.
[c] Corrected factor. It means the ratio: B_{th}/B_{exp}, where B is the rotational constant; *A*, *B* and *C*.
[d] Relative error calculated as follows:$100\cdot(B_{th}/B_{exp})/B_{exp}$, where B is the rotational constant; *A*, *B* and *C*.
[e] Theoretical values for the deuterated isotopic species calculated at CCSD/aug-cc-pVTZ level of theory.
[f] Experimental values for the deuterated isotopic species. Green color means color that the values are well assigned to the predicted values. Red color means a hypothetical assignment.
[g] Values obtained using the corrected factor from the parent species and the theoretical values calculated at CCSD/aug-cc-pVTZ level of theory.

Table S2. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for *anti*-HPEF-I conformer.

H	-0.12632	-1.60333	-0.91046
O	-0.14668	-1.96174	-0.00677
O	0.52042	-0.91494	0.71472
C	-0.29474	0.21306	0.77656
H	-1.31387	-0.06547	0.51616
C	-0.16155	0.83612	2.14346
H	0.89029	1.02470	2.35554
H	-0.70808	1.77662	2.18221
H	-0.55864	0.14937	2.88821
O	0.15244	1.23635	-0.15365
C	0.12627	0.96959	-1.45343
H	0.44326	1.84958	-2.01812
O	-0.19204	-0.07154	-1.97049

Table S3. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for *anti*-HPEF-II conformer.

H	-1.61148	-0.46139	1.84762
O	-1.10651	0.34965	1.98458
O	0.21955	-0.09689	1.66631
C	0.44734	0.19842	0.32702
H	0.11617	1.20790	0.09497
C	1.91540	-0.02653	0.06258
H	2.18483	-1.04888	0.32522
H	2.11882	0.14559	-0.99252
H	2.50524	0.66770	0.65869
O	-0.35749	-0.72554	-0.43567
C	-0.66326	-0.35172	-1.68323
H	-1.31597	-1.10128	-2.13953
O	-0.28245	0.64490	-2.23173

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

H	-0.97228	-1.64793	-1.31537
O	-0.42317	-1.05469	-1.84096
O	0.63825	-0.77564	-0.91208
C	0.39594	0.46944	-0.31893
H	1.29267	0.62511	0.27774
C	0.13732	1.59089	-1.29426
H	-0.79960	1.43155	-1.82109
H	0.08873	2.53409	-0.75176
H	0.95261	1.63385	-2.01488
O	-0.73997	0.38347	0.55167
C	-0.50548	-0.05269	1.80355
H	-1.45184	-0.09419	2.35027
O	0.56009	-0.34178	2.26493

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

H	-1.57948	-0.35254	0.34411
O	-1.32686	-0.16368	1.26508
O	-0.34440	0.86078	1.06340
C	0.84226	0.34565	0.55641
H	1.60011	1.04710	0.89827
C	1.17312	-1.07496	0.94951
H	0.49516	-1.78489	0.48408
H	2.19409	-1.29151	0.63836
H	1.09358	-1.17374	2.03052
O	0.94370	0.50491	-0.89406
C	-0.00170	0.04806	-1.70115
H	0.28952	0.22555	-2.73935
O	-1.04107	-0.48109	-1.39230

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

O	-1.41775	-0.33497	-0.69366
O	-0.65087	0.77532	-1.08421
C	0.47810	0.50266	-1.53796
H	1.05208	1.38897	-1.78466
C	0.95391	-0.87116	-1.76682
H	0.19844	-1.40460	-2.34635
H	1.91568	-0.86156	-2.27152
H	1.03067	-1.37052	-0.80188
O	1.23706	0.26189	1.10941
C	0.44602	0.02558	1.99839
H	0.72971	0.05144	3.05503
O	-0.82028	-0.28683	1.85453
H	-1.07204	-0.31346	0.88065

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

O	0.22123	-1.78904	-0.06514
O	-0.37250	-0.91037	-1.01605
C	0.35751	0.04786	-1.32975
H	1.37083	0.04759	-0.94946
C	-0.14802	1.06244	-2.27820
H	-1.19181	0.88166	-2.52017
H	-0.02848	2.04189	-1.81664
H	0.45983	1.03302	-3.18463
O	0.14208	1.36927	0.69831
C	-0.05520	0.85035	1.78571
H	-0.19188	1.45697	2.68574
O	-0.13328	-0.42240	2.03950
H	0.00553	-0.99229	1.19065

Table S8. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for TS-*syn* conformer.

O	-2.85726	-0.51973	-1.42526
O	-1.16868	1.48751	-2.04179
C	1.10969	0.84822	-2.31540
H	2.32642	2.47108	-2.61596
C	2.01565	-1.73865	-2.81113
H	1.68241	-2.11093	-4.82394
H	4.03028	-1.85999	-2.43824
H	0.96654	-3.13119	-1.73740
O	2.26696	0.67165	1.89241
C	0.69980	0.03164	3.48414
H	1.22537	0.00495	5.48952
O	-1.61568	-0.66288	3.11893
H	-2.21813	-0.64692	1.17288

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

O	0.35713	-3.47683	0.27995
O	-0.67704	-1.85236	-1.58525
C	0.66347	-0.00761	-2.25766
H	2.63383	0.01812	-1.72383
C	-0.25803	1.72732	-4.19952
H	-2.25954	1.46888	-4.55574
H	0.14066	3.64357	-3.59500
H	0.78446	1.32453	-5.95875
O	0.24631	2.65571	0.82401
C	-0.14800	1.83376	2.99208
H	-0.44360	3.19466	4.52556
O	-0.17911	-0.47136	3.65709
H	0.08952	-2.04953	2.16362

Table S10. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for VHP species.

H	-0.67896	-0.83524	-1.58219
O	-0.59473	0.06345	-1.24158
O	0.68888	-0.00528	-0.61343
C	0.54710	-0.00042	0.74803
C	-0.57343	-0.00660	1.46077
H	1.53826	0.01348	1.18081
H	-0.49053	-0.00114	2.53618
H	-1.54946	-0.01676	1.00561

Table S11. Observed transition frequencies for *anti*-HPEF-I conformer.

J′	K_a'	K_c'	J′′	K_a''	K_c''	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
3	0	3	2	1	2	10708.502	0.000
3	1	2	2	2	1	10772.866	0.000
3	1	3	2	1	2	10851.025	0.000
3	0	3	2	0	2	11149.288	0.000
3	1	3	2	0	2	11291.811	0.000
2	1	1	1	0	1	11336.496	0.000
2	2	1	1	1	0	12274.920	-0.001
3	2	2	2	2	1	12584.638	-0.001
2	2	0	1	1	0	12741.987	0.000
2	2	1	1	1	1	13265.921	0.000
3	1	2	2	1	1	13667.010	-0.001
2	2	0	1	1	1	13732.989	0.001
3	2	1	2	2	0	14019.999	0.000
4	0	4	3	1	3	14123.995	0.000
4	1	4	3	1	3	14161.787	0.001
4	0	4	3	0	3	14266.519	0.000
4	1	4	3	0	3	14304.310	0.000
3	2	2	2	1	1	15478.782	-0.001
4	1	3	3	2	2	15542.276	0.000
4	2	3	3	2	2	16395.578	0.000
3	1	2	2	0	2	17080.793	0.000
4	1	3	3	1	2	17354.050	0.001
3	2	1	2	1	1	17381.210	0.000
5	0	5	4	1	4	17391.962	-0.001
5	1	5	4	1	4	17400.962	0.001
5	0	5	4	0	4	17429.751	-0.002
5	1	5	4	0	4	17438.752	0.001
4	2	3	3	1	2	18207.351	0.000

Table SX12. Observed transition frequencies for *syn*-HPEF-I conformer.

J′	K_a'	K_c'	J′′	K_a''	K_c''	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	1	1	1	0	1	10091.032	0.001
4	0	4	3	1	2	10268.889	0.001
4	0	4	3	1	3	11890.140	0.000
3	1	3	2	0	2	12391.152	0.000
5	0	5	4	1	3	12902.055	0.000
4	1	4	3	1	3	13455.796	-0.001
4	0	4	3	0	3	13836.401	0.000
3	1	2	2	0	2	14012.403	0.000
4	1	3	3	1	2	14531.325	-0.001
2	2	1	1	1	0	14886.132	-0.001
2	2	0	1	1	0	14906.642	0.000
2	2	1	1	1	1	15156.519	0.000
2	2	0	1	1	1	15177.029	0.000
4	1	4	3	0	3	15402.055	-0.001
5	0	5	4	1	4	15598.835	0.000
4	1	3	3	0	3	18098.838	0.001
3	2	2	2	1	1	18124.398	0.000
3	2	1	2	1	1	18226.164	0.000
5	1	5	4	0	4	18352.983	0.000

Table S13. Observed transition frequencies for *anti*-d-HPEF-I conformer.

J′	K_a'	K_c'	J′′	K_a''	K_c''	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
3	1	3	2	0	2	11029.812	-0.005
2	2	1	1	1	0	11990.457	-0.001
2	2	1	1	1	1	12960.001	0.004
2	2	0	1	1	1	13417.742	-0.002
4	0	4	3	1	3	13797.738	-0.002
4	1	4	3	0	3	13972.824	-0.001
3	2	2	2	1	1	15119.937	0.000
5	0	5	4	1	4	16989.501	0.002
5	1	5	4	0	4	17034.834	0.003

Table S14. Observed transition frequencies for *syn*-d-HPEF-I conformer.

J′	K_a'	K_c'	J′′	K_a''	K_c''	F′	F′′	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
3	1	3	2	0	2	2	1	12180.027	-0.004
						4	3	12180.048	0.002
						3	2	12180.057	0.003
3	1	2	2	0	2	2	1	13656.195	-0.003
						4	3	13656.217	-0.001
						3	2	13656.238	0.002
2	2	0	1	1	0	3	2	14638.978	0.007
						1	0	14638.988	0.002
						2	1	14639.001	0.002
2	2	1	1	1	1	3	2	14867.889	-0.003
						2	1	14867.931	0.002
2	2	0	1	1	1	3	2	14885.136	-0.004
						2	1	14885.176	-0.003
4	1	4	3	0	3	5	4	15150.939	-0.004
						3	2	17607.069	-0.001
						5	4	17607.087	0.007
3	2	1	2	1	1	2	1	17888.340	0.003
						4	3	17888.361	0.008
						3	2	17888.379	0.000
3	2	2	2	1	2	2	1	18541.138	-0.003
						4	3	18541.158	-0.003
						3	2	18541.188	-0.009