

SUPPLEMENTARY MATERIAL

to

Characterization and Atmospheric Implication of Hydrotrioxy Radical-Water-Methylamine-Formic Acid-Sulphuric Acid Complexes

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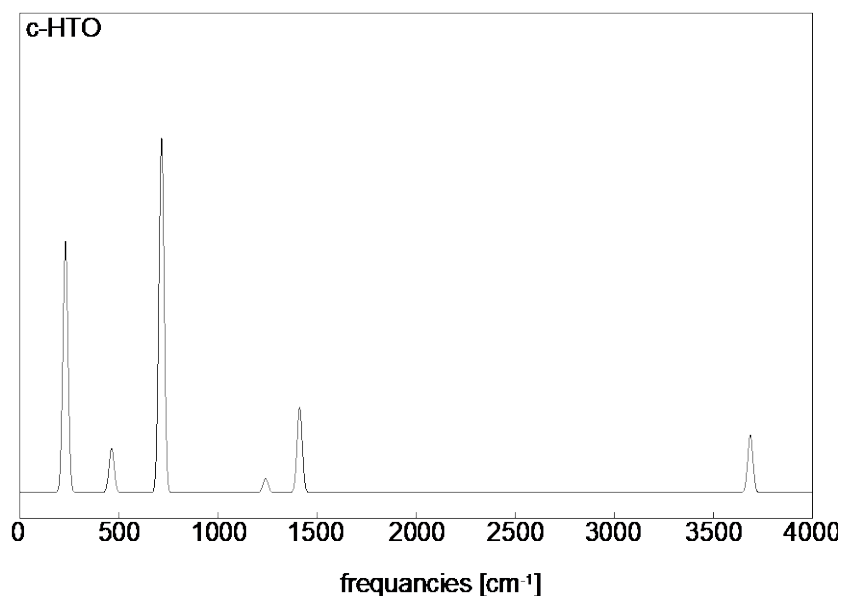


Figure S1: Harmonic IR absorption spectra of *cis*-HOOO' radical calculated on B3LYP/6-311++G(3df,3pd) level of theory.

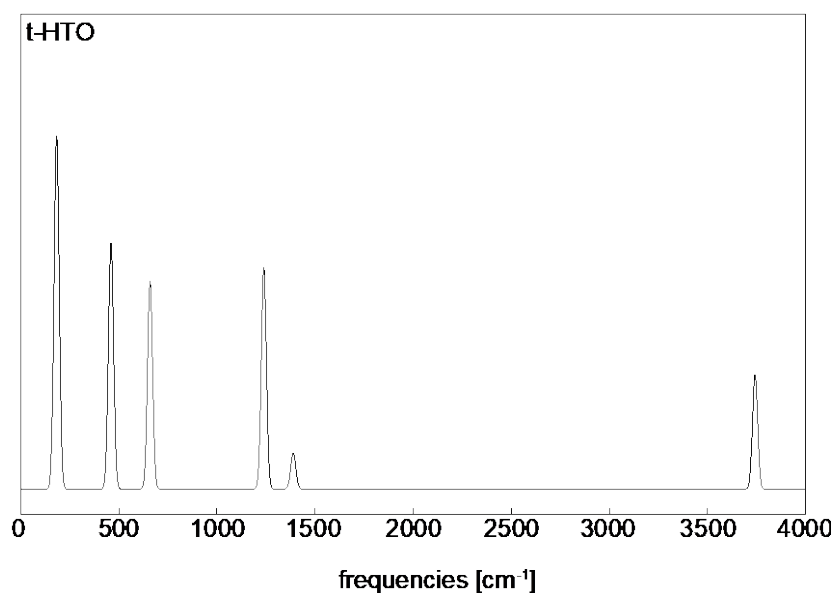


Figure S2: Harmonic IR absorption spectra of *trans*-HOOO' radical calculated on B3LYP/6-311++G(3df,3pd) level of theory.

Table S1: B3LYP/6-311++G(3df,3pd) calculated harmonic and anharmonic frequencies (ν) in cm^{-1} and IR absorption intensities (I) in km mol^{-1} of c-HTO and T-HTO radicals and precursors (water, methylamine, formic acid and sulphuric acid) . Available experimental values are given.

	Mode:	harmonic		anharmonic		experiment ^{a, b}
		ν	I	ν	I	ν
t-HTO	1	3742	70	3582	59	3569
	2	1389	22	1353	36	-
	3	1239	136	1199	113	1202
	4	659	64	636	53	482
	5	460	76	445	74	244
	6	183	109	193	98	129

c-HTO	1	3687	49	3521	42	-
	2	1413	72	1362	72	-
	3	1240	12	1219	8	-
	4	715	150	691	138	-
	5	463	19	450	22	-
	6	230	106	163	93	148
H₂O	1	3913	59	3728	55	3756
	2	3814	5	3641	3	3657
	3	1627	72	1573	74	1595
CH₃NH₂	1	3505	1	3355	1	3361
	2	3060	31	2957	16	2961
	3	2969	89	2791	49	2820
	4	1660	21	1630	15	1623
	5	1499	7	1461	5	1473
	6	1461	2	1425	3	1430
	7	1168	6	1123	5	1130
	8	1055	12	1029	14	1044
	9	823	149	760	152	780
	10	3578	2	3405	1	3427
	11	3096	28	2968	22	2985
	12	1519	5	1476	4	1485
	13	1344	0	1309	0	1419
	14	972	0	959	0	1195
	15	294	32	262	29	268
HCOOH	1	3730	60	3540	50	3569
	2	3053	40	2896	38	2942
	3	1819	372	1786	353	1777
	4	1403	2	1375	3	1381
	5	1300	9	1294	2	1223
	6	1125	263	1092	260	1104
	7	631	42	624	40	625
	8	1052	2	1033	1	1033
	9	676	139	641	137	642
H₂SO₄	1	3768	49	3595	148	3609
	2	3764	201	3591	215	-
	3	1467	297	1438	281	1465
	4	1221	170	1199	174	1220
	5	1162	91	1134	64	1157
	6	1145	73	1113	57	1138
	7	862	332	842	302	891
	8	811	110	793	94	834
	9	551	25	542	18	568
	10	538	40	533	32	550
	11	493	40	486	31	-
	12	433	14	403	6	-
	13	370	2	346	1	281
	14	326	60	291	59	-
	15	248	101	229	111	216

^a Derro et al., values for isolated radical (*cis*- and *trans*-HOOO[•] radicals) in gas-phase¹;

^b Shimanouchi et. al., IR absorption spectra of gase-phase precursor molecules.²

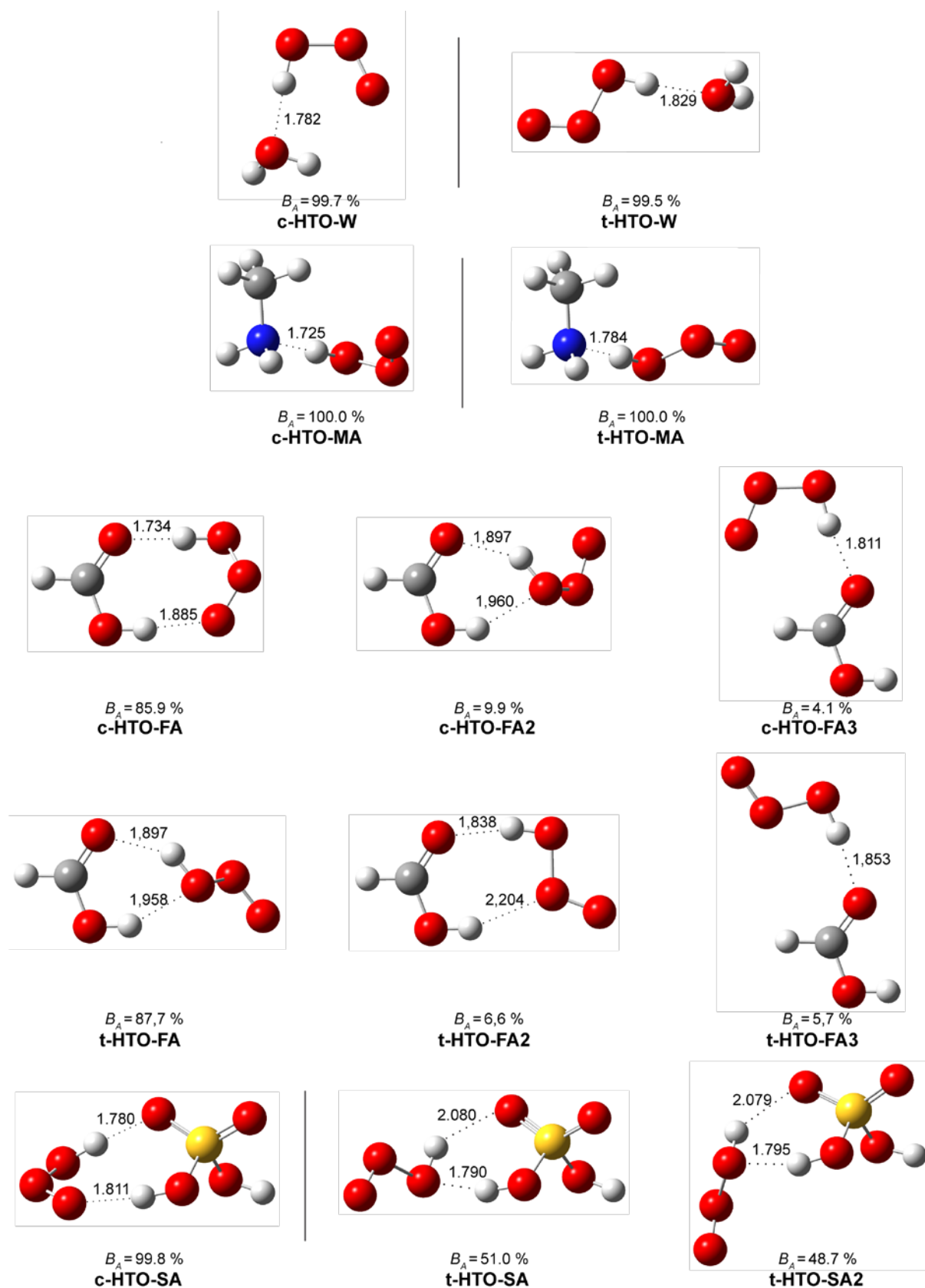


Figure S3: Optimised structures of the stable binary complexes with the B3LYP/6-311++G(3df,3pd) bond lengths and the CBS-QB3 binding energies. Dotted lines represent intermolecular formation of H-bonds.

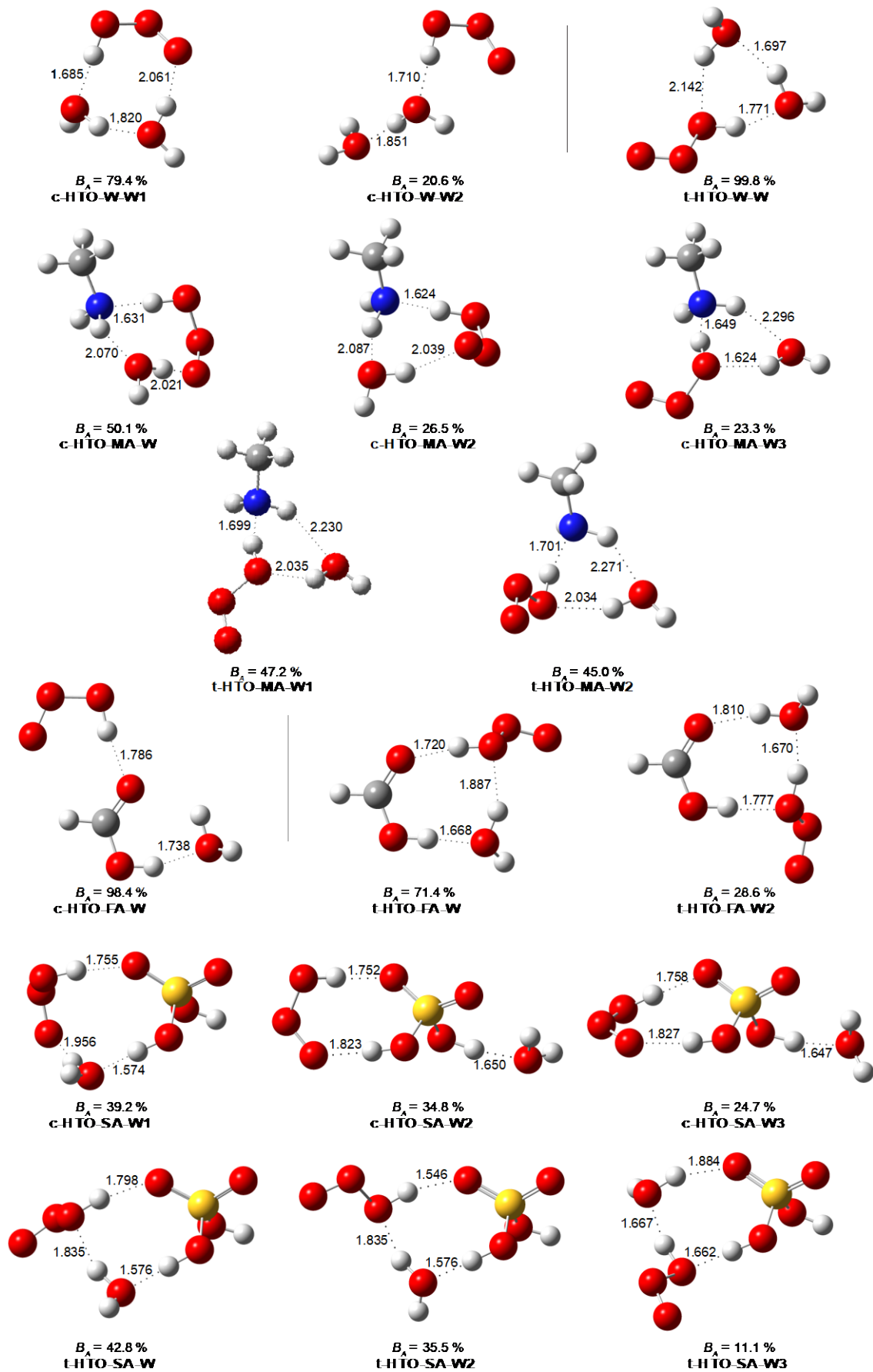


Figure S4: Optimised structures of the stable ternary complexes with the B3LYP/6-311++G(3df,3pd) bond lengths and the CBS-QB3 binding energies. Dotted lines represent intermolecular formation of H-bonds.

Table S2: Thermodynamic properties (ΔH , $T\Delta S$ and ΔG) in kcal mol⁻¹ and calculated K_c values in cm³ molecules⁻¹ at different altitude (h) [km], temperature (T) [K] and pressure (p) [atm]. Calculated values correspond to the reaction: x -HTO-PR + W \rightarrow x -HTO-PR-W (where x stands for the corresponding conformation of HOOO' radical and RP for the corresponding precursor molecule).

Complex	h	T	p	ΔH	$T\Delta S$	ΔG	K_c
Ternary Complexes							
t-HTO-W-W	0	298.15	1	-7.73	-10.78	3.05	5.7×10^{-24}
	0	278.15	1	-7.74	-10.09	2.35	1.3×10^{-23}
	5	255.15	0.533	-7.73	-9.57	1.84	2.3×10^{-23}
	8	236.15	0.351	-7.71	-9.03	1.32	4.7×10^{-23}
c-HTO-MA-W	0	298.15	1	-5.54	-2.14	-3.40	3.2×10^{-24}
	0	278.15	1	-5.57	-2.77	-2.80	5.8×10^{-24}
	5	255.15	0.533	-5.61	-3.19	-2.42	7.1×10^{-24}
	8	236.15	0.351	-5.63	-3.61	-2.02	1.0×10^{-23}
t-HTO-FA-W	0	298.15	1	-10.64	-10.22	-0.42	2.0×10^{-21}
	0	278.15	1	-10.65	-9.55	-1.10	6.7×10^{-21}
	5	255.15	0.533	-10.66	-9.09	-1.57	1.9×10^{-20}
	8	236.15	0.351	-10.66	-8.61	-2.05	6.2×10^{-20}
c-HTO-SA-W	0	298.15	1	-12.25	-8.71	-3.54	3.9×10^{-19}
	0	278.15	1	-12.26	-8.13	-4.13	1.6×10^{-19}
	5	255.15	0.533	-12.27	-7.79	-4.48	8.8×10^{-19}
	8	236.15	0.351	-12.28	-7.41	-4.87	2.7×10^{-18}

References

1. C. Murray, E. L. Derro, T. D. Sechler, M. I. Lester, *J. Phys. Chem. A* **2007**, *111*, 11592.
2. T. Shimanouchi, Tables of Molecular Vibrational Frequencies Consolidated. National Bureau of Standards, Washington, United States, **1972**.