Interaction of water, alkyl hydroperoxide, and allylic alcohol with a single-site homogeneous Ti-Si epoxidation catalyst: A spectroscopic and computational study

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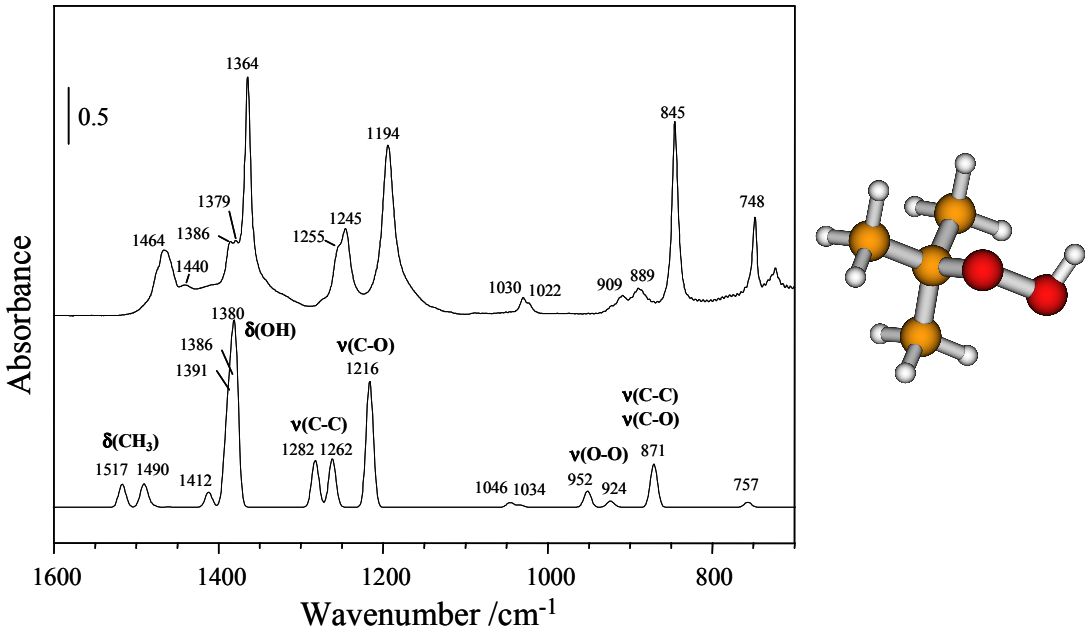
Supporting Information

Equilibrium Geometry of TBHP

Optimization and frequency calculations were done with the B3PW91 functional but with higher basis sets, 6-31++G(2d,2p) instead of 6-311G(d). The geometry and IR spectrum at the different basis sets were nearly identical, except the scaling factor of about 0.955 was necessary to compare with experimental spectrum in the case of 6-311G(d) basis set.

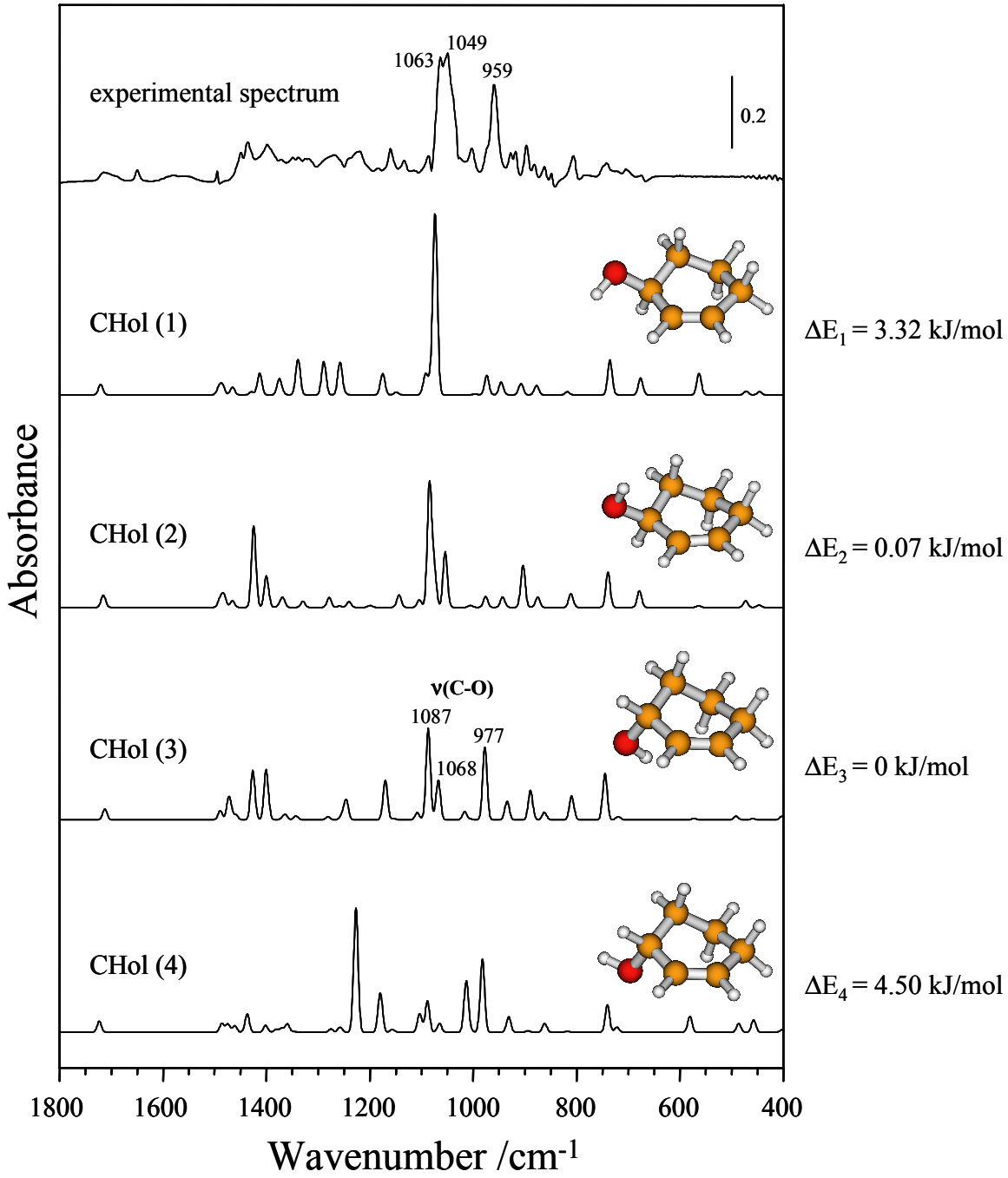
Figure 1(S). Comparison between experimental and calculated IR spectra. 5.5 M TBHP in nonane at 300 K (above) and calculated (B3PW91/6-31++G(2d,2p), without scaling) spectrum.



Conformation Analysis of CHol

A conformational analysis was carried out for four possible conformations of CHol. The spectrum of the conformation (3) was in best agreement with the experimental CHol spectrum in toluene, especially the C-O stretching peak at 977 cm^{-1} of conformation (3) in comparison with 959 cm^{-1} of the experimental spectrum strongly supports CHol(3) as the most probable conformation. The electronic energy calculations at the same level of theory supported the stability of conformation (3), although the conformation (2) is as stable as (3) and it is expected to exist to some extent by the ring structure fluctuation.

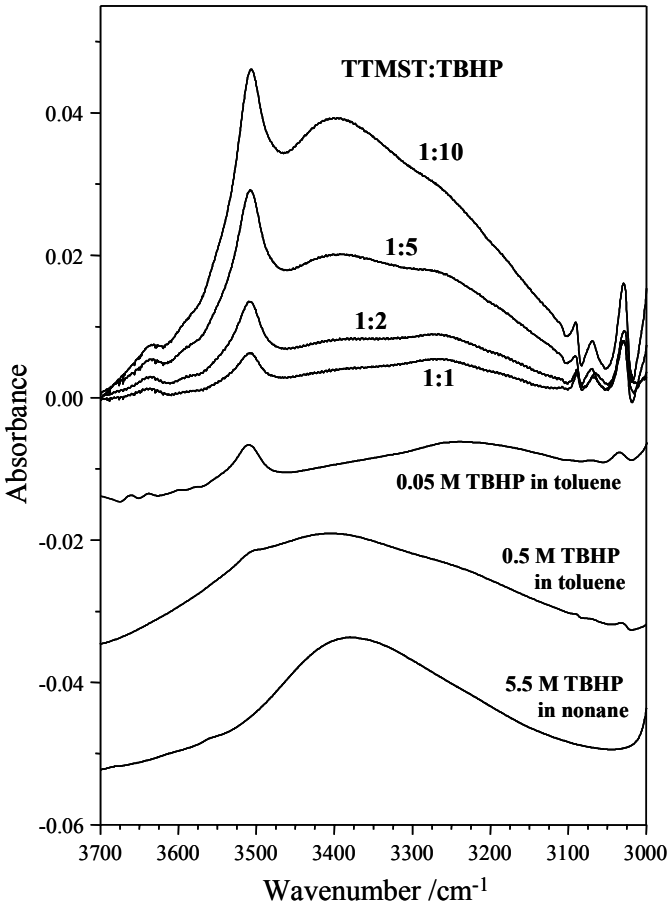
Figure 2(S). Comparisons between experimental IR spectrum (0.5M in toluene at 300 K) and calculated IR spectra (B3PW91/6-31++G(2d,2p), without scaling) and relative electronic energies (with respect to CHol (3)) of four possible CHol conformers.



Interaction of TBHP with TTMST: IR study of OH stretching region.

When TBHP concentration is high, TBHP molecules form hydrogen-bonds leading to the broad peak at 3380 cm^{-1} (e.g. 5.5 M TBHP in nonane). When concentration is decreased, for example at 0.05 M in toluene, the OH stretching at 3510 cm^{-1} of free TBHP molecules is observed. At a higher concentration, 0.5 M TBHP in toluene, the broad feature of intermolecular interactions is more pronounced than the sharp peak of free TBHP. However, the trend changes remarkably in the presence of TTMST. The sharp peak at 3380 cm^{-1} is pronounced, which indicates free TBHP or TBHP interacting very weakly with TTMST. Also, the shape of the broad band due to hydrogen-bonded TBHP changes, indicating hydrogen-bonding interaction between TBHP and TTMST.

Figure 3(S). ATR-IR spectra of TBHP and TTMST-TBHP in toluene (0.05 M TTMST for the TTMST-TBHP solutions, at 300 K). The spectra of 0.5 M TBHP in toluene and 5.5 M TBHP in nonane are scaled by 1/20.

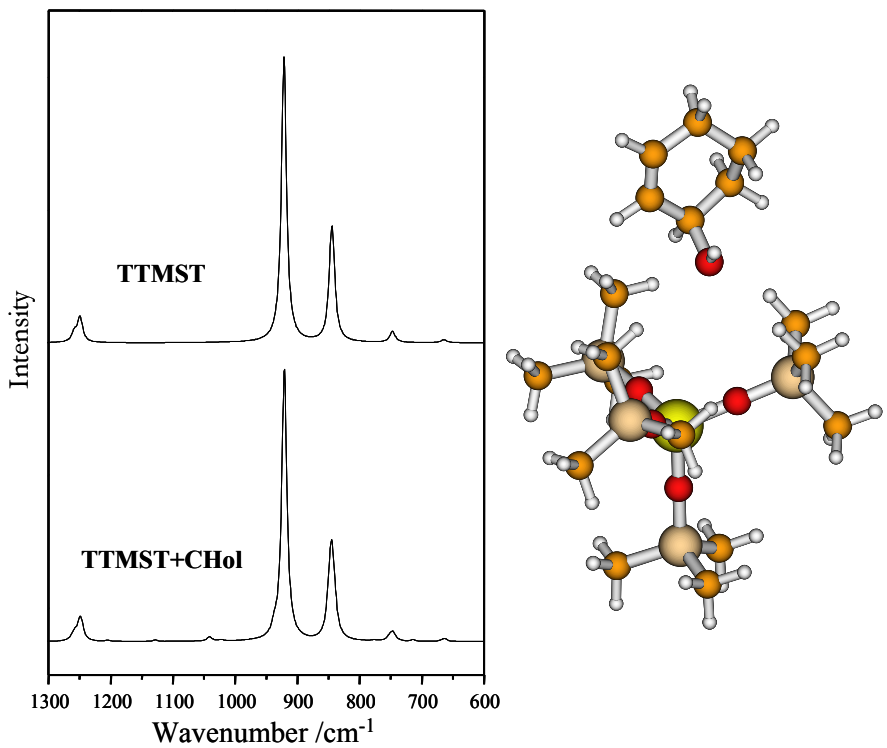


Interaction of CHol with TTMST

Similar to the study of TTMST-TBHP interaction, TTMST-CHol interaction was studied starting from several initial geometries using CHol(3) as the conformation of CHol with B3PW91/3-21G. The most stable complex was further optimised with the method described in the experimental section. The optimised geometry and calculated IR spectrum are shown below.

It should be noted that a hydrogen-bonded complex was found when conformer 1 (CHol(1)) was used as a starting geometry of TTMST-CHol complex. However, when the most stable and probable conformation CHol(3) was chosen as a starting geometry, no hydrogen-bonded complex was found. These results and our IR and NMR results imply that CHol is rather stable when isolated or weakly interacting with TTMST in the absence of TBHP. This indicates that a change in conformation from CHol(1) to CHol(3), which involves a rotation of the O-H group and which would allow hydrogen-bonding with TTMST, does not occur.

Figure 4(S). Calculated IR spectra of TTMST and TTMST-CHol complex (scaled by 0.955) and the optimised structure.



Orbital Analysis

Table 1(S). Orbital energies of HOMO-10 to LUMO+9 of the molecules and complexes are shown below. The values are in hartree.

	TTMST	TBHP	TTMST+TBHP	TTMST+2TBHP	TTMST+3TBHP	TTMST+4TBHP	TTMSS	TTMSS+TBHP
LUMO+9	0.06557	0.15902	0.04899	0.04328	0.04241	0.03126	0.07477	0.07512
LUMO+8	0.04352	0.15519	0.04480	0.04205	0.03025	0.02596	0.07455	0.07471
LUMO+7	0.04345	0.12119	0.04135	0.03006	0.02526	0.02362	0.07434	0.07188
LUMO+6	0.04331	0.11576	0.02777	0.02735	0.02331	0.02270	0.07162	0.06434
LUMO+5	0.01422	0.11225	0.01514	0.01429	0.01328	0.01223	0.07157	0.05182
LUMO+4	-0.00008	0.10756	-0.00380	-0.00913	-0.01233	-0.01568	0.05641	0.04808
LUMO+3	-0.00018	0.09116	-0.00575	-0.00988	-0.01340	-0.01645	0.04260	0.04709
LUMO+2	-0.00023	0.08445	-0.00690	-0.01039	-0.01543	-0.01734	0.04257	0.04256
LUMO+1	-0.03736	0.04566	-0.04182	-0.04488	-0.04871	-0.05084	0.04249	0.02671
LUMO	-0.03741	0.02438	-0.04417	-0.04973	-0.05480	-0.05892	0.01678	0.01772
HOMO	-0.27576	-0.26397	-0.23473	-0.24034	-0.23976	-0.24536	-0.27571	-0.23571
HOMO-1	-0.27580	-0.29538	-0.27673	-0.24252	-0.24158	-0.24570	-0.27575	-0.27641
HOMO-2	-0.27582	-0.33814	-0.27782	-0.27854	-0.24540	-0.24610	-0.27576	-0.27781
HOMO-3	-0.28914	-0.35312	-0.28107	-0.28081	-0.27836	-0.24695	-0.29248	-0.28464
HOMO-4	-0.28918	-0.37179	-0.28963	-0.28234	-0.28037	-0.27878	-0.29252	-0.29117
HOMO-5	-0.28922	-0.37953	-0.29088	-0.28955	-0.28261	-0.28026	-0.29332	-0.29311
HOMO-6	-0.29519	-0.39085	-0.29188	-0.29081	-0.28968	-0.28317	-0.29337	-0.29455
HOMO-7	-0.29527	-0.39506	-0.29624	-0.29224	-0.29133	-0.28860	-0.29338	-0.29622
HOMO-8	-0.33282	-0.42006	-0.29648	-0.29517	-0.29255	-0.28938	-0.33367	-0.29824
HOMO-9	-0.33285	-0.44548	-0.31043	-0.29698	-0.29511	-0.29105	-0.33368	-0.31399
HOMO-10	-0.33286	-0.46573	-0.32985	-0.30442	-0.29740	-0.29314	-0.33370	-0.33097

Figure 5(S). Kohn-Sham orbitals (LUMO-LUMO+5) of TTMST and the TTMST-TBHP complex.