

Electronic supplementary information

**Vibrational Spectroscopy and Dissociation Dynamics of
Cyclohexyl Hydroperoxide**

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S1. Synthesis of Cyclohexyl Hydroperoxide

S1.1. General Methods

All reactions were performed under normal atmosphere unless otherwise noted with oven-dried glassware. The plastic reactor used with pyridine·HF was made of high-density polyethylene (HDPE) and was stored in a desiccator for at least 24 h prior to use. All reactions mixtures were stirred using RCT Digital IKA Magnetic Stirrer Plates. Dry THF and dichloroethane (DCE) were obtained using a Solvent Purification System from Pure Process Technology, LLC. Commercially available reagents were obtained from Sigma-Aldrich, TCI America, or Acros Organics, and solvents were obtained from Fisher Scientific. Co(modp)₂ was prepared using previously established literature precedent.¹⁻² Analytical thin-layer chromatography (TLC) was used to monitor reaction progress and was performed using Silicycle 250 μm precoated 60 Å silica gel plates with F254 indicator using potassium permanganate stain, or an iodine chamber to visualize spots. Purification via flash chromatography was done using 230 – 400 mesh silica gel obtained from Silicycle. ¹H NMR spectra were obtained using a 400 MHz spectrometer. Decoupled ¹³C{¹H} NMR spectra were recorded at 101 MHz. Chemical shifts are reported in parts per million (ppm) from the solvent resonance, CDCl₃ 7.26 ppm ¹H NMR, and CDCl₃ 77.16 ppm, for ¹³C NMR. Data are reported as follows: chemical shift, multiplicity (s = singlet, t = triplet, q = quartet, m = multiplet), coupling constants, and number of protons. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc.

S1.2. Synthesis Procedures

Oxygen Gas:

Hazards:

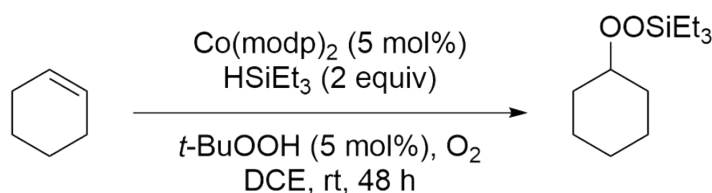
- Greatly **increased fire risk** with **flammable solvents**.
- **Exothermically** reacts with **alkali metals** potentially leading to **fire**.

Precautions:

- **Avoid** large scale reactions with **flammable** solvents.
- **Avoid** the use of oxygen gas in reactions producing **flammable gases** as this can create an **explosive** environment (e.g. methyl lithium).

Disposal:

- **Generally** safe to open reaction to **atmosphere** and allow oxygen gas to naturally disperse. An active purge with argon can also be done.



(Cyclohexylperoxy)triethylsilane. Was prepared using a literature procedure.³ To a dry 1 L rbf was added Co(modp)₂ (1.72 g, 3.20 mmol) followed by dry DCE (215 mL). The flask was sealed with a rubber septum. With an outlet needle attached, O₂ gas was bubbled through the solution using two balloons for ~10 minimum before adding triethylsilane (20.0 mL, 125 mmol), cyclohexene (6.5 mL, 64 mmol), and t-BuOOH (~5.5 M in decane, 0.58 mL, 3.2 mmol). O₂ gas was once again bubbled through the solution for ~10 min before removing the outlet needle and leaving two balloons filled with O₂ gas attached. After 48 h, the reaction was deemed complete as determined by GC. The reaction mixture was filtered through a pad of silica and washed with CH₂Cl₂ (~100 mL). The resultant mixture was directly concentrated to remove residual starting materials (cyclohexene and triethylsilane) to yield pure **(cyclohexylperoxy)triethylsilane** as a clear oil (13.3 g, 57.7 mmol, 90% yield). In some runs, residual triethylsilane remained after concentrating, the impure material can be further purified via column

chromatography using 0-2.5% EtOAc in hexanes as eluent. This material is safer to store in bulk compared to the unprotected hydroperoxide and can be safely stored at ~-4 °C for several weeks without noticeable decomposition.⁴

¹H NMR (400 MHz, CDCl₃) δ 3.91 – 3.80 (m, 1H), 2.03 – 1.90 (m, 2H), 1.82 – 1.67 (m, 2H), 1.61 – 1.49 (m, 1H), 1.36 – 1.12 (m, 5H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 8.6 Hz, 6H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 83.3, 30.6, 26.0, 24.1, 6.9, 4.0.

Organic Peroxides:

Hazards:

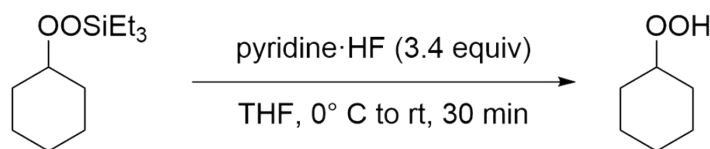
- Potential for *explosive* decomposition.
- *Oxidizing* and can violently react with reductants.

Precautions:

- *Avoid* storing large amounts of material in one batch. Store <50-100 mg in multiple *small* vials, or as a solution in an appropriate solvent (e.g. hexanes). Store at low temperature.
- *Avoid* mixing with transition metals as this may catalyze an *explosive* reaction.

Disposal:

- *Small* amounts of diluted material can be quenched with a reductant such as sodium bisulfite.
- *Contact* local *EHS* department for advice on how to safely store and dispose of organic peroxides.



Cyclohexylhydroperoxide. To a 500 mL HDPE plastic bottle was added (cyclohexylperoxy)triethylsilane (5.00 g, 21.7 mmol) followed by dry THF (140 mL). The mixture was cooled to 0 °C using an ice bath. Using a plastic pipette, pyridine·HF (70% HF by weight, 2 mL, 75 mmol (HF)) was added dropwise over the course of ~1 min. Following the addition, the reaction mixture was removed from the ice bath and allowed to warm to rt. After 30 min, the reaction was deemed complete by TLC and the mixture cooled back down to 0 °C with an ice bath before adding 12 M KOH (10 mL). After vigorously stirring the mixture for ~5 min, the bottom layer was transferred to an Erlenmeyer flask using a plastic pipette and additional 12 M KOH (10 mL) was added. After an additional ~5 min of stirring the bottom layer was once again transferred to the same Erlenmeyer flask and this process was repeated for a total of five times. The combined basic washings were washed with hexanes (3 x 10 mL) and cooled to 0 °C with an ice bath. With stirring, conc HCl was added until a pH of 1 was achieved while the temperature of the solution was monitored to ensure the temperature did not exceed 40 °C. Once at a pH of 1, the aqueous mixture was extracted with hexanes (5 x 15 mL). The organic washings were combined, washed with satd NaCl (10 mL), dried with anhydrous MgSO₄, filtered, and concentrated to yield pure **cyclohexylhydroperoxide** as a clear oil (0.500 g, 4.30 mmol, 20%). The product was separated into multiple small vials (~50-100 mg each) and brought into a glovebox to be stored in a -20 °C freezer. The NMR spectra are consistent with those reported in literature.⁵

¹H NMR (400 MHz, CDCl₃) δ 7.67 (s, 1H), 4.02 – 3.89 (m, 1H), 2.02 – 1.89 (m, 2H), 1.82 – 1.69 (m, 2H), 1.64 – 1.50 (m, 1H), 1.43 – 1.17 (m, 5H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 83.4, 30.2, 25.9, 23.8.

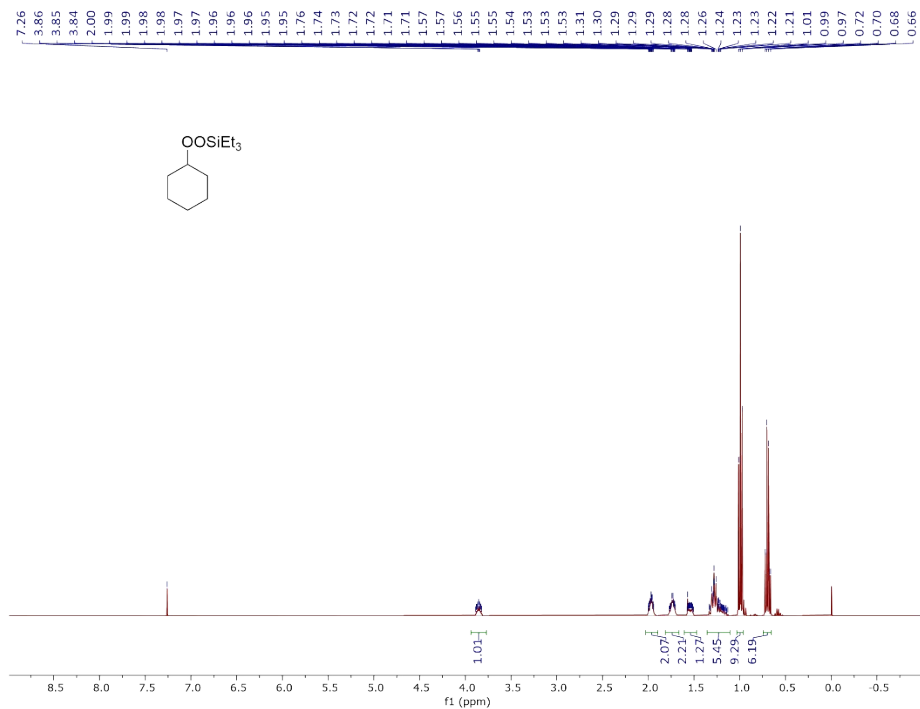


Figure S1. (cyclohexylperoxy)triethylsilane: ¹H NMR (400 MHz, CDCl₃) δ 3.91 – 3.80 (m, 1H), 2.03 – 1.90 (m, 2H), 1.82 – 1.67 (m, 2H), 1.61 – 1.49 (m, 1H), 1.36 – 1.12 (m, 5H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 8.6 Hz, 6H).

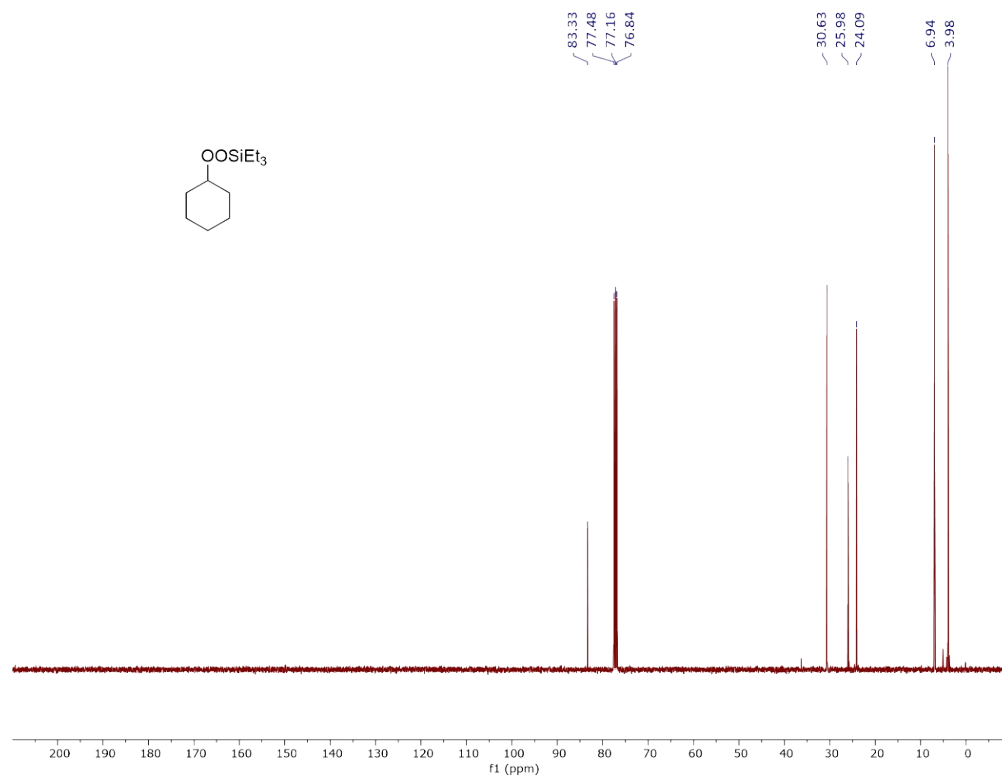


Figure S2. (cyclohexylperoxy)triethylsilane: ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 83.3, 30.6, 26.0, 24.1, 6.9, 4.0.

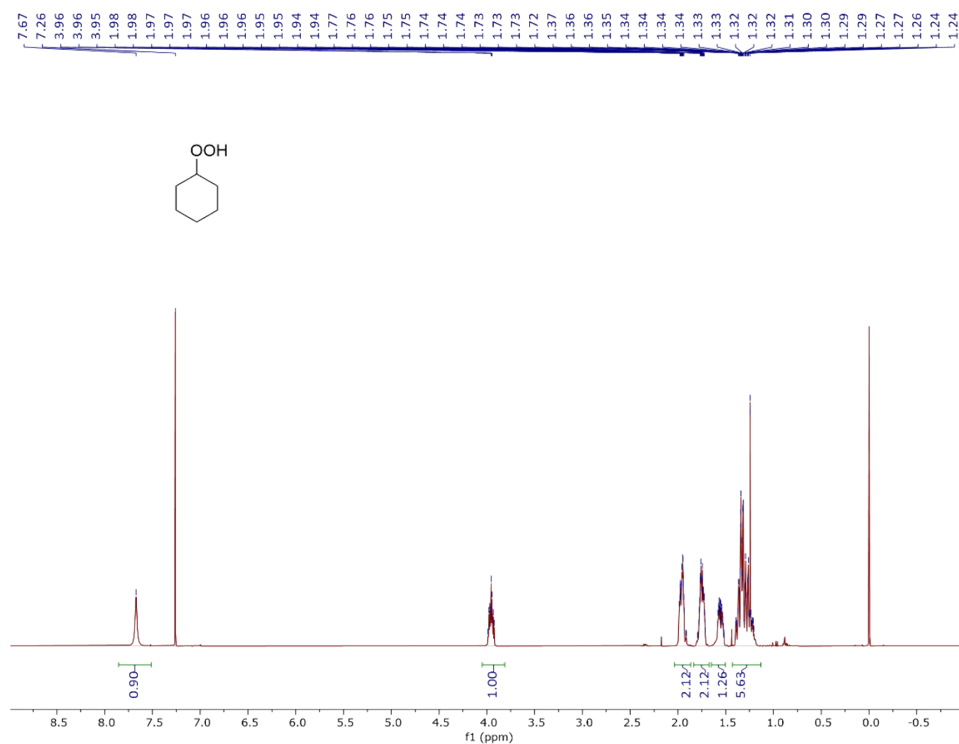


Figure S3. Cyclohexylhydroperoxide: ^1H NMR (400 MHz, CDCl_3) δ 7.67 (s, 1H), 4.02 – 3.89 (m, 1H), 2.02 – 1.89 (m, 2H), 1.82 – 1.69 (m, 2H), 1.64 – 1.50 (m, 1H), 1.43 – 1.17 (m, 5H).

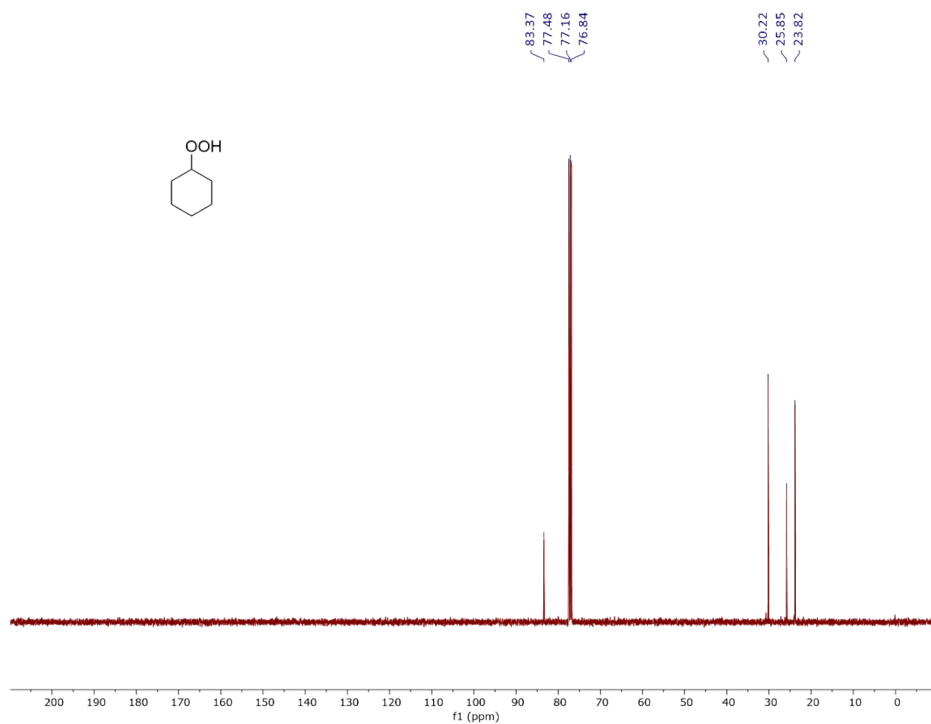


Figure S4. Cyclohexylhydroperoxide: $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 83.4, 30.2, 25.9, 23.8.

S2. Molecular orbitals of CHHP

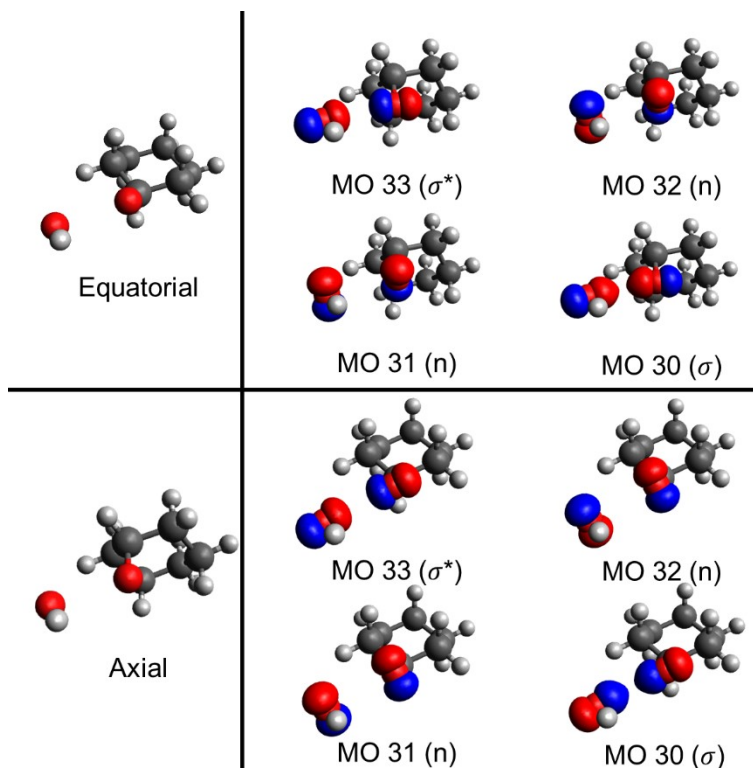


Figure S5. Complete set of molecular orbitals in the active space of CHHP utilized in the CASPT2 calculations. The R_{O-O} distance is elongated to 2.5 Å for visual clarity of orbitals.

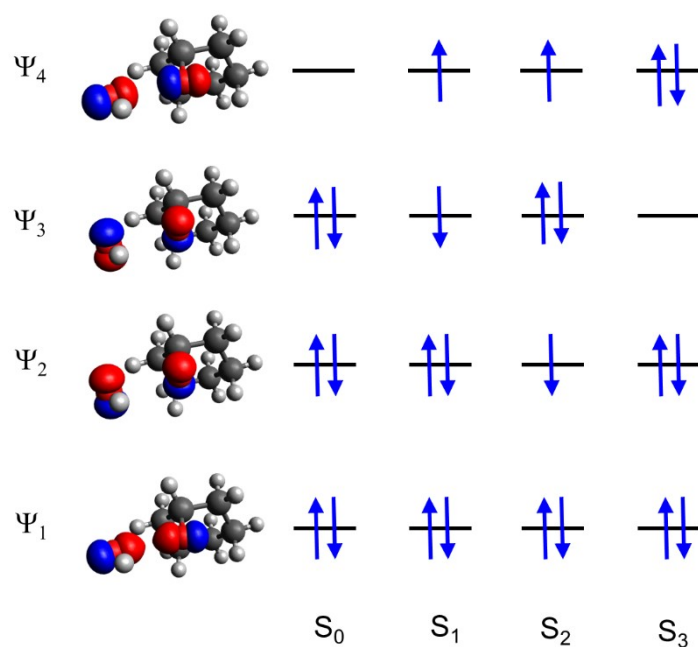


Figure S6. Orbital occupancies for the dominant configurations of the ground and excited electronic states of CHHP. The ground electronic state of CHHP involves an electronic configuration in which all orbitals are doubly occupied. The excited electronic states all involve promotion of an electron to a common σ^* orbital localized along the O-O bond. Configuration interaction (CI) vectors for each state are given in Table S4.

S3. Temporal Profile

The overtone OH stretch ($2\nu_{\text{OH}}$) of CHHP is identified via IR multiphoton dissociation with UV LIF detection of OH products. Temporal profiles for the appearance of OH radical product upon IR activation of $\bullet\text{QOOH}$ are collected and fit with a dual exponential function with rate constants k_{rise} and k_{fall} convoluted with Gaussian functions for the IR and UV pulses, as described previously.⁶⁻⁷ k_{rise} is the exponential appearance of OH products upon unimolecular dissociation of CHHP. k_{fall} is purely experimental in nature arising from OH products moving out of the UV detection region. k_{fall} is determined separately by measuring the OH temporal profile for *syn*- CH_3CHOO at 6080 cm^{-1} ($k_{\text{fall}} = 8.5 \times 10^5\text{ s}^{-1}$), which has a prompt risetime. The overall time resolution is $3.9 \pm 0.1\text{ ns}$, derived from the Gaussian widths of $\Delta t_{\text{IR}} = 2.5 \pm 0.1\text{ ns}$ and $\Delta t_{\text{UV}} = 3.1 \pm 0.1\text{ ns}$, with a corresponding full width at half maximum (FWHM) of $6.5 \pm 0.1\text{ ns}$.

The temporal profile of OH products resulting from IR multiphoton excitation of CHHP at 7012.5 cm^{-1} , obtained by changing the time delay between IR and UV lasers, is shown in Figure S6. Simulations of the temporal profile indicate a lower limit for the OH appearance rate of $k_{\text{rise}} \leq 6.7 \times 10^5\text{ s}^{-1}$ ($\tau_{\text{rise}} \geq 1500\text{ ns}$) with a similar rate as the separately determined k_{fall} . This slow k_{rise} leads to a significant reduction (at least 4-fold) in the peak OH signal intensity, which is consistent with the relatively weak IR signal observed in the $2\nu_{\text{OH}}$ region.

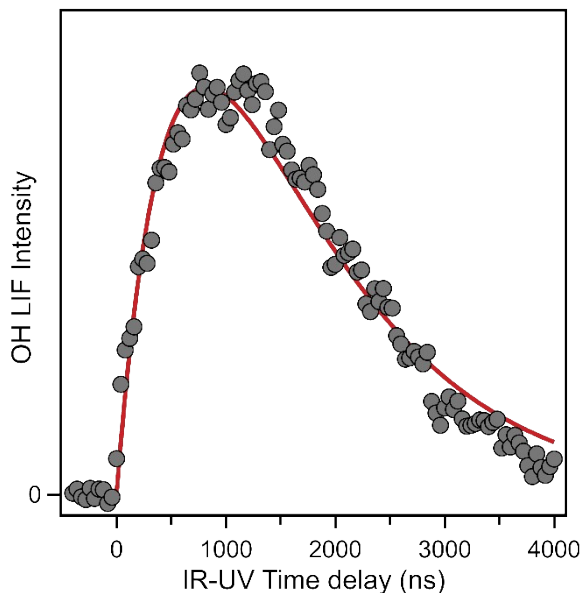


Figure S7. Experimental temporal profile (gray circles) of OH products arising from CHHP unimolecular dissociation upon IR multiphoton excitation at 7012.5 cm^{-1} superimposed with a simulated OH temporal profile (red line, $k_{\text{rise}} \sim k_{\text{fall}}$).

S4. Spectral simulations

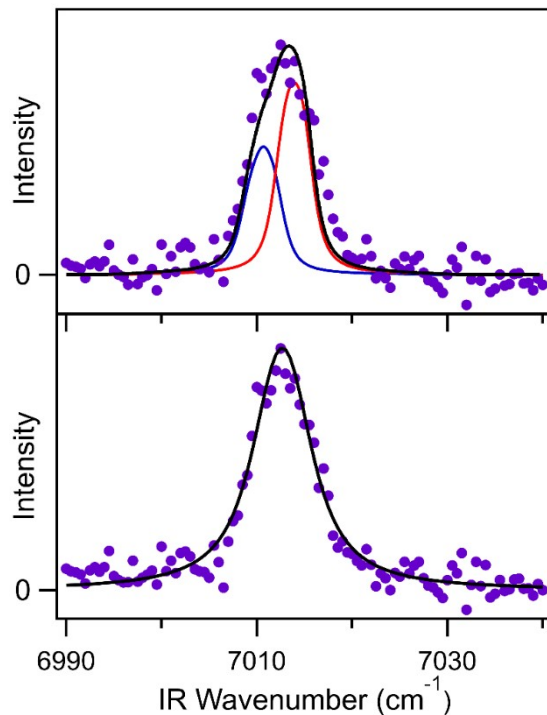


Figure S8. Experimental IR action spectrum obtained for the overtone OH stretch ($2\nu_{\text{OH}}$) of CHHP upon supersonic jet cooling (purple points). Nearly indistinguishable simulations of the rotational band contour (black) are shown for two limiting scenarios: (Top) Closely spaced $2\nu_{\text{OH}}$ transitions, ca. 3 cm^{-1} apart, for equatorial and axial conformer with 60:40 population ratio of equatorial (red) and axial (blue) conformers estimated for a Boltzmann distribution at 300 K, which merge into a single feature (black) utilizing a typical homogeneous linewidth of 1.7 cm^{-1} associated with rapid (ps) intramolecular vibrational energy redistribution. (Bottom) IR power broadening of the $2\nu_{\text{OH}}$ transition for the equatorial conformer with homogeneous linewidth of 6.0 cm^{-1} . Spectral simulations in both panels include experimental rotational constants,⁸ a rotational temperature of 10 K, and the OPO bandwidth (0.9 cm^{-1}). The spectral shift of the observed feature (ca. $10 \pm 2\text{ cm}^{-1}$) is within the accuracy of the theoretical predictions ($10\text{-}20\text{ cm}^{-1}$).

S5. Relaxed potential energy profiles

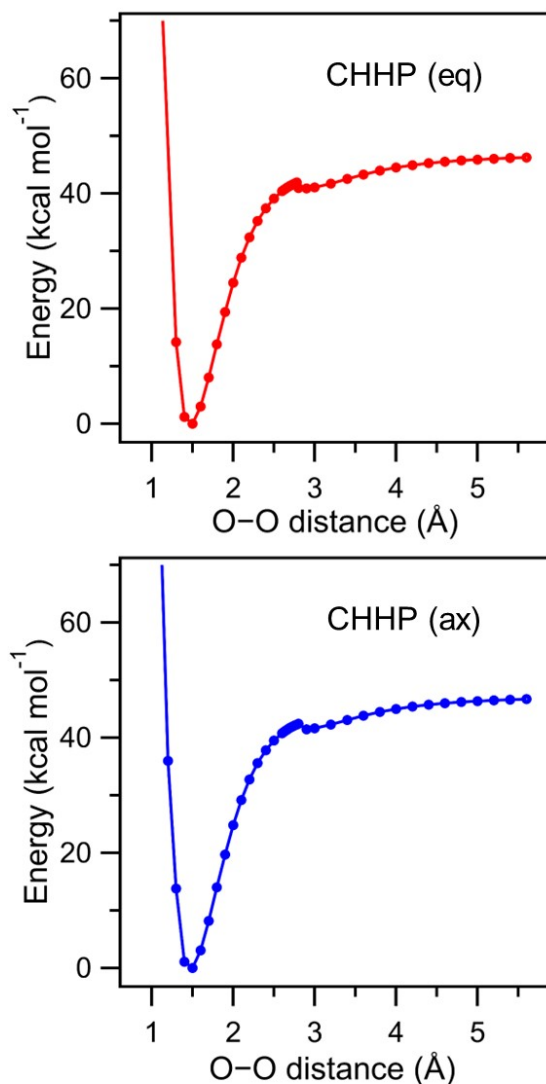


Figure S9. Relaxed potential energy profiles along the O–O stretch coordinate (R_{OO}) for equatorial (red) and axial (blue) conformers of CHHP computed at the CASPT2/aug-cc-pVTZ level of theory. The profiles exhibit a weak saddle point at $R_{OO} = 2.78$ Å followed by a shallow minimum at $R_{OO} = 2.8$ Å, which is attributed to the hydrogen bonding between the H-atom of the OH unit and the O lone pair of the cyclohexoxy radical (RO). The potential energy profile for equatorial CHHP is also shown in Figure 4 of the main text with fewer data points between $R_{OO} = 2.60$ and 2.80 Å.

S6. Supplementary Theoretical Tables

Table S1. Calculated relative energies computed at the CCSD(T)-F12/cc-pVTZ-F12//B2PLYP-D3/cc-pVTZ level of theory for the seven conformers of cyclohexyl hydroperoxide (CHHP). All energies are zero-point energy (ZPE) corrected with harmonic frequencies.

Species	CCSD(T)-F12/cc-pVTZ- F12//B2PLYPD3/cc-pVTZ (kcal mol ⁻¹)
equatorial	0.00
half-chair	11.49
twist-boat	5.83
boat	7.70
twist-boat	6.40
half-chair	10.52
axial	0.21

Table S2. Observed $2\nu_{\text{OH}}$ transition (cm^{-1}) of CHHP along with anharmonic frequencies (cm^{-1}) and intensities (km mol^{-1}) computed for the equatorial and axial conformers of CHHP using the VPT2 method.

Transition	Observed (cm^{-1})	CHHP	
		Calculated ^a (cm^{-1}) (km mol^{-1})	
		Equatorial	Axial
$2\nu_{\text{OH}}$	7012.5	7006.0 (5.7)	6999.0 (5.7)

a. Calculated at the B2PLYP-D3/cc-pVTZ level of theory

Table S3. Computed transition moments of CHHP along principle axes computed using VPT2.

Transition	CHHP ^a					
	Equatorial			Axial		
	A	B	C	A	B	C
$2\nu_{\text{OH}}$	0.803	0.016	0.179	0.948	0.045	0.006

a. Calculated at B2PLYP-D3/cc-pVTZ level of theory.

Table S4. Major contributing CI coefficients for the orbital occupancies of equatorial CHHP at ROO = 2.5 Å. Ψ_n refers to the orbitals in Figure S6.

State	Energy (Hartree)	$\Psi_1\Psi_2\Psi_3\Psi_4^a$							
		2220	2202	2022	0222	22ba/22ab	2b2a/2a2b	b2a2/a2b2	ba22/ab22
S ₀	-385.134	0.80	-	-	0.60	-	-	-	-
S ₁	-385.122	-	-	-	-	+/- 0.43	+/- 0.31	+/- 0.28	+/- 0.36
S ₂	-385.118	-	-	-	-	+/- 0.32	+/- 0.43	+/- 0.38	+/- 0.27
S ₃	-385.109	-	0.72	0.68	-	-	-	-	-

a. description of the 4 active orbitals follows Molpro notation in which:

2= doubly occupied

0 = unoccupied

a = singly occupied with spin up electronic configuration

b = singly occupied with spin down electronic configuration

Table S5. Optimized geometry of each conformer of cyclohexyl hydroperoxide (CHHP) at the B2PLYP-D3/cc-pVTZ level of theory.

<i>equatorial</i>			
C	0.603454	-0.217012	0.219353
C	-0.322869	-1.353537	-0.189103
C	0.102729	1.124263	-0.294960
C	-1.317731	1.395188	0.202901
C	-1.747792	-1.086037	0.300698
C	-2.266062	0.264265	-0.193400
O	1.877792	-0.565171	-0.323513
O	2.841936	0.410935	0.165550
H	3.373854	-0.160232	0.733189
H	0.687512	-0.185456	1.311580
H	0.054773	-2.295459	0.207956
H	-0.313435	-1.432241	-1.278476
H	-2.405289	-1.890960	-0.028203
H	-1.761390	-1.097966	1.393893
H	-3.265603	0.450089	0.201283
H	-2.356361	0.237337	-1.282716
H	-1.673939	2.347468	-0.190271
H	-1.308732	1.492267	1.292357
H	0.784476	1.912666	0.017367
H	0.115933	1.093600	-1.387186
<i>axial</i>			
C	0.217870	0.455758	-0.016627
C	1.496898	-0.049785	-0.674616
C	-0.671763	-0.690781	0.455561
C	0.082832	-1.689725	1.334719
C	2.245301	-1.037169	0.219532
C	1.343963	-2.198639	0.637254
O	0.491821	1.207572	1.173345
O	1.260221	2.380804	0.787179
H	0.600218	3.066677	0.947118
H	-0.332548	1.100045	-0.707926
H	2.126380	0.800418	-0.929561
H	1.217220	-0.536442	-1.613046
H	3.128875	-1.408609	-0.300352
H	2.596859	-0.513834	1.110182
H	1.885208	-2.882350	1.292180
H	1.059499	-2.772218	-0.250383
H	-0.574918	-2.521910	1.588140
H	0.359569	-1.205681	2.272240

H	-1.535342	-0.283834	0.981612
H	-1.047077	-1.196566	-0.437051
<hr/>			
<i>half chair</i>			
C	-0.581975	-0.365850	0.284310
C	-0.170754	1.112633	0.102464
C	0.436422	-1.358447	-0.265594
C	1.779959	-1.087227	0.418517
C	1.327740	1.405930	-0.223726
C	2.367091	0.256143	-0.043417
O	-1.859688	-0.449427	-0.366367
O	-2.429519	-1.755600	-0.061271
H	-3.163099	-1.481805	0.518302
H	-0.732666	-0.588205	1.351551
H	-0.474262	1.665681	0.997368
H	-0.785375	1.508370	-0.714371
H	1.383081	1.748299	-1.262203
H	1.637736	2.267112	0.377767
H	3.154979	0.569721	0.651526
H	2.866588	0.091062	-1.006218
H	2.495118	-1.892261	0.212172
H	1.628751	-1.084280	1.508402
H	0.084476	-2.377558	-0.077810
H	0.523285	-1.235012	-1.354053
<hr/>			
<i>twist-boat</i>			
C	-0.570869	0.181423	0.237140
C	-0.054780	-1.017705	-0.537232
C	0.311072	1.414346	0.006255
C	1.769158	1.024278	-0.289524
C	1.319748	-1.443917	0.008448
C	2.157478	-0.237195	0.479028
O	-1.875242	0.590920	-0.179472
O	-2.802873	-0.468775	0.191981
H	-3.314842	-0.005154	0.866068
H	-0.617369	-0.065758	1.301817
H	0.018424	-0.736181	-1.589118
H	-0.768529	-1.835416	-0.472743
H	1.188483	-2.141871	0.835700
H	1.856465	-1.985822	-0.770091
H	3.219944	-0.448469	0.362981
H	1.993763	-0.062012	1.544677
H	2.429315	1.853026	-0.036166
H	1.896250	0.843710	-1.358292

H	-0.106967	1.974266	-0.831048
H	0.259574	2.062217	0.880700
<hr/>			
<i>boat</i>			
C	0.562254	-0.209999	0.168009
C	0.122167	1.112384	-0.447033
C	-0.317468	-1.360939	-0.300095
C	-1.816034	-1.090131	-0.010115
C	-1.384603	1.389429	-0.215812
C	-2.060323	0.289626	0.604871
O	1.881916	-0.572348	-0.240857
O	2.795716	0.413587	0.321008
H	3.275455	-0.148792	0.941366
H	0.553680	-0.145598	1.259325
H	0.342248	1.055264	-1.513658
H	0.735675	1.913026	-0.041632
H	-1.521291	2.351428	0.276364
H	-1.892719	1.463366	-1.178338
H	-3.132132	0.478472	0.668789
H	-1.685221	0.309404	1.629911
H	-2.212504	-1.860124	0.650499
H	-2.381574	-1.162333	-0.939720
H	-0.152205	-1.484911	-1.370742
H	0.013571	-2.281342	0.177685
<hr/>			
<i>twist-boat</i>			
C	-0.60013	0.196093	0.414523
C	-0.08781	-1.12983	-0.16442
C	0.285371	1.355582	-0.01032
C	1.687717	1.199059	0.605806
C	1.439488	-1.12395	-0.34973
C	2.109451	-0.27791	0.730905
O	-1.9066	0.521618	-0.05681
O	-2.79915	-0.54094	0.388426
H	-3.32968	-0.04892	1.027145
H	-0.63548	0.146874	1.507756
H	-0.58796	-1.28679	-1.11993
H	-0.38639	-1.94803	0.488354
H	1.8196	-2.14473	-0.33359
H	1.696105	-0.71548	-1.32917
H	3.194211	-0.36251	0.675424
H	1.820207	-0.66563	1.710179
H	1.712176	1.671058	1.588206
H	2.404029	1.737373	-0.01469

H	0.343288	1.361456	-1.09945
H	-0.16539	2.300041	0.289984
<hr/>			
<i>half chair</i>			
C	0.632298	-0.372422	0.626084
C	0.116108	1.054783	0.732982
C	-0.371921	-1.405512	0.073658
C	-1.823736	-0.955867	-0.242412
C	-0.837094	1.390351	-0.404587
C	-2.102804	0.560004	-0.233162
O	1.712295	-0.448076	-0.328864
O	2.820496	0.339898	0.187508
H	3.434702	-0.370508	0.410816
H	1.029687	-0.695862	1.589916
H	0.976388	1.719841	0.763802
H	-0.409359	1.168831	1.685171
H	-1.079875	2.452867	-0.399087
H	-0.356379	1.177653	-1.362170
H	-2.835677	0.797569	-1.003897
H	-2.556198	0.843484	0.719205
H	-2.507042	-1.442241	0.452259
H	-2.075693	-1.350162	-1.225844
H	0.079060	-1.779359	-0.844854
H	-0.398479	-2.256248	0.751349

Table S6. Optimized geometry of organic hydroperoxides (ROOH) and associated RO and OH radicals at the W1DB method.

OH			
O	0.000000	0.000000	0.108291
H	0.000000	0.000000	-0.866331
H₂O₂			
O	0.000000	0.725759	-0.057570
O	0.000000	-0.725759	-0.057570
H	0.796208	0.901293	0.460564
H	-0.796208	-0.901293	0.460564
CH₃O			
O	0.790934	0.004664	0.000277
C	-0.572014	0.013310	0.000481
H	-1.026673	1.011238	0.007419
H	-0.931945	-0.555784	-0.873919
H	-0.936768	-0.572630	0.861397
CH₃O-OH			
O	0.015385	-0.607571	-0.024283
O	1.166672	0.275255	-0.098209
H	1.602984	0.063064	0.737639
C	-1.126867	0.225624	0.023439
H	-1.142907	0.835879	0.930402
H	-1.183503	0.869831	-0.856371
H	-1.971828	-0.463985	0.027634
(CH₃)₃CO			
O	0.001178	0.269283	1.426002
C	-0.000205	-0.027070	0.082431
C	0.008062	1.383280	-0.582500
C	1.269288	-0.799568	-0.311357
C	-1.278176	-0.785119	-0.311766
H	1.299501	-0.982878	-1.386397
H	2.156852	-0.237711	-0.023229
H	1.292984	-1.762713	0.199138
H	0.898254	1.936537	-0.290620
H	-0.876057	1.946592	-0.291343
H	0.007728	1.246282	-1.664183
H	-2.159614	-0.213231	-0.024575
H	-1.309802	-0.968561	-1.386777
H	-1.313076	-1.747717	0.199115
(CH₃)₃C-OH			
O	-0.734244	-0.056425	-0.881151
C	0.387993	-0.000106	0.034590

C	1.572470	-0.137696	-0.921299
C	0.409274	1.347345	0.753804
C	0.332705	-1.167524	1.018860
H	1.287794	1.420985	1.396201
H	0.439822	2.162030	0.030381
H	-0.478993	1.467787	1.370920
H	1.571705	0.671025	-1.651302
H	1.531602	-1.086995	-1.455039
H	2.505687	-0.096532	-0.359662
H	0.296302	-2.117434	0.483615
H	1.217234	-1.169673	1.656687
H	-0.544103	-1.091568	1.660149
O	-1.975629	0.101792	-0.141902
H	-2.362716	-0.774676	-0.263261
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(CH₃)₂CHO			
O	0.000063	1.421610	-0.145279
C	-0.000012	0.124829	0.292467
C	-1.285225	-0.626697	-0.077715
C	1.285181	-0.626779	-0.077714
H	-1.315835	-1.607536	0.398054
H	-2.158603	-0.055218	0.232148
H	-1.332428	-0.770209	-1.158080
H	2.158582	-0.055406	0.232273
H	1.315662	-1.607675	0.397943
H	1.332430	-0.770165	-1.158093
H	0.000026	0.265208	1.395760
<hr/>			
(CH₃)₂CHO-OH			
O	0.657270	-0.691750	-0.322613
C	-0.407880	0.013482	0.331625
C	-1.655668	-0.779403	-0.027693
C	-0.476690	1.470295	-0.102754
H	-1.564139	-1.813810	0.300285
H	-1.821014	-0.770252	-1.105861
H	-2.526431	-0.336382	0.455745
H	-0.663621	1.541847	-1.175914
H	-1.283295	1.985616	0.420951
H	0.454537	1.985218	0.128396
O	1.915493	-0.180561	0.193552
H	2.293347	0.204542	-0.607830
H	-0.230057	-0.044534	1.409648
<hr/>			
cyc-C₆H₁₁O			
C	-1.104943	-0.074075	0.329164
C	-0.437830	1.249185	-0.189298

C	-0.327521	-1.292521	-0.192511
C	1.147825	-1.234630	0.209449
C	1.038294	1.291172	0.214002
C	1.808739	0.060293	-0.269980
O	-2.391772	-0.019747	-0.101959
H	-1.052423	-0.027700	1.430940
H	-0.986607	2.097321	0.217106
H	-0.542965	1.272018	-1.275426
H	1.483685	2.202248	-0.192630
H	1.114717	1.365864	1.302628
H	2.843336	0.108930	0.075492
H	1.844190	0.064110	-1.364089
H	1.675167	-2.101390	-0.193712
H	1.232961	-1.303189	1.298989
H	-0.797011	-2.199721	0.192238
H	-0.428256	-1.317056	-1.280830
cyc-C₆H₁₁O-OH			
C	0.604708	-0.224970	0.230810
C	-0.329289	-1.358151	-0.185493
C	0.112443	1.127657	-0.277278
C	-1.318743	1.405658	0.197420
C	-1.763662	-1.083253	0.282655
C	-2.271653	0.276654	-0.205825
O	1.884776	-0.584282	-0.298713
H	0.686126	-0.201675	1.323282
H	0.039161	-2.300639	0.221326
H	-0.305695	-1.447635	-1.275545
H	-2.420857	-1.882381	-0.065399
H	-1.797640	-1.109429	1.376444
H	-3.272188	0.467416	0.188124
H	-2.364680	0.256294	-1.296594
H	-1.665194	2.359235	-0.205702
H	-1.324816	1.511894	1.287184
H	0.787460	1.914559	0.060679
H	0.143851	1.115145	-1.371686
O	2.879014	0.294199	0.297170
H	3.181325	0.776312	-0.483502

Table S7. Optimized geometry of organic hydroperoxides (ROOH) and associated RO and OH radicals at the B2PLYP-D3/cc-pVTZ level of theory.

OH			
O	0.000000	0.000000	0.107885
H	0.000000	0.000000	-0.863082
H₂O₂			
O	0.000000	0.726222	-0.057231
O	0.000000	-0.726222	-0.057231
H	0.797683	0.893229	0.457845
H	-0.797683	-0.893229	0.457845
CH₃O			
O	0.791570	-0.000100	-0.007750
C	-0.575790	-0.000290	-0.012880
H	-1.005510	-0.908610	-0.447190
H	-0.867520	0.010990	1.050750
H	-1.004790	0.900150	-0.464260
CH₃O-OH			
O	-0.017470	0.609500	-0.000020
O	-1.132250	-0.338420	-0.000030
H	-1.860130	0.294260	0.000210
C	1.127660	-0.211560	0.000020
H	1.162880	-0.837460	-0.892520
H	1.966180	0.481230	-0.000040
H	1.162900	-0.837360	0.892620
(CH₃)₃CO			
O	-0.000100	0.273050	1.426160
C	0.000010	-0.024770	0.078680
C	-0.000370	1.374640	-0.585240
H	0.885950	1.933280	-0.295980
H	-0.000330	1.236140	-1.665180
H	-0.886980	1.932810	-0.295970
C	1.268210	-0.790280	-0.308950
H	2.151030	-0.221120	-0.026010
H	1.297220	-1.749570	0.205390
H	1.294860	-0.977250	-1.381930
C	-1.267770	-0.790960	-0.308980
H	-2.150910	-0.222270	-0.026100
H	-1.294270	-0.977990	-1.381950
H	-1.296290	-1.750250	0.205400
(CH₃)₃C-OH			
O	-0.731125	0.000226	-0.877219
O	-1.950030	-0.000004	-0.057492

H	-2.590760	0.000658	-0.777477
C	0.386124	-0.000011	0.028945
C	1.567893	0.000871	-0.932947
H	1.546931	0.886505	-1.565006
H	2.497195	0.000008	-0.366140
H	1.546562	-0.883364	-1.566965
C	0.373363	1.261283	0.884710
H	0.361478	2.145528	0.249756
H	-0.504025	1.282994	1.525265
H	1.262572	1.295249	1.513040
C	0.373877	-1.262394	0.883130
H	0.363630	-2.145883	0.247093
H	1.262365	-1.296226	1.512481
H	-0.504257	-1.285742	1.522613
<hr/>			
(CH₃)₂CHO			
O	-0.228786	1.365942	-0.157206
C	0.020148	0.122683	0.371804
C	-1.174408	-0.740203	-0.094047
H	-1.189811	-0.796826	-1.179961
H	-1.053714	-1.741126	0.315615
H	-2.112700	-0.319699	0.256418
C	1.348289	-0.455680	-0.102121
H	1.349809	-0.553173	-1.186519
H	2.170175	0.196475	0.186573
H	1.517792	-1.436029	0.342917
H	-0.015434	0.162042	1.468788
<hr/>			
(CH₃)₂CHO-OH			
O	-0.663130	-0.663440	-0.354350
O	-1.911060	-0.034650	0.049480
H	-2.302620	-0.760480	0.550650
C	0.399110	0.007720	0.334090
C	1.633090	-0.807380	-0.008190
H	1.805880	-0.796300	-1.083230
H	2.503800	-0.378830	0.484770
H	1.521520	-1.839610	0.316200
C	0.509360	1.458390	-0.096650
H	0.727950	1.516920	-1.162300
H	-0.420120	1.985950	0.098560
H	1.310520	1.953810	0.451220
H	0.197210	-0.049120	1.407600

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