Supplementary Information

Experimental and Computational Investigations of C-H Activation of Cyclohexane by Ozone in Liquid CO_2

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1. Peng- Robinson EOS parameters

Table S1: Fitted binary interaction parameters for cyclohexane/O_2/CO_2 system

Binary Pair	k_{ij}
CO_2-cyclohexane	0.166
CO_2-O_2	0.156
O_2-cyclohexane	0.208

2. Analysis of hydrocarbons in vented gas from the reactor

Table S1: Gas phase hydrocarbons detected during cyclohexane ozonation (corresponding to Table 2, Entries#1&2)

Cyclohexane conversion (%)	11.6	12.4
Cyclohexane (mol)	6.7 (10^{-4})	1.2 (10^{-3})
Cyclohexanone (mol)	9.5 (10^{-6})	1.8 (10^{-5})
Cyclohexanol (mol)	Not detectable	Not detectable

*Reaction conditions: 9.22×10^{-3} mol cyclohexane, O_3/cyclohexane = 49-51%. 280 K, 6.7 MPa, 400 rpm, 1 hr). The number in the parentheses are the percentage of gaseous cyclohexane in total cyclohexane (liquid + gas phases)

3. GC-MS spectra of cyclohexanone and cyclohexanol

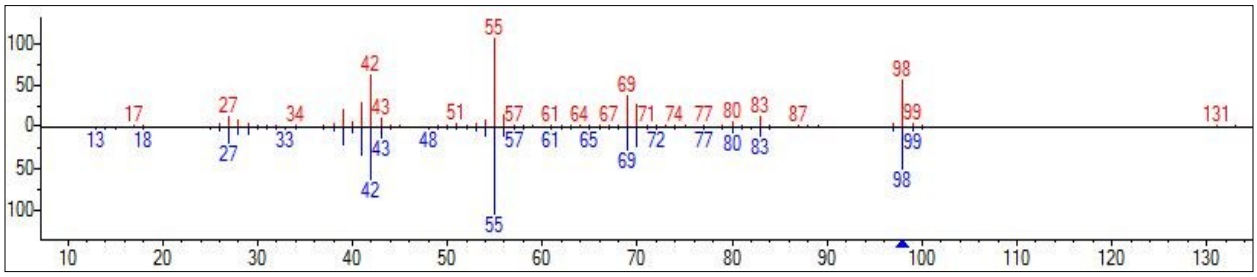

Figure S1: Mass fragmentation pattern of cyclohexanone

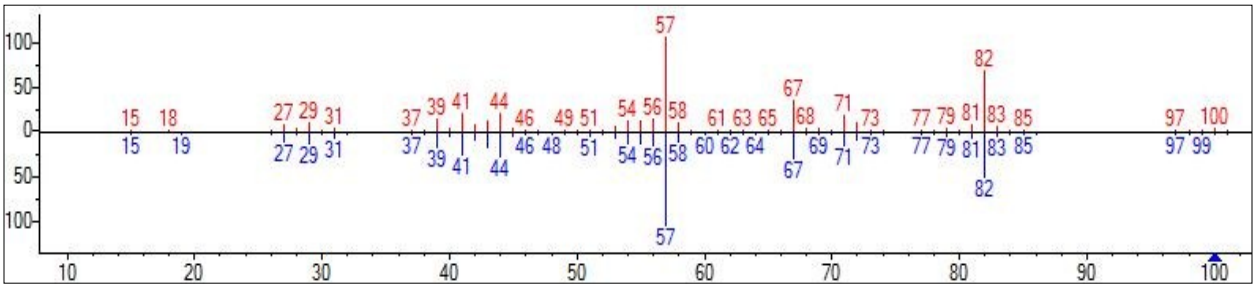

Figure S2: Mass fragmentation pattern of cyclohexanol

4. GC-FID chromatograph of product mixture from the reactor

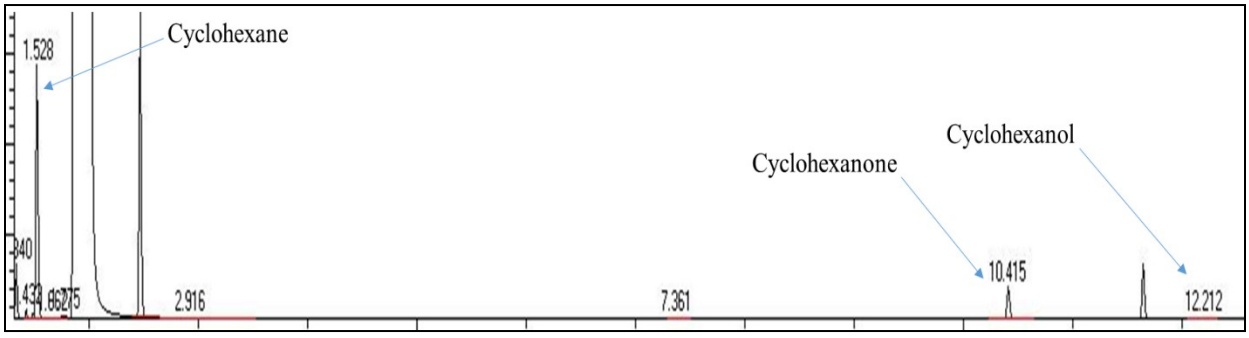

Figure S3: GC-FID chromatogram of liquid phase reaction mixture showing cyclohexanone and cyclohexanol

5. Ceric sulfate titration method for hydrogen peroxide quantification

The reaction stoichiometry for titration is described in Eq. S2.

$$H_2O_2 + 2\ Ce(SO_4)_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2 \qquad \text{(Eq. S2)}$$

A few drops of ferroin indicator solution were added to 150 mL of 5 (v/v) % sulfuric acid. The pink-colored solution was then titrated by ceric sulfate solution (0.1N) to a bright green color. A

known amount of product solution was added to this bright green solution, which then changed back to pink color. This pink colored solution was titrated by ceric sulfate solution back to bright green color as end point. The mass of chemicals consumed during the titration procedure was used to quantify hydrogen peroxide according to Eq. S3.

$$H_2O_2\ (wt.\%) = \frac{Volume\ of\ Ce(SO_4)_2\ (L)\ \times\ 0.1\ mol\ L^{-1}\ \times\ 0.5 \frac{mole\ H_2O_2}{mole\ Ce(SO_4)_2} \times \frac{34.01\ g\ H_2O_2}{mol\ H_2O_2}}{Weight\ of\ sample\ (g)} \quad \text{(Eq. S3)}$$

Table S2: Example of H_2O_2 measurement by ceric sulfate titration

Entry	Sample amount (g)	Sulfuric acid (mL)	Ceric sulfate solution (g)	Mass percentage (%)	Mass in 35 mL product solution (g)	Mol. of H_2O_2 in 35 mL product solution
1	5.2896	150	0.3423	0.0138	3.3×10^{-3}	9.6×10^{-5}
2	5.2284	150	0.3267	0.0133	3.2×10^{-3}	9.3×10^{-5}

*Reaction condition: 9.22×10^{-3} mol cyclohexane, O_3/cyclohexane = 51%. 280 K, 6.9 MPa, 400 rpm, 1 hr (corresponding to Table 1, entry#2). The titration was repeated twice for each product sample, as shown in the two entries above.

6. IR spectra of cyclohexane, cyclohexanol and cyclohexanone

The IR absorbance spectra for cyclohexane, cyclohexanol and cyclohexanone in toluene were obtained with the ReactIR15 instrument at 293 K and 0.1 MPa (Figure S4). The IR absorbance peaks 2857 cm^{-1}, 1723 cm^{-1} and 1067 cm^{-1} were chosen to identify cyclohexane, cyclohexanone and cyclohexanol as there are no overlapping solvents peaks in these regions. To verify the ReactIR detection of cyclohexane in liquid CO_2, the following experiment was performed. Approximately 15 mL of CO_2 from an ISCO pump (3.64 MPa, 293 K, 266 mL) was pumped as liquid into the 50 mL Parr reactor where the CO_2 was allowed equilibrium at 280 K, 4.14 MPa. The liquid CO_2 formed at this condition was scanned and taken as IR background. Next,

a small amount liquid cyclohexane (1 mL) was pumped into the reactor by another ISCO pump at 293 K, and the binary mixture was stirred at 400 rpm to reach equilibrium followed by IR scan. The recorded IR spectra are shown in Figure S5. The IR absorbance peaks assigned to cyclohexane occur at 2857 cm^{-1} and 2939 cm^{-1}. The prominent peak at ~ 2300 cm^{-1} corresponds to CO_2.

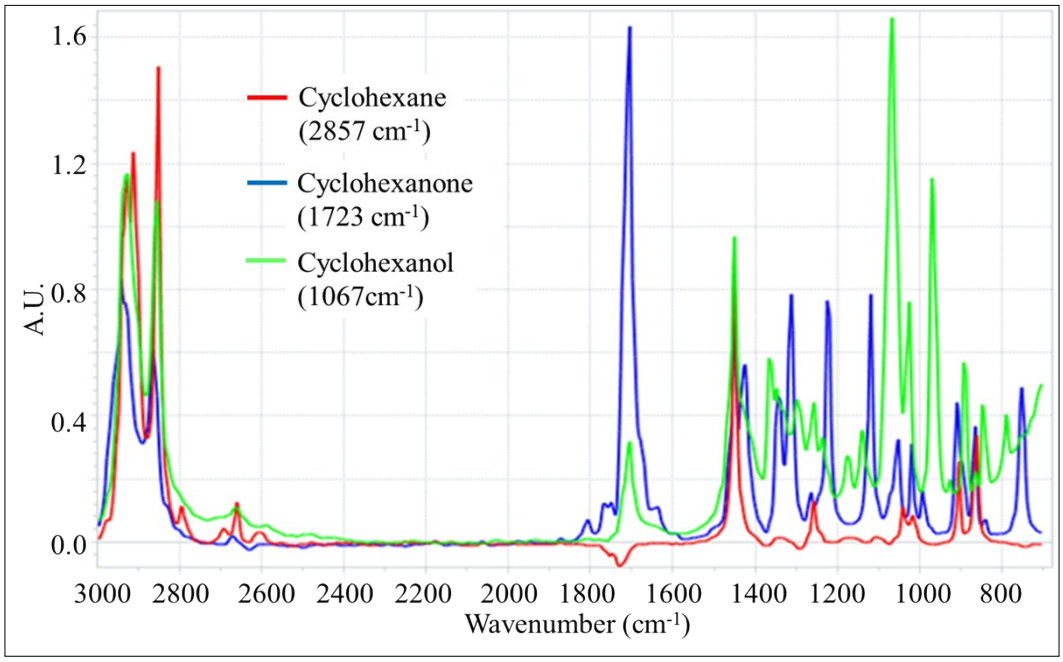

Figure S4: IR spectra of cyclohexane, cyclohexanone and cyclohexanol.

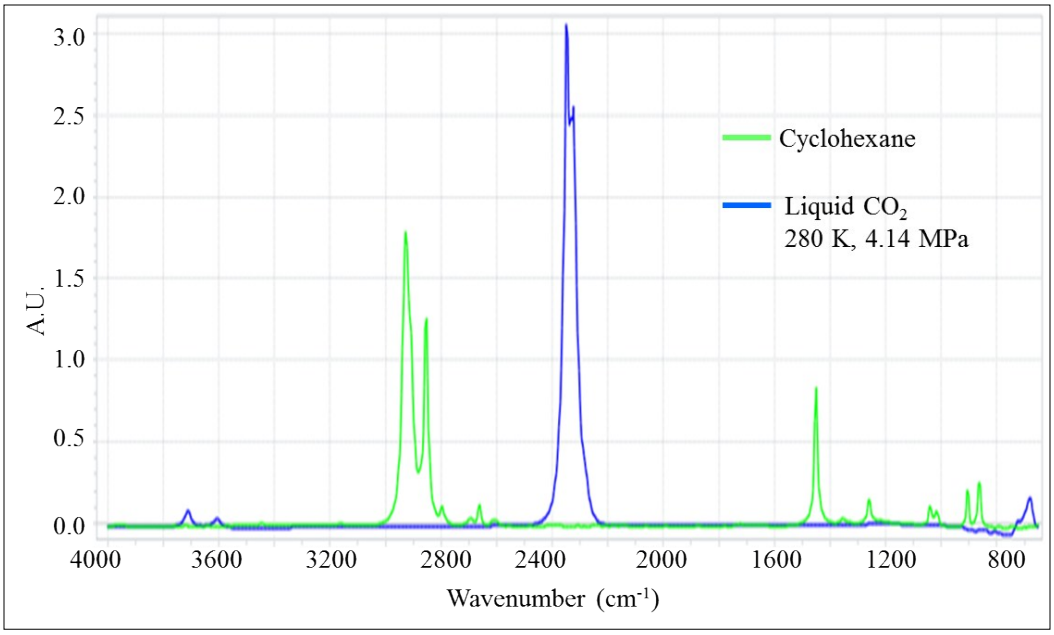

Figure S5: IR spectra of cyclohexane in liquid CO_2 (280 K, 4.14 MPa)

7. Minor Products from ozonation of cyclohexane

Table S3: Distribution of minor products from ozonation of cyclohexane based on FC/FID chromatogram (operating conditions correspond to Table 2, entry#1)

Products	Peak Area Counts	Total Area	Area Ratio to Cyclohexane[a]	Yield [b]
Acetic acid	1,071,372	9.12 (10)^6	1:100 (1%)	0.80 mol%
Oxalic acid	191,981			
Butyrolactone	288,999			
Pentanoic acid	194,451			
Tetrahydro-2-pyranone	598,308			
Hexanoic acid	118,531			
1,4-cyclohexanedione	754,383			
Succinic anhydride	73,849			
Propanoic acid	494,363			
Butanoic acid	1,162,297			
Heptanoic acid	2,368,298			
Hexanoic acid, 6-hydroxy-	774,322			
Butanal, 3- hydroxy-	173,771			
2-Oxepanone	313,330			
Cyclohexanone, 2-hydroxy-	134,870			
Cyclohexanone,4-hydroxy-	135,655			

Cyclohexanone,3- hydroxy-	273,334			

[a] Area Ratio to Cyclohexane: total area of minor products/area of cyclohexane in product sample; [b] Yield = moles of minor products / initial moles of cyclohexane.

8. Computational details

Table S4**:** Comparison of Experimental and Computationally-Predicted Metric Parameters for O_3.

method	*d*(O–O) (Å)	∠ (O–O–O) (°)
experiment[a]	1.27276	116.7542
CAS(18,12)	1.2772	116.57
TPSS-D3	1.2759	118.12

[a] Experimental data from Tyuterev, V. G.; Tashkun, S.; Jensen, P.; Barbe, A.; Cours, T., Determination of the Effective Ground State Potential Energy Function of Ozone from High-Resolution Infrared Spectra. *J. Mol. Spectrosc.* 1999, *198*, 57-76.

Table S5: Zero-Point-Energy (ZPE)-Corrected Electronic Energies (*E*) of Transitions States and Reaction Products for Cyclohexane (C_6H_{12}) Oxidation by Ozone (O_3).

Structure	*E* + ZPE (kcal/mol)	Relative *E* + ZPE (kcal/mol)
C_6H_{12} + O_3 (reactant complex)	-289501.8	0.0
HAT TS (DFT)	-289484.8	17.0
HAT TS (CASSCF/NEVPT2)	-289482.7	19.1
$C_5H_{11}C$• + •OOOH	-289497.2	4.6
$C_5H_{11}COOOH$	-289546.4	-44.6
$C_5H_{11}CO$• + •OOH	-289532.7	-31.0
$C_5H_{10}CO$ + H_2O_2 (ketone product)	-289591.7	-89.9
$C_5H_{11}COH$ + O_2 (alcohol product)	-289577.5	-75.7

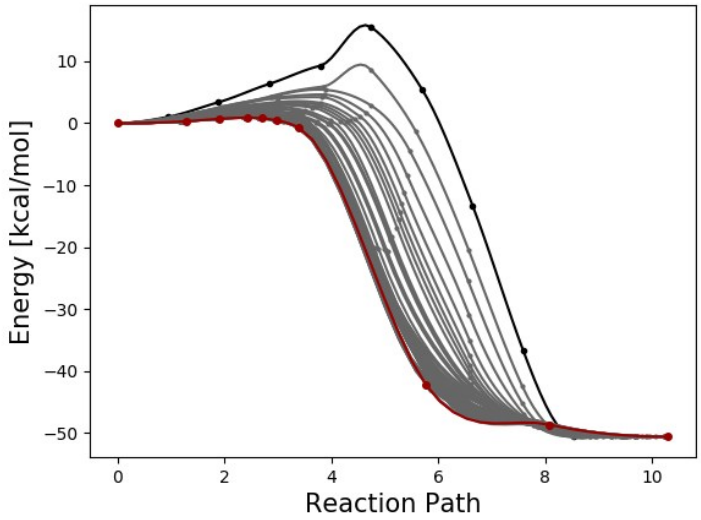

Figure S6: Reaction paths for recombination of hydrotrioxyl and cyclohexyl radicals from a nudged elastic band calculation. The black and red circles are for the initial and final paths; the grey circles are intermediate paths. The solid lines are a spline interpolation through the path points.

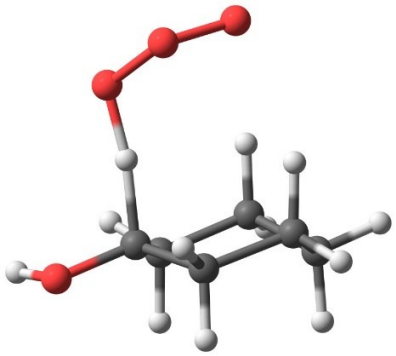

Figure S7: Optimized transition-state structure for cyclohexanol oxidation by O_3. The energy (E + ZPE) of this transition-state relative to the reactant complex is 10.3 kcal/mol.

Cartesian Coordinates of All DFT Models

HAT1 RC

	x	y	z
C	-0.005702414	-5.370607200	-1.057911047
C	0.358397463	-5.141774553	0.417794434
C	1.810124865	-5.555303818	0.711607401
C	2.068565508	-7.014188343	0.294667059
C	1.704655077	-7.245736727	-1.181750695
C	0.252809668	-6.829763721	-1.473678204
H	-1.062195796	-5.100835813	-1.239487637
H	0.605903717	-4.697053993	-1.690278389

H	-0.326502363	-5.731232499	1.059395390
H	0.206207145	-4.077958416	0.688692968
H	2.041490154	-5.416329173	1.783863915
H	2.497226597	-4.891582195	0.149204700
H	1.456001038	-7.685635953	0.929025695
H	3.125448893	-7.282288058	0.478174087
H	1.861871521	-8.306132791	-1.452883125
H	2.387155083	-6.650130800	-1.820465518
H	0.021009924	-6.968290683	-2.545868041
H	-0.434212158	-7.494307686	-0.912319569
O	1.740060739	-1.599384788	0.252261440
O	2.269277676	-1.886291992	-0.874146839
O	0.477352275	-1.747056991	0.375303618

HAT1 TS

	x	y	z
C	-0.839337031	-5.387449853	0.469978190
C	-0.069709048	-4.798574531	1.625691777
C	1.336173612	-5.318503350	1.792511729
C	1.274388993	-6.864287774	1.971831378
C	0.510842316	-7.522227077	0.812634747
C	-0.898716539	-6.932539468	0.654033975
H	-1.858618139	-4.970170309	0.407492411
H	-0.323369633	-5.164639773	-0.482200597
H	-0.642585754	-4.713537335	2.566278407
H	0.066493238	-3.412012662	1.369583747
H	1.841238900	-4.852631575	2.655639511
H	1.934105274	-5.096356857	0.889078105
H	0.769680371	-7.095825046	2.929071746
H	2.303698540	-7.259817605	2.043113141
H	0.445817015	-8.613523917	0.977458114
H	1.076565604	-7.375039071	-0.128019618
H	-1.419266611	-7.379138078	-0.212421802
H	-1.502580807	-7.166409883	1.551583149
O	1.471231288	-2.084504856	0.573474147
O	1.452063430	-2.426350713	-0.660512692
O	0.180683867	-2.258346462	1.248646108

HAT1 PC

	x	y	z
C	1.101840168	-5.364443343	0.038293382

C	-0.308336237	-5.128710225	0.491683983
C	-0.629111314	-5.518206376	1.904686194
C	-0.281106363	-7.024571859	2.101497267
C	1.171323786	-7.309616359	1.687076867
C	1.449445590	-6.870647956	0.240624833
H	1.247200924	-5.074400764	-1.016093345
H	1.802647061	-4.766064527	0.652233185
H	-1.109932346	-5.227319759	-0.257723608
H	-0.582178584	-3.280164975	0.359712468
H	-1.687927255	-5.330997224	2.150965285
H	-0.009142066	-4.932398166	2.610713950
H	-0.968967465	-7.636271654	1.487016116
H	-0.451559118	-7.304787087	3.156935998
H	1.390312678	-8.387185283	1.801506684
H	1.857702133	-6.771347845	2.370102876
H	2.508712389	-7.040195817	-0.025367699
H	0.838169136	-7.477344380	-0.454481764
O	-0.262785718	-1.767916629	1.625584883
O	0.914198678	-2.172090570	1.825630817
O	-0.881707195	-2.307203810	0.304346240

cyclohexyltrioxidane

	x	y	z
C	0.310655000	0.340360000	-0.949609000
C	-0.926688000	0.412236000	-0.047708000
C	-0.570187000	0.167912000	1.424187000
C	0.153584000	-1.180725000	1.591173000
C	1.397071000	-1.266015000	0.692172000
C	1.032017000	-1.009896000	-0.778453000
H	0.014388000	0.465371000	-2.008352000
H	0.992176000	1.170360000	-0.683750000
H	-1.675650000	-0.333911000	-0.377227000
H	-0.598150000	2.346881000	-2.465060000
H	-1.488018000	0.202273000	2.035564000
H	0.086451000	0.990013000	1.765747000
H	-0.542059000	-2.002974000	1.333608000
H	0.430086000	-1.319153000	2.651439000
H	1.879485000	-2.254240000	0.799129000
H	2.137890000	-0.510987000	1.021097000
H	1.935104000	-1.031924000	-1.413943000

H	0.371329000	-1.822935000	-1.137923000
O	-2.116923000	1.981787000	-1.370893000
O	-1.563457000	1.717518000	-0.041171000
O	-1.259103000	2.938051000	-2.040027000

Peroxyl Cleavage

	x	y	z
C	1.621720043	-5.365505174	0.480962563
C	0.330023043	-4.674879174	0.936166563
C	-0.274170957	-5.378569174	2.193403563
C	-0.494723957	-6.873775174	1.898994563
C	0.792469043	-7.566932174	1.427095563
C	1.386073043	-6.858117174	0.199061563
H	2.004275043	-4.848791174	-0.416227437
H	2.378672043	-5.240711174	1.278493563
H	-0.448214957	-4.748694174	0.138371563
H	-0.971723043	-2.304593826	-0.898017563
H	-1.217087957	-4.879407174	2.470980563
H	0.435263043	-5.253905174	3.031234563
H	-1.275834957	-6.978615174	1.121445563
H	-0.884442957	-7.359292174	2.812655563
H	0.587196043	-8.628470174	1.198206563
H	1.534443043	-7.555008174	2.249591563
H	2.332027043	-7.340471174	-0.105916437
H	0.688715043	-6.963344174	-0.655633437
O	0.765432957	-2.443191826	-0.231555563
O	0.484628043	-3.352347174	1.321063563
O	-0.184283043	-2.861557826	-1.112959563

cyclohexanol

	x	y	z
C	1.998214000	-5.699908000	0.600258000
C	0.838689000	-4.707161000	0.691480000
C	-0.127686000	-5.086846000	1.822126000
C	-0.651117000	-6.523994000	1.649408000
C	0.509310000	-7.527936000	1.549827000
C	1.484669000	-7.139674000	0.426099000
H	2.662214000	-5.413521000	-0.234492000
H	2.592345000	-5.622095000	1.531198000
H	0.282444000	-4.722401000	-0.271381000
H	0.679273000	-2.761115000	0.957935000

H	-0.970517000	-4.369568000	1.851716000
H	0.413051000	-4.995541000	2.783856000
H	-1.262947000	-6.581833000	0.727374000
H	-1.320305000	-6.785823000	2.488826000
H	0.119061000	-8.548564000	1.383422000
H	1.055120000	-7.548226000	2.513803000
H	2.337979000	-7.840801000	0.395781000
H	0.968346000	-7.228432000	-0.550265000
O	1.414147000	-3.396820000	0.887302000

cyclohexanone

	x	y	z
C	0.957908000	-5.708662000	0.173714000
C	-0.184625000	-5.109600000	0.982926000
C	-0.243971000	-5.548905000	2.439374000
C	-0.156918000	-7.086365000	2.572759000
C	1.059206000	-7.648481000	1.821424000
C	1.027584000	-7.243804000	0.339895000
H	0.846638000	-5.409111000	-0.880684000
H	1.897899000	-5.264462000	0.558811000
H	-1.157792000	-5.142455000	2.901541000
H	0.629070000	-5.095746000	2.951041000
H	-1.080895000	-7.535204000	2.160623000
H	-0.118777000	-7.361601000	3.641721000
H	1.085483000	-8.749207000	1.913098000
H	1.989357000	-7.267500000	2.288080000
H	1.914579000	-7.632132000	-0.191424000
H	0.141741000	-7.697706000	-0.144165000
O	-1.000731000	-4.335376000	0.495120000

9. Isooctane ozonation

Table S6. Operating Conditions for *Iso*octane Ozonation

P_{tot}/T	6.2 MPa/280 K
*iso*octane	0.012 mol (2 mL)
CO_2	0.29 mol (14 mL)
p_{O3}	1.3 bar
Initial [O_3/C_8H_{18}]	0.38
Reaction time	1 h

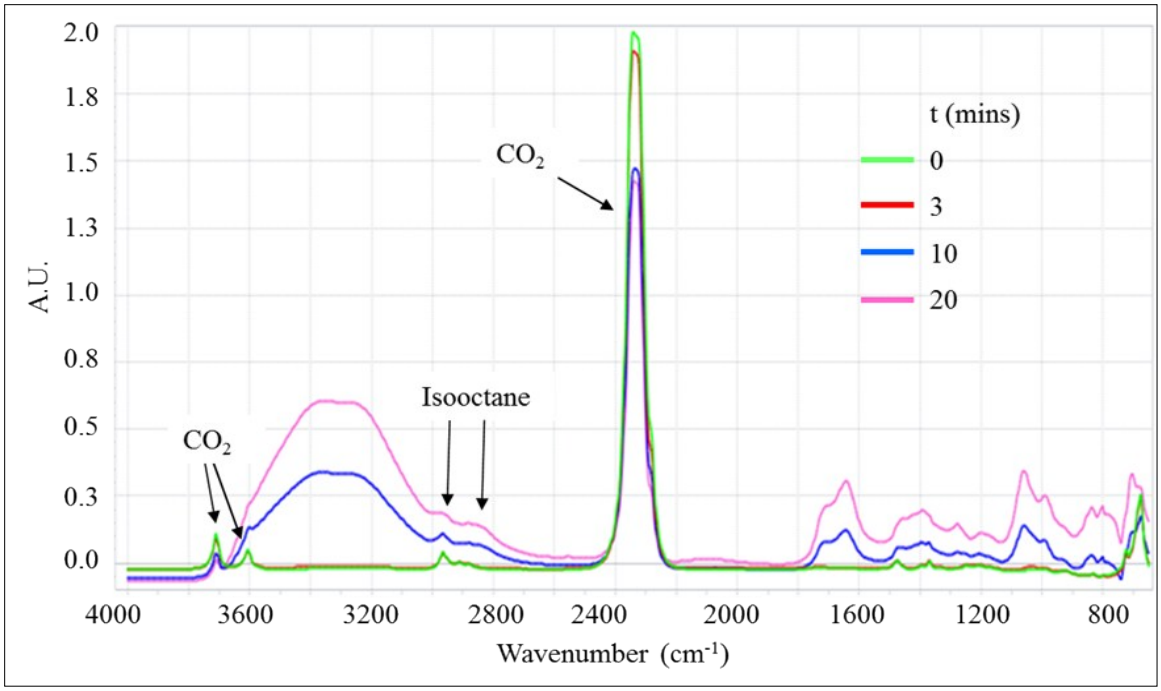

Figure S8: IR absorbance peaks during ozonation of *iso*octane. (operating conditions are given in Table S6).

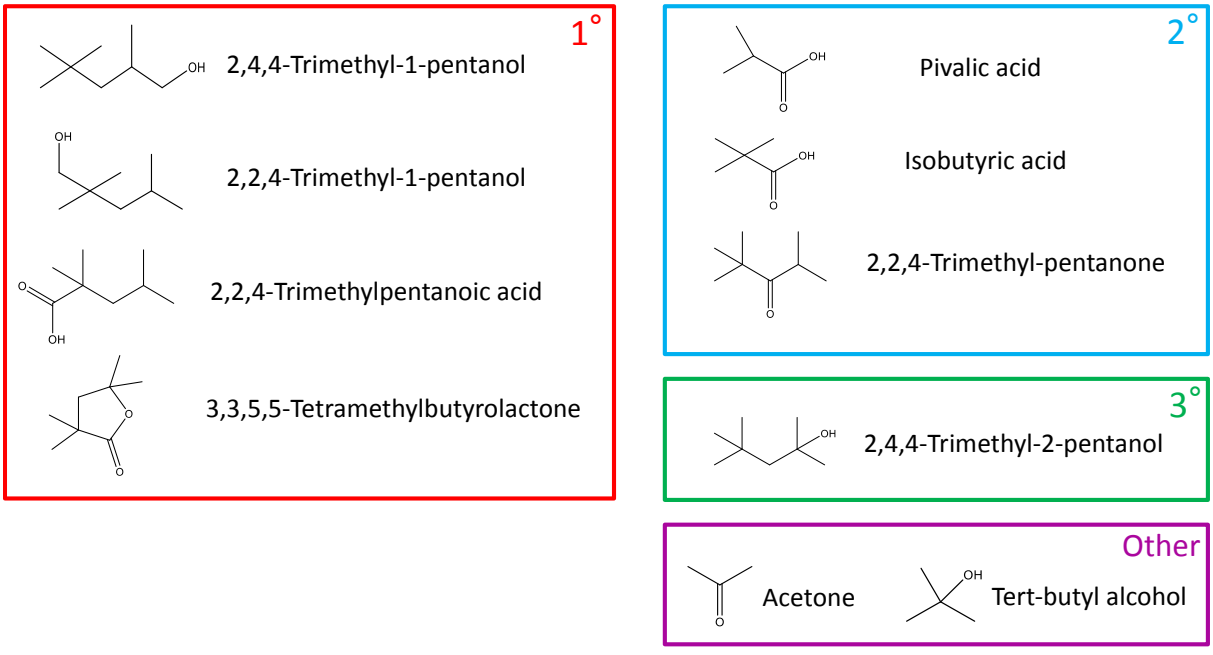

Figure S9. Variety of oxygenated species detected in the GC/MS spectra of product mixture from *iso*octane ozonation in liquid CO_2. Product distribution suggests that ozone prefers attack at the primary carbon.