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Kinetic Analysis for HO_2 Addition to Ethylene, Propene, and Isobutene, and Thermochemical Parameters of Alkyl Hydroperoxides and Hydroperoxide Alkyl Radicals

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Thermochemical kinetic analysis for the reactions of HO_2 radical addition to the primary, secondary, and tertiary carbon−carbon double bonds of ethylene, propene, and isobutene are studied using canonical transition state theory (TST). Thermochemical properties of reactants, alkyl hydroperoxides (ROOH), hydroperoxy alkyl radicals (R•OOH), and transition states (TSs) are determined by ab initio and density functional calculations. Enthalpies of formation ($\Delta H_f°_{298}$) of product radicals (R•OOH) are determined using isodesmic reactions with group balance at MP4(full)/6-31G(d,p)//MP2(full)/6-31G(d), MP2(full)/6-31G(d), complete basis set model chemistry (CBS-q with MP2(full)/6-31g(d) and B3LYP/6-31g(d) optimized geometries), and density functional (B3LYP/6-31g(d) and B3LYP/6-311+g(3df,2p)//B3LYP/6-31g(d)) calculations. $\Delta H_f°_{298}$ of TSs are obtained from the $\Delta H_f°_{298}$ of reactants plus energy differences between reactants and TSs. Entropies ($S°_{298}$) and heat capacities ($Cp(T)$ $300 \leq T/\mathrm{K} \leq 1500$) contributions from vibrational, translational, and external rotational are calculated using the rigid-rotor-harmonic-oscillator approximation based on geometric parameters and vibrational frequencies obtained at MP2(full)/6-31G(d) and B3LYP/6-31G(d) levels of theory. Selected potential barriers of internal rotations for hydroperoxy alkyl radicals and TSs are calculated at MP2(full)/6-31G(d) and CBS-Q//MP2(full)/6-31G(d) levels. Contributions from hindered rotors of $S°_{298}$ and $Cp(T)$ are calculated by the method of Pitzer and Gwinn and by summation over the energy levels obtained by direct diagonalization of the Hamiltonian matrix of hindered internal rotations when the potential barriers of internal rotations are available. Calculated rate constants obtained at CBS-q//MP2(full)/6-31G(d) and CBS-q//B3LYP/6-31G(d) levels of theory show similar trends with experimental data: HO_2 radical addition to the tertiary carbon−carbon double bond (HO_2 addition at CD/C2 carbon atom of isobutene) has a lower activation energy than addition to the secondary carbon−carbon double bond CD/C/H, which is lower than addition to the primary carbon−carbon bond CD/H2; the values are 12.11(11.56), 11.08(10.34), and 7.63(7.03) kcal/mol, respectively, at CBS-q//MP2 (full)/ 6-31G(d) level. Data in parentheses are calculations at the CBS-q//B3LYP/6-31G(d) level. The E_a for addition to primary carbon−carbon double bonds of ethylene, propene, and isobutene also show a decreasing trend 13.49(12.89), 12.16(11.20), and 10.70(10.59) kcal/mol, respectively. The high-pressure limit rate constants are (based on CBS-q//MP2(full)/6-31G(d) calculations) (Q = OOH): $k_{1,\infty}(HO_2 + C{=}C \Rightarrow C{\bullet}CQ) = 4.13 \times 10^4\ T^{2.332} \exp(-13.49\ \mathrm{kcal\ mol^{-1}}/RT)\ \mathrm{cm^3/mol\text{-}s}$; $k_{2,\infty}(HO_2 + C{=}CC \Rightarrow CC{\bullet}CQ) = 2.47 \times 10^4\ T^{2.132} \exp(-12.16\ \mathrm{kcal\ mol^{-1}}/RT)\ \mathrm{cm^3/mol\text{-}s}$; $k_{3,\infty}(HO_2 + C{=}CC \Rightarrow C{\bullet}CQC) = 7.74 \times 10^3\ T^{2.285} \exp(-11.08\ \mathrm{kcal\ mol^{-1}}/RT)\ \mathrm{cm^3/mol\text{-}s}$; $k_{4,\infty}(HO_2 + C_2C{=}C \Rightarrow C_2C{\bullet}CQ) = 3.45 \times 10^5\ T^{1.765} \exp(-10.70\ \mathrm{kcal\ mol^{-1}}/RT)\ \mathrm{cm^3/mol\text{-}s}$; $k_{5,\infty}(HO_2 + C_2C{=}C \Rightarrow C_3{\bullet}CQ) = 2.78 \times 10^4\ T^{2.106} \exp(-7.63\ \mathrm{kcal\ mol^{-1}}/RT)\ \mathrm{cm^3/mol\text{-}s}$. Enthalpies of formation for alkyl hydroperoxides are determined to be $\Delta H_f°_{298}$ (CCQ) = −39.70 ± 0.3 kcal/mol, $\Delta H_f°_{298}$ (CCCQ) = −44.77 ± 0.41 kcal/mol, $\Delta H_f°_{298}$ (CCQC) = −48.99 ± 0.32 kcal/mol, $\Delta H_f°_{298}$ (C_2CCQ) = −51.32 ± 0.38 kcal/mol, and $\Delta H_f°_{298}$ (C_3CQ) = −57.91 ± 0.47 kcal/mol. $\Delta H_f°_{298}$ of hydroperoxy alkyl radicals are $\Delta H_f°_{298}$ (C•CQ) = 10.96 ± 1.06 kcal/mol, $\Delta H_f°_{298}$ (CC•CQ) = 2.62 ± 1.29 kcal/mol, $\Delta H_f°_{298}$ (C•CQC) = 0.68 ± 1.54 kcal/mol, $\Delta H_f°_{298}$ (C_2C•CQ) = −7.24 ± 1.25 kcal/mol, and $\Delta H_f°_{298}$ (C_3•CQ) = −6.42 ± 1.28 kcal/mol.

Introduction

The addition of an HO_2 radical to alkenes plays an important role in combustion kinetics and atmospheric chemistry.[1−4] Hydroperoxides and alkyl hydroperoxides are also important in biochemical synthesis and metabolism.[5−9] HO_2 is a relative nonreactive radical having weak HOO−H and HOO−CH_3 bonds of 88.2 and 70.1 kcal/mol, respectively; its low reactivity is responsible for the buildup in concentration in atmospheric and moderate-temperature combustion systems. HO_2 radical addition to carbon−carbon double bonds of alkenes is part of a complex chemical reaction system that results in a number of different products. These include oxiranes (cyclic oxygenates) and OH radicals; peroxy radicals (formed via two paths—direct reaction and isomerization), a biradical plus OH radical (chain branching); or stabilized hydroperoxy alkyl adduct radicals that can further react with O_2. The hydroperoxy alkyl radicals are also formed via reactions of alkyl radicals with O_2 (Scheme 1). The reactions of these stabilized adducts are important in controlling the negative temperature regime of hydrocarbon oxidation,[10] and include isomerization, HO_2 elimination, and

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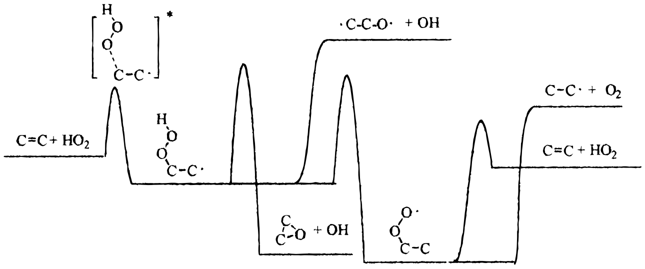
SCHEME 1: Energy vs Reaction Pathways



further addition with O_2. The peroxy radicals can dissociate to alkyl radicals + O_2, or they can undergo reaction with nitric oxides or the radical pool.

Under moderately low-temperature, precombustion conditions, the alkyl radical + O_2, hydroperoxy radical + olefin and the two adducts often exist in near-equilibria, with slower rate (bleed) reactions, to the oxiranes and biradical + OH controlling the process(es) (Scheme 1):

The research group of Baldwin and Walker[4a-e] has studied relative rate constants on the addition of HO_2 radicals to alkenes, and reported Arrhenius parameters based on measurements of product−reactant ratios, i.e., [oxirane]/[reactants]. Accurate kinetic parameters are often difficult to derive from a complex reaction system using an overall, stable product slate resulting from several minutes of oxidation reaction. This problem is amplified when thermochemistry is uncertain and equilibrium constants are important to the kinetic analysis.

In this study we use ab initio and density functional calculations with isodesmic reactions that retain group balance to estimate thermochemical properties for the alkyl hydroperoxides; and for kinetic parameters in HO_2 radical addition to ethylene, propene, and isobutene carbon−carbon double bonds forming the hydroperoxy alkyl radicals.

Method

The geometries of reactants, transition states, and product radicals were pre-optimized using UHF/PM3 in MOPAC,[11] followed by optimization and vibrational frequency calculation at the MP2(full)/6-31G(d) and B3LYP/6-31G(d) levels of theory using the GAUSSIAN94[12] program. Zero-point vibrational energies (ZPVE), vibrational frequencies, and thermal contributions to enthalpy from harmonic frequencies were scaled as recommended by Scott et al.[13] Transition state (TS) geometries were identified by the existence of only one imaginary frequency in the normal mode coordinate analysis, evaluation of the TS geometry, and coordinate information on the vibration movement.

Total energy for all species were calculated at the MP2(full)/6-31G(d), MP4(full)/6-31G(d,p)//MP2(full)/6-31G(d), B3LYP/6-31G(d), and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) levels of theory. Complete basis set (CBS-q) model chemistry[14a-c] based on MP2(full)/6-31G(d) and B3LYP/6-31G(d) geometries are also calculated. CBS-q//MP2(full)/6-31G(d), CBS-q//B3LYP/6-31G(d), MP4(full)/6-31G(d,p)//MP2(full)/6-31G(d), and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) are abbreviated in the remainder of the text as CBSlqM, CBSlqB, MP4F, and B3LYP311, respectively.

Contributions of vibration, translation, and external rotation to entropies and heat capacities were calculated from scaled vibrational frequencies, molecular mass, and moments of inertia of the optimized structures. Potential barriers of internal rotations for 2-hydroperoxy-1-ethyl radical (C•−COOH, C•C−OOH, and C•CO−OH bonds) and TS1 (CC−OOH and CCO−OH bonds) were calculated at the MP2(full)/6-31G(d) and CBS-Q//MP2-(full)/6-31G(d) (abbreviated as CBSQM) levels. The C•−COOH bond in other hydroperoxy radicals and the C−C single bond in TSs were calculated at the MP2(full)/6-31G(d) level. The geometries and harmonic vibrational frequencies were calculated for all rotational conformers at the MP2(full)/6-31G(d) level.

Contributions from hindered rotors to $S°_{298}$ and $Cp(T)$ were determined by the method of Pitzer and Gwinn[15] and by direct integration over energy levels of the calculated intramolecular rotation potential energy curves.[16] The number of optical isomers and spin degeneracy of unpaired electrons were also incorporated for calculation of $S°_{298}$ and $Cp(T)$.

A Fourier series was used to represent the potential calculated at discrete torsional angles:

$$V(\Phi) = a_0 + a_i \cos(i\Phi) + b_i \sin(i\Phi),\ i = 1,2,3... \qquad \text{(F1)}$$

where values of the coefficients were calculated to provide the true minima and maxima of the torsional potentials with allowance of a shift of the theoretical extrema of angular positions. Further description on this method to calculate contributions from the internal rotors are reported by method of Lay et al.[16-17]

Reaction enthalpy $(\Delta H^{\ddagger}_{\text{TS}-\text{reactants}})_{298}$ was obtained from the differences of total energies, ZPVE, and thermal correction for entropies between the TS and the reactants. Enthalpies of formation for the TSs are estimated from experimental data on $\Delta H_f°_{298}$ of the reactants plus the reaction enthalpy $(\Delta H^{\ddagger}_{\text{TS}-\text{reactants}})_{298}$. Two sets of isodesmic reactions with group balance, shown in Schemes 2 and 3, were used in this study to accurately estimate the enthalpy of formation of the hydroperoxide alkyl radicals, $CH_2{\bullet}CH_2OOH$ (C•CQ), $CH_3CH{\bullet}CH_2OOH$ (CC•CQ), $CH_2{\bullet}CH(OOH)CH_3$ (C•CQC), $(CH_3)_2C{\bullet}CH_2OOH$ ($C_2C{\bullet}CQ$), and $CH_2{\bullet}C(OOH)(CH_3)_2$ ($C_3{\bullet}CQ$). An isodesmic reaction with group balance is characterized by conservation of both bonds and the number of groups of each group type in the reactants and products, where a group is defined as a polyvalent atom (ligancy ≥ 2) in a molecule.[18] To obtain $\Delta H_f°_{298}$ of hydroperoxy alkyl radicals, we also needed the $\Delta H_f°_{298}$ of corresponding hydroperoxide alkanes (Scheme 2). Reactions in

SCHEME 2

CCQ + COH = CQ + CCOH (IR1)

CCCQ + COH = CQ + CCCOH (IR2)

CCQC + COH = CQ + CC(OH)C (IR3)

C_2CCQ + COH = CQ + C_2CCOH (IR4)

C_3CQ + COH = CQ + C_3COH (IR5)

(Q = OOH)

SCHEME 3

CCQ + C•C = C•CQ + CC (IR6)

CCCQ + C•CQ = CC•CQ + CCQ (IR7)

CCQC + C•CQ = C•CQC + CCQ (IR8)

C_2CCQ + C•CQ = $C_2C{\bullet}CQ$ + CCQ (IR9)

C_3CQ + C•CQ = $C_3{\bullet}CQ$ + CCQ (IR10)

TABLE 1: Enthalpy Data Used in Isodesmic Reactions to Determine $\Delta H_f°_{298}$ of Other Species

compound	$\Delta H_f°_{298}$ in kcal/mol	source
COOH	−31.8	ref 19
COH	−48.08	ref 20
CCOH	−56.21	ref 21
CCCOH	−60.97	ref 21
C2COH	−65.20	ref 21
C2CCOH	−67.85	ref 21
C3COH	−74.69	ref 21
HOO•	3.5	ref 22

Scheme 2 are based on the reaction of CH_3OOH with the alcohols to form the desired hydroperoxides alkanes and CH_3OH. The value of $\Delta H_f°_{298}$ (CH_3OOH) = −31.8 kcal/mol was taken from Lay et al.[19] Enthalpies of formation for the alcohols used in reactions IR1−IR5 were obtained from literature data[19−22] and listed in Table 1.

Calculated enthalpies of formation of hydroperoxy alkyl radicals, C•CQ, CC•CQ, C•CQC, C_2C•CQ and C_3•CQ, were derived from the reactions in Scheme 3 and bond dissociation enthalpy of D$H°_{298}$ (QCC−H). (Q = OOH hydroperoxide group).

High-Pressure Limit A Factors (A_∞) and Rate Constants (k_∞) Determination. The high-pressure limit rate constant (k_∞) of HO_2 addition reactions were fit by three parameters A_∞, n, and E_a over the temperature range from 298 to 2000 K:

$$k_\infty = A_\infty (T)^n \exp(-E_a/RT)$$

Entropy differences between reactants and TS were used to determine the Arrhenius preexponential factor, A_∞, via canonical transition state theory[23] (TST) for unimolecular and bimolecular reactions $A_\infty = (kT/h)\exp(\Delta S^‡/R)$ and $A_\infty = (ekT/h)\exp(\Delta S^‡/R)$, respectively, where h is Plank's constant, and k is the Boltzmann constant. The activation energy was calculated from the difference in the enthalpies of formation of the reactants and the TS.

Results and Discussion

Geometries. Optimized structures and selected geometric parameters for reactants, transition states, and product radicals of ethylene, propene, and isobutene reactions with HO_2 radical are illustrated in Table 2. Vibration frequencies and moments of inertia for all species are listed in Table 3, the calculated vibrational frequencies were scaled by the factor 0.9427 and 0.9614 for MP2(full)/6-31G(d) and B3LYP/6-31g(d) theoretical frequencies, respectively, in the calculation of ZPVEs and thermal energies, as recommended by Scott et al.[13] Torsion frequencies are not included in Table 3.

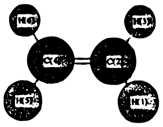
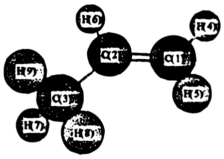
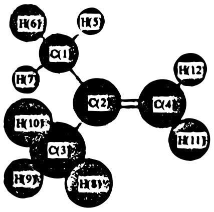
Reactants and Product Radicals. Structures from the MP2(full)/6-31G(d) and B3LYP/6-31g(d) calculations are similar for both reactants and product radicals. C═C double bonds in MP2(full)/6-31G(d) geometries are slightly longer (∼0.004 Å) than B3LYP/6-31g(d) for olefin reactants only; other bond lengths in MP2(full)/6-31G(d) are slightly shorter (∼0.006 Å) than B3LYP/6-31g(d). The differences of bond length and angles for olefin reactants between MP2(full)/6-31G(d) and B3LYP/6-31g(d) are less than 0.006 Å and 1 degree, respectively. Both calculated reactant geometries are in good agreement with experimental results (Table 2). Differences between the calculated and measured bond lengths and angles are within 0.015 Å and 1.2 degrees, respectively.

Bond lengths of hydroperoxy alkyl radicals in B3LYP/6-31g(d) geometries are longer than those in MP2(full)/6-31G(d) geometries except R•O−OH and R•OO−H bonds. The R•OO−H and R•O−OH bonds (except C3•CQ radical) in MP2(full)/6-31G(d) geometries are longer than B3LYP/6-31g(d) by 0.003 Å and 0.021−0.003 Å, respectively. The R•−COOH bond in the hydroperoxy alkyl radicals is ca. 0.16 Å longer than the experimental C═C double bond in ethylene, propylene, and isobutene (average value ca. 1.329 Å[24]) and 0.04 Å shorter than experimental C−C single bond in ethanol (1.530 Å[24]). The new-formed R•C−OOH bond lengths in product radicals are between 1.434 Å (C•CQ) and 1.466 Å (C3•CQ) in B3LYP/6-31g(d) geometries, while MP2(full)/6-31G(d) geometries yield slightly shorter bond length between 1.431 Å (C•CQ) and 1.459 Å (C3•CQ). Differences of bond angles and dihedral angles are within 1.9° and 13.6° between B3LYP/6-31g(d) and MP2(full)/6-31G(d) geometries.

Transition States. MP2(full)/6-31g(d) and B3LYP/6-31g(d) calculations both show structures of the hydrocarbon in the transition states having a near-planar ethylene configuration with HO_2 addition perpendicular to the plane. The ∠CCO bond angle varies from 96.1° (TS of HO_2 addition at CD/C2 carbon atom of isobutene) to 104.07° (TS of HO_2 addition at CD/H2 carbon atom of propene) for MP2(full)/6-31G(d) geometry. The ∠CCO of B3LYP/6-31g(d) is 2.1∼3.9° larger than those calculated by MP2(full)/6-31G(d). The forming RC−OOH bond lengths range from 1.9365 Å (TS of HO_2 addition ethylene) to 1.9743 Å (TS of HO_2 addition at CD/C2 carbon atom of isobutene) for MP2(full)/6-31G(d) geometry. RC−OOH bond lengths from B3LYP/6-31G(d) geometries are shorter than those of MP2(full)/6-31G(d) by 0.02−0.046 Å. The breaking C═C bond length is 1.35 and 1.38 Å from MP2(full)/6-31G(d) and B3LYP/6-31G(d) geometries, respectively (in case of HO_2 addition isobutene forming C_3•COOH, it is slightly longer than other TSs by 0.01 Å for both MP2 and DFT geometries). This distance is longer than average C═C double bonds, 1.33 Å, and shorter than average C−C single bonds 1.51 Å. The bond lengths of RO−OH in transition states are shorter than the R•O−OH bond in hydroperoxy alkyl radicals, but the ROO−H bond in TSs are slightly longer than the R•OO−H bond in hydroperoxy alkyl radicals.

Rotational Barriers. *2-Hydroperoxy-1-ethyl Radical and TS1.* Potential barriers of internal rotations for 2-hydroperoxy-1-ethyl radical (C•−COOH, C•C−OOH, and C•CO−OH bonds) and TS1 (CC−OOH and CCO−OH bonds) are calculated at MP2(full)/6-31G(d) and CBSQM levels. Calculation of the potential energy as a function of the dihedral angle is performed by varying the torsion angle in 30° intervals and allowing other parameters to be optimized (except the C•−COOH bond in the C•CQ radical, where the HCCH dihedral angle is fixed as 174°). The minimum and maximum on the torsional potential are full optimized for 2-hydroperoxy-1-ethyl radical. The geometries and harmonic vibrational frequencies are calculated for all rotational conformers and transition states at MP2(full)/6-31G(d) level. The barriers for internal rotations are calculated from the differences between the total energy of each conformation and that of the most stable conformer, where the zero-point vibrational energy (ZPVE) and thermal correction to 298 K are also included. Total energies, ZPVE, thermal correction to 298 K, and calculated rotation barriers for each rotational conformer of 2-hydroperoxy-1-ethyl radical and TS1 are listed in Table 4. Potential barrier diagrams for internal rotations about C•−COOH, C•C−OOH and C•CO−OH bonds of 2-hydroperoxy-1-ethyl radical are shown in Figure 1, parts a, b, and c, respectively. Figure 2a, b shows the diagrams about CC−OOH and CCO−OH bonds of TS1. Points are calculated values at

TABLE 2: Geometrical Parameters (distances in Å, angles in deg)

	bond length				bond angle				dihedral angle		
		B3LYP	MP2	expt[24]		B3LYP	MP2	expt[24]		B3LYP	MP2
Reactants: Ethylene, Propene, and Isobutene											
	r21	1.087	1.085	1.085	a321	116.3	116.6	117.8	d4213	180.0	180.0
	r32	1.087	1.085		a421	121.9	121.7		d5421	0.0	0.0
	r42	1.331	1.335	1.339	a542	121.9	121.7		d6421	180.0	180.0
	r54	1.087	1.085		a642	121.9	121.7				
	r64	1.087	1.085								
	r21	1.333	1.337	1.318	a321	125.2	124.6	124.3	d4123	180.0	180.0
	r32	1.502	1.498		a412	121.8	121.7		d5123	0.0	360.0
	r41	1.087	1.085		a512	121.6	121.5		d6213	180.0	180.0
	r51	1.089	1.086		a621	118.9	119.0		d7321	239.3	239.5
	r62	1.091	1.089		a732	111.2	111.1		d8321	0.0	360.0
	r73	1.099	1.095		a832	111.5	111.0		d9321	120.7	120.4
	r83	1.095	1.093		a932	111.2	111.1				
	r93	1.099	1.095								
	r21	1.509	1.503	1.507	a321	115.8	115.8		d4213	180.0	180.0
	r32	1.509	1.503		a421	122.1	122.1	122.4	d5123	180.0	180.0
	r42	1.337	1.339	1.330	a512	111.9	111.6		d6123	59.1	59.2
	r51	1.094	1.093		a612	111.0	110.8		d7123	300.9	300.8
	r61	1.099	1.096		a712	111.0	110.8		d8321	180.0	180.0
	r71	1.099	1.096		a832	111.9	111.6		d9321	59.1	59.3
	r83	1.094	1.093		a932	111.0	110.8		d10321	300.9	300.8
	r93	1.099	1.096		a1032	111.0	110.8		d11421	180.0	180.0
	r103	1.099	1.096		a1142	121.8	121.7		d12421	0.0	0.0
	r114	1.087	1.086		a1242	121.8	121.7				
	r124	1.087	1.086								

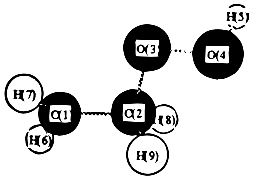
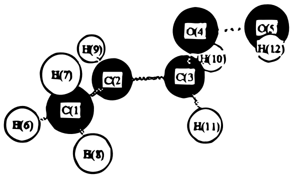
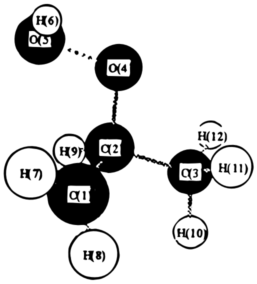
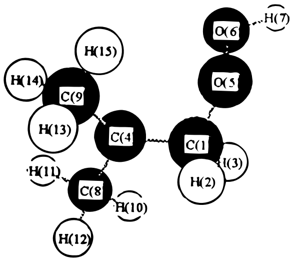
	bond length			bond angle			dihedral angle		
		B3LYP	MP2		B3LYP	MP2		B3LYP	MP2
Product Radicals Corresponding to HO_2 Addition to Ethylene, Propene, and Isobutene									
	r21	1.484	1.483	a321	107.1	106.2	d4321	169.9	171.9
	r32	1.434	1.431	a432	106.4	104.9	d5432	112.7	120.5
	r43	1.457	1.467	a543	99.8	98.5	d6123	137.7	147.4
	r54	0.974	0.977	a612	121.2	120.8	d7123	314.9	317.8
	r61	1.084	1.081	a712	119.6	119.5	d8213	238.8	239.6
	r71	1.084	1.081	a821	111.8	111.9	d9213	118.2	118.3
	r82	1.100	1.097	a921	111.8	112.2			
	r92	1.104	1.100						
	r21	1.491	1.488	a321	121.9	119.9	d4321	283.7	293.9
	r32	1.488	1.486	a432	106.9	106.4	d5432	181.3	179.5
	r43	1.445	1.442	a543	106.6	105.2	d6123	206.8	199.4
	r54	1.461	1.464	a612	111.7	111.6	d7123	87.6	79.3
	r61	1.097	1.093	a712	111.5	111.2	d8123	328.3	320.4
	r71	1.104	1.099	a812	111.6	110.9	d9213	194.4	197.3
	r81	1.097	1.095	a921	118.6	119.2	d10321	164.4	174.3
	r92	1.087	1.084	a1032	112.0	112.4	d11321	42.5	52.1
	r103	1.097	1.094	a1132	111.4	111.3	d12543	250.4	244.0
	r113	1.101	1.099	a1254	99.9	98.9			
	r125	0.974	0.977						
	r21	1.492	1.489	a321	113.1	113.1	d4213	243.7	244.3
	r32	1.534	1.525	a421	111.5	111.1	d5421	291.3	291.3
	r42	1.445	1.439	a542	107.8	106.4	d6542	96.2	98.9
	r54	1.452	1.465	a654	100.7	99.6	d7123	245.2	258.8
	r65	0.975	0.977	a712	122.0	121.6	d8123	61.5	66.8
	r71	1.085	1.082	a812	119.4	118.9	d9213	123.6	124.1
	r81	1.087	1.084	a921	110.4	110.5	d10321	62.5	61.6
	r92	1.097	1.096	a1032	110.0	109.9	d11321	302.7	302.0
	r103	1.094	1.092	a1132	110.6	110.0	d12321	182.6	181.9
	r113	1.095	1.092	a1232	110.1	110.1			
	r123	1.095	1.092						
	r21	1.104	1.103	a312	108.5	108.1	d4123	123.6	123.6
	r31	1.097	1.096	a412	112.0	111.9	d5123	245.2	244.7
	r41	1.497	1.493	a512	101.9	101.5	d6512	169.2	169.6
	r51	1.436	1.433	a651	105.6	104.9	d7651	96.1	95.0
	r65	1.454	1.465	a765	99.7	97.8	d8412	253.2	265.3
	r76	0.975	0.978	a841	119.0	117.6	d9412	59.0	61.7
	r84	1.495	1.491	a941	117.7	118.2	d10841	332.7	321.7
	r94	1.498	1.493	a1084	111.5	111.6	d11841	211.5	200.8
	r108	1.096	1.094	a1184	111.1	110.9	d12841	92.9	81.8
	r118	1.099	1.095	a1284	111.8	111.9	d13941	265.8	273.2
	r128	1.105	1.102	a1394	111.1	111.4	d14941	147.1	154.3
	r139	1.105	1.102	a1494	111.4	110.9	d15941	25.6	32.7
	r149	1.098	1.095	a1594	111.2	110.9			
	r159	1.095	1.093						

TABLE 2: continued

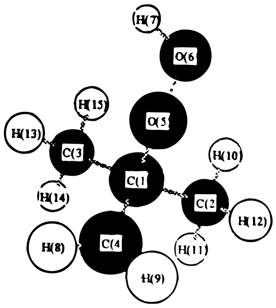
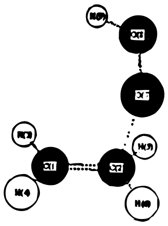
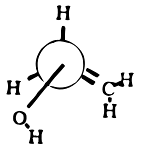
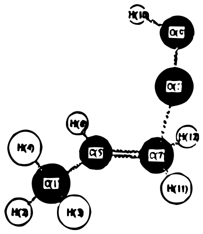
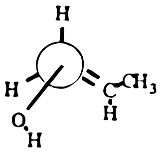
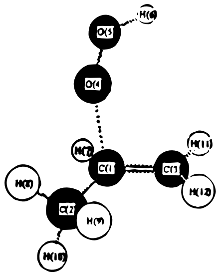
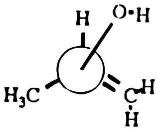
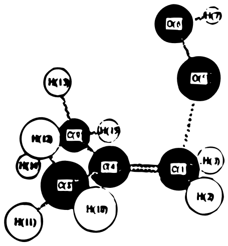
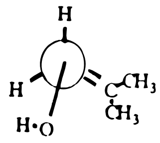
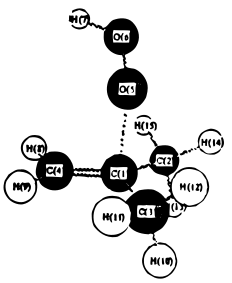
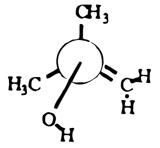
		bond length			bond angle			dihedral angle		
			B3LYP	MP2		B3LYP	MP2		B3LYP	MP2
Product Radicals Corresponding to HO_2 Addition to Ethylene, Porpene, and Isobutene										
		r21	1.533	1.522	a312	112.2	112.1	d4123	125.9	125.3
		r31	1.533	1.522	a412	111.6	111.2	d5123	237.7	237.7
		r41	1.496	1.494	a512	109.5	109.4	d6512	61.2	60.3
		r51	1.466	1.459	a651	109.1	107.7	d7651	110.1	114.0
		r65	1.467	1.458	a765	99.6	98.9	d8412	205.8	206.2
		r76	0.974	0.977	a841	120.7	120.5	d9412	35.9	39.3
		r84	1.085	1.083	a941	120.2	119.9	d10213	60.1	58.6
		r94	1.085	1.083	a1021	110.3	110.3	d11213	299.8	298.1
		r102	1.093	1.091	a1121	110.6	110.2	d12213	179.7	178.2
		r112	1.096	1.094	a1221	110.2	109.7	d13312	181.1	182.7
		r122	1.095	1.093	a1331	110.4	109.9	d14312	61.3	63.1
		r133	1.096	1.094	a1431	110.6	110.3	d15312	301.4	303.2
		r143	1.095	1.093	a1531	110.4	110.4			
		r153	1.094	1.091						
Transition States Corresponding to HO_2 Addition to Ethylene, Propene, and Isobutene										
	 **TS1**	r21	1.379	1.352	a312	121.3	121.3	d4123	186.8	185.7
		r31	1.086	1.083	a521	120.1	120.7	d5213	343.1	346.2
		r52	1.085	1.082	a721	105.6	103.5	d7213	87.7	87.7
		r72	1.909	1.937	a872	109.2	108.7	d8721	273.5	280.8
		r87	1.393	1.387	a987	102.5	102.2	d9872	106.3	102.9
		r98	0.976	0.978						
	 **TS2A**	r21	1.099	1.095	a312	108.2	108.5	d4123	244.4	243.7
		r31	1.095	1.092	a412	106.3	106.9	d5123	123.0	122.3
		r41	1.100	1.096	a512	111.2	111.0	d6512	57.3	58.0
		r51	1.496	1.492	a651	116.9	117.0	d7512	230.7	231.9
		r65	1.090	1.088	a751	124.3	124.0	d8751	275.1	275.0
		r75	1.381	1.351	a875	106.1	103.1	d9875	272.3	278.8
		r87	1.918	1.943	a987	109.1	108.6	d10987	104.7	102.5
		r98	1.396	1.390	a1098	102.5	102.2	d11751	16.8	13.9
		r109	0.976	0.977	a1175	119.3	120.2	d12751	170.4	173.1
		r117	1.087	1.085	a1275	120.1	120.8			
		r127	1.085	1.082						
	 **TS2B**	r21	1.506	1.498	a312	121.7	122.6	d4123	250.9	254.7
		r31	1.384	1.353	a412	97.8	95.9	d5412	209.8	200.5
		r41	1.920	1.954	a541	119.3	109.8	d6541	251.0	254.3
		r54	1.396	1.388	a654	102.4	102.2	d7123	154.0	159.9
		r65	0.976	0.978	a712	115.7	116.1	d8213	152.9	146.2
		r71	1.087	1.085	a821	110.6	110.4	d9213	32.1	25.5
		r82	1.093	1.091	a921	111.2	110.8	d10213	272.5	265.7
		r92	1.095	1.092	a1021	110.1	109.9	d11312	169.4	172.1
		r102	1.098	1.094	a1131	121.3	121.3	d12312	342.2	346.2
		r113	1.086	1.083	a1231	121.1	121.2			
		r123	1.087	1.084						
	 **TS3A**	r21	1.086	1.085	a312	115.3	115.7	d4123	154.4	159.9
		r31	1.087	1.085	a412	119.9	120.7	d5123	262.5	262.9
		r41	1.382	1.349	a512	91.2	90.1	d6512	170.4	179.4
		r51	1.933	1.953	a651	110.4	110.8	d7651	275.2	274.8
		r65	1.399	1.394	a765	102.8	102.4	d8412	17.6	15.4
		r76	0.977	0.978	a841	121.2	121.3	d9412	187.5	184.9
		r84	1.501	1.495	a941	120.8	121.2	d10841	350.3	349.6
		r94	1.500	1.494	a104	112.1	111.7	d11841	228.8	228.0
		r108	1.094	1.092	a1184	111.2	110.9	d12841	110.6	109.7
		r118	1.099	1.096	a1284	111.7	109.9	d13941	261.9	259.5
		r128	1.100	1.096	a1394	110.1	109.3	d14941	143.2	140.6
		r139	1.101	1.097	a1494	111.6	111.2	d15941	21.2	18.9
		r149	1.098	1.095	a1594	112.1	111.8			
		r159	1.095	1.092						
	 **TS3B**	r21	1.511	1.503	a312	116.0	115.9	d4123	206.9	200.3
		r31	1.512	1.504	a412	119.4	120.6	d5123	100.0	98.2
		r41	1.392	1.357	a312	100.1	98.3	d6512	46.1	48.4
		r51	1.928	1.974	a651	111.9	111.8	d7651	107.0	107.0
		r65	1.399	1.391	a765	102.2	102.0	d8412	341.8	345.5
		r76	0.975	0.978	a841	121.1	121.1	d9412	168.8	171.5
		r84	1.086	1.085	a941	121.1	121.3	d10312	296.2	296.8
		r94	1.086	1.084	a1031	110.0	109.6	d11312	176.2	176.6
		r103	1.098	1.095	a1131	111.5	111.3	d12312	55.4	55.8
		r113	1.094	1.092	a1231	11.4	110.1	d13213	73.2	71.3
		r123	1.094	1.092	a1321	110.0	109.5	d14213	313.6	311.9
		r132	1.098	1.095	a1421	110.7	110.3	d15213	193.3	191.6
		r142	1.094	1.092	a1521	111.1	110.9			
		r152	1.09.3	1.091						

TABLE 3: Harmonic Vibrational Frequencies (cm^{-1}) for Transition States Corresponding to HO_2 Addition to Ethylene, Propene, and Isobutene

	Frequencies (based on MP2(full)/6-31g(d) level)											moments of inertia (amu-Bohr∧2)
TS1	−783.7	287.0	422.3	476.4	807.5	867.6	955.2	1048.7	1110.1	1210.3	1276.0	1347.3	103.1
	3052.6	3058.4	3139.6	3158.9	3470.9	1438.5	1546.5						411.9
													445.7
TS2A	−774.1	200.4	336.7	417.5	431.7	696.0	897.5	921.6	954.9	1019.3	1039.0	1110.0	175.6
	1169.3	1267.5	1341.5	1379.4	1413.1	1451.5	1466.6	1565.5	2917.5	2984.8	3019.5	3046.7	723.3
	3049.4	3143.4	3471.9										757.9
TS2B	−759.2	275.3	297.1	419.5	433.1	575.2	853.4	891.6	925.8	990.4	1029.1	1105.3	224.4
	1169.2	1262.2	1343.6	1371.2	1417.0	1453.9	1468.9	1546.4	2935.0	3015.6	3037.2	3044.9	541.3
	3070.7	3141.5	3471.6										689.8
TS3A	−737.7	176.3	285.2	367.8	424.4	436.2	457.3	800.0	851.8	935.3	945.6	972.0	380.3
	1010.4	1055.7	1070.2	1114.3	1288.1	1336.1	1378.8	1385.5	1399.1	1443.4	1452.6	1459.5	762.5
	1470.9	1595.6	2912.1	2916.0	2983.9	2986.4	3020.2	3026.0	3035.2	3123.1	3456.8		878.6
TS3B	−731.2	227.0	291.0	375.3	380.8	424.3	453.6	626.1	784.7	841.2	936.6	954.9	395.5
	987.1	1001.8	1053.0	1103.0	1282.5	1337.5	1368.7	1382.3	1407.3	1446.2	1457.5	1458.9	703.3
	1474.1	1541.4	2927.4	2931.9	3009.5	3014.9	3032.3	3037.5	3043.7	3133.1	3469.5		731.4
C•CQ	286.7	417.8	475.2	801.5	895.7	979.7	1059.4	1122.9	1186.6	1299.8	1344.4	488.4	54.1
	1483.4	2880.5	2939.5	3070.8	3181.7	3510.6							411.6
													444.3
CC•CQ	252.2	348.4	445.6	507.5	883.2	920.5	950.0	984.2	1117.2	1123.4	1135.3	1207.1	125.7
	1297.4	1326.3	1368.8	1393.4	1453.3	1465.2	1489.3	2897.9	2900.6	2971.0	2974.8	3011.5	708.2
	3083.9	3505.9											768.6
C•CQC	269.0	317.2	442.0	453.6	532.5	809.8	879.8	900.7	930.0	1040.5	1134.8	1149.1	218.6
	1281.9	1302.3	1343.3	1370.6	1428.3	1459.5	1470.3	2938.5	2941.3	3031.3	3033.7	3046.9	459.9
	3158.0	3496.3											611.8
C2C•CQ	250.0	295.4	346.3	387.4	540.2	766.3	817.5	908.7	920.4	953.0	981.3	1007.2	333.1
	1057.1	1207.9	1251.4	1282.6	1303.1	1346.2	1379.2	1390.2	1436.4	1450.0	1456.8	1464.9	802.7
	1473.5	2871.5	2872.9	2876.0	2958.7	2960.6	2962.3	3005.4	3014.8	3488.5			896.3
C3C•CQ	269.2	333.9	340.5	375.0	443.3	506.5	536.4	733.2	864.0	896.0	928.9	977.1	395.1
	1001.8	1146.3	1240.5	1263.7	1282.5	1317.5	1364.2	1377.8	1432.3	1452.3	1467.1	1471.5	624.0
	1485.2	2931.9	2936.8	3016.6	3022.6	3033.9	3039.9	3048.2	3157.7	3505.9			634.0

	Frequencies (based on B3lyp/6-31g(d) level)											moments of inertia (amu-Bohr∧2)
TS1	−496.8	291.8	404.5	455.9	786.4	790.7	897.8	995.4	1041.5	1202.4	1229.8	1354.5	103.1
	1430.7	1514.8	3044.6	3049.7	3119.2	3141.3	3501.8						412.0
													445.7
TS2A	−483.0	210.6	333.3	396.9	415.4	671.1	877.3	885.2	912.4	977.7	1006.1	1027.7	165.1
	1158.8	1236.5	1348.0	1373.1	1397.7	1445.2	1459.3	1515.9	2903.2	2943.1	2998.4	3037.5	768.7
	3042.0	3129.2	3502.7										795.5
TS2B	−476.0	280.6	300.8	400.8	422.2	507.9	765.2	869.4	913.5	932.3	992.9	1045.6	231.0
	1155.7	1230.3	1350.5	1364.2	1398.6	1449.8	1464.4	1500.0	2932.0	2992.0	3020.6	3041.9	546.9
	3060.3	3129.4	3508.7										696.7
TS3A	−466.4	166.1	285.4	362.0	407.6	426.6	442.8	778.0	835.5	889.0	939.0	959.1	368.3
	988.9	1010.1	1039.9	1046.3	1272.6	1347.1	1362.8	1379.0	1386.3	1439.6	1447.3	1454.5	818.4
	1467.0	1522.0	2900.5	2906.5	2945.6	2952.8	3001.2	3007.3	3032.9	3112.2	3483.2		953.7
TS3B	−457.9	231.0	300.6	364.6	378.9	409.0	431.4	516.5	743.9	769.2	911.7	922.6	404.2
	947.3	993.3	1032.4	1051.4	1265.2	1342.8	1348.3	1376.2	1390.0	1444.2	1452.1	1454.9	708.2
	1472.5	1493.7	2929.7	2934.0	2994.1	2999.4	3019.7	3029.5	3041.3	3128.1	3512.4		734.1
C•CQ	287.6	443.3	490.3	791.3	895.8	965.0	1037.5	1115.3	1190.9	1326.9	1344.0	459.0	53.9
	1469.9	2857.1	2910.9	3063.3	3166.3	3555.2							415.5
													445.8
CC•CQ	260.9	346.8	455.3	518.0	858.2	869.8	917.4	927.5	971.0	1121.9	1125.1	1203.4	118.2
	1311.1	1327.5	1367.2	1380.9	1445.3	1456.1	1482.4	2871.6	2890.3	2943.6	2957.0	2984.5	748.6
	3067.2	3549.4											795.5
C•CQC	269.5	320.4	436.2	460.7	541.5	807.6	881.1	896.3	916.8	1010.9	1122.9	1141.2	220.6
	1281.0	1334.7	1341.3	1367.5	1423.0	1453.9	1467.1	2941.1	2942.2	3015.2	3018.2	3040.4	464.0
	3144.3	3542.2											618.8
C2C•CQ	234.8	293.8	350.0	384.4	534.6	750.7	835.2	911.0	917.1	946.0	971.6	982.7	343.7
	1028.2	1203.9	1254.4	1269.4	1331.4	1342.2	1372.4	1387.3	1429.0	1442.3	1448.1	1457.8	805.4
	1466.8	2848.3	2853.0	2866.2	2926.7	2934.3	2955.8	2985.6	2993.1	3540.6			903.2
C3C•CQ	258.7	328.6	336.2	372.8	439.7	505.1	556.6	724.0	826.3	843.2	879.4	926.9	401.5
	966.5	998.1	1123.1	1220.0	1255.6	1309.4	1363.2	1377.0	1427.2	1448.4	1463.1	1467.7	633.3
	1481.6	2936.5	2943.2	3002.2	3008.1	3018.3	3027.0	3047.1	3148.3	3560.5			643.2

MP2(full)/6-31g(d) (circles) and CBSQM (triangles). Lines are results of Fourier expansions F1. Coefficients of the Fourier expansion components, a_i and b_i in eq F1 are presented in the Supporting Information (Table S1).

Contributions from hindered rotors of $S°_{298}$ and $Cp(T)$ calculated using the method of Pitzer and Gwinn[15] and by direct integration over energy levels of the exact potential curve are listed in Table 5. The differences between rotational barriers calculated at MP2(full)/6-31g(d) and CBSQM levels are less than 1.6 kcal/mol. Direct diagonalization of the Hamiltonian matrix of rotational potential energy and the Pitzer and Gwinn approximation method both lead to similar results in determi-

TABLE 4: Total Energy, Zero-Point Vibrational Energies, Thermal Correction, and Internal Rotation Barriers of TS1 and 2-Hydroperoxy-1-ethyl Radical

		total energy (hartree)		ZPVE^{a}	H_{thermal}^{b}	rotational barrier (kcal/mol)^{c}	
	torsion angle	MP2(full)/6-31g(d)	CBS-Q^{d}	(kcal/mol)	(kcal/mol)	MP2(full)/6-31g(d)	CBS-Q^{d}
TS1	CC−OOH						
	−5	−228.7621645	−229.1274687	42.18	3.41	2.71	3.43
	0	−228.7620629	−229.1272540	42.18	3.41	2.77	3.56
	5	−228.7620359	−229.1271514	42.18	3.41	2.78	3.63
	30	−228.7628320	−229.1281435	42.17	3.42	2.28	3.02
	60	−228.7644161	−229.1303841	42.18	3.44	1.33	1.52
	75.20	−228.7647060	−229.1311215	42.23	3.44	1.19	1.05
	90	−228.7644496	−229.1307296	42.28	3.43	1.38	1.31
	115	−228.7634505	−229.1297802	42.29	3.41	2.01	1.98
	120	−228.7632756	−229.1297161	42.28	3.41	2.11	2.02
	125	−228.7631293	−229.1297196	42.27	3.41	2.19	2.02
	150	−228.7628813	−229.1303355	42.20	3.42	2.28	1.64
	175	−228.7630742	−229.1300503	42.16	3.42	2.13	1.78
	180	−228.7630975	−229.1296801	42.16	3.42	2.11	2.01
	210	−228.7633215	−229.1293380	42.21	3.41	2.01	2.26
	240	−228.7647700	−229.1301744	42.32	3.4	1.21	1.73
	270	−228.7665092	−229.1323222	42.33	3.42	0.14	0.27
	280.70	−228.7666916	−229.1327393	42.30	3.43	0.00	0.00
	300	−228.7660909	−229.1322836	42.23	3.43	0.31	0.29
	330	−228.7636625	−229.1297477	42.19	3.41	1.77	2.01
	360	−228.7620629	−229.1272616	42.18	3.41	2.77	3.56
	CCO−OH						
	0	−228.7474757	−229.1151436	42.09	3.75	12.17	11.51
	30	−228.7517307	−229.1191947	41.65	3.72	9.03	8.93
	60	−228.7609838	−229.1274317	42.04	3.44	3.34	3.35
	90	−228.7661446	−229.1322706	42.23	3.43	0.27	0.29
	103.01	−228.7666916	−229.1327375	42.30	3.43	0.00	0.00
	120	−228.7657577	−229.1317874	42.36	3.43	0.66	0.61
	150	−228.7600745	−229.1264396	42.33	3.55	4.31	4.07
	180	−228.7523517	−229.1180858	42.37	3.77	9.42	9.68
	190	−228.7509029	−229.1156923	42.39	3.81	10.38	11.22
	195	−228.7507782	−229.1160681	42.31	3.83	10.41	11.01
	200	−228.7511861	−229.1151786	42.16	3.85	10.01	11.58
	210	−228.75318	−229.1188890	41.92	3.84	8.51	9.24
	240	−228.7605883	−229.1273410	42.08	3.54	3.73	3.53
	270	−228.7645911	−229.1310102	42.22	3.45	1.26	1.12
	275.73	−228.764706	−229.1311229	42.23	3.44	1.19	1.05
	300	−228.7626601	−229.1287587	42.22	3.44	2.46	2.53
	330	−228.755464	−229.1244116	42.01	3.58	6.91	5.40
	360	−228.7474757	−229.1151436	42.09	3.75	12.17	11.51
C•CQ	C•−COOH						
	0	−228.8124851	−229.1598939	41.82	3.93	0.46	0.27
	0.28	−228.8124854	−229.1598863	41.83	3.93	0.46	0.27
	30	−228.8129459	−229.1598838	41.87	3.90	0.19	0.10
	42.24	−228.8130662	−229.1597073	41.97	3.89	0.20	0.16
	60	−228.8128063	−229.1592828	42.30	3.85	0.65	0.57
	90	−228.8121396	−229.1584321	42.59	3.82	1.33	1.07
	92.31	−228.8121347	−229.1584197	42.59	3.82	1.33	1.08
	120	−228.8127581	−229.1590216	42.46	3.83	0.82	0.71
	147.35	−228.8134071	−229.1599021	42.02	3.86	0.00	0.00
	180	−228.8126679	−229.1599364	41.84	3.93	0.36	0.23
	197.04	−228.8124388	−229.1597525	41.83	3.93	0.49	0.35
	210	−228.8125460	−229.1597816	41.84	3.92	0.43	0.32
	240	−228.8129126	−229.1592929	42.39	3.84	0.66	0.53
	248.92	−228.8129302	−229.1591378	42.53	3.82	0.78	0.63
	263.58	−228.8129203	−229.1589532	42.66	3.81	0.91	0.74
	270	−228.8129270	−229.1589273	42.69	3.81	0.92	0.75
	300	−228.8131254	−229.1592107	42.55	3.82	0.67	0.58
	308.86	−228.8131546	−229.1592939	42.42	3.83	0.53	0.47
	330	−228.8129498	−229.1596399	41.98	3.89	0.28	0.25
	360	−228.8124854	−229.1598902	41.83	3.93	0.46	0.27
	C•C−OOH						
	−1.02	−228.8037463	−229.1498706	42.03	3.80	6.83	6.48
	30	−228.8071461	−229.1542549	41.80	3.37	3.68	3.76
	66.98	−228.813076	−229.1589102	41.77	3.41	0.58	0.62
	90	−228.8111734	−229.1577259	41.79	3.42	1.51	1.54
	116.52	−228.8090495	−229.1559429	42.06	3.77	3.02	2.70
	150	−228.8119317	−229.1589051	41.77	3.44	0.67	0.68
	172.03	−228.8134071	−229.1597629	41.81	3.45	0.00	0.00
	210	−228.8095028	−229.1567332	41.99	3.78	2.95	2.63
	239.16	−228.8087762	−229.1558283	41.99	3.84	3.34	2.95
	240	−228.8083101	−229.1553129	41.99	3.78	3.60	3.27
	270	−228.8123781	−229.1585331	42.11	3.72	1.39	1.12
	300	−228.813511	−229.1592246	42.22	3.75	1.04	0.74
	289.36	−228.8141222	−229.159871	42.14	3.74	0.52	0.23
	330	−228.8067175	−229.1541645	41.90	3.88	4.42	4.00
	358.98	−228.8037463	−229.1498706	42.03	3.80	6.83	6.48

TABLE 4 (Continued)

torsion angle	total energy (hartree)		ZPVE[a] (kcal/mol)	H_{thermal}[b] (kcal/mol)	rotational barrier (kcal/mol)[c]	
	MP2(full)/6-31g(d)	CBS-Q[d]			MP2(full)/6-31g(d)	CBS-Q[d]
C•CO−OH						
0	−228.8016037	−229.1517770	41.97	3.93	7.42	5.84
0.17	−228.8016036	−229.1517754	41.97	3.93	7.42	5.84
30	−228.8044058	−229.1539892	41.90	3.94	5.61	4.45
60	−228.8095432	−229.1570267	42.06	3.77	2.38	1.94
90	−228.8126289	−229.1594660	42.09	3.77	0.47	0.41
120	−228.8134069	−229.1601160	42.02	3.86	0.00	0.00
120.49	−228.8134071	−229.1601187	42.02	3.86	0.00	0.00
150	−228.8131274	−229.1610336	42.03	3.90	0.23	0.03
180	−228.8128132	−229.1606958	42.06	3.90	0.46	0.25
191.07	−228.8127838	−229.1605611	42.05	3.91	0.47	0.33
210	−228.8128679	−229.1605997	42.01	3.92	0.39	0.31
238.88	−228.8130701	−229.1598785	41.97	3.90	0.21	0.15
238.99	−228.8130699	−229.1598915	41.97	3.90	0.20	0.14
240	−228.8130694	−229.1598873	41.97	3.89	0.20	0.15
270	−228.8123060	−229.1593540	42.06	3.79	0.66	0.49
300	−228.8092943	−229.1705722	42.03	3.78	2.52	1.92
330	−228.8043895	−229.1541411	41.87	3.94	5.59	4.36
360	−228.8016037	−229.1517764	41.97	3.93	7.42	5.84

[a] ZPVE with the frequency of the torsion motion about CC−OOH bond excluded. [b] Thermal correction to 298 K with the frequency of the torsion motion about CC−OOH bond excluded. [c] Rotational barriers are calculated as the difference in total energies + scaled (0.9661) zero-point vibrational energies + thermal correction to 298 K, where the corresponding torsional frequencies are excluded in the calculation of ZPVE and thermal correction. [d] Based on MP2(full)/6-31g(d) geometry.

TABLE 5: Calculation of $S°_{298}$ and $C_p(T)$ Contribution from Internal Rotor for 2-Hydroperoxy-1-ethyl Radical and TS1

rotors	method	$S°_{298}$ cal/mol K	C_{p300} cal/mol K	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}	I_r[e] amu-Å^2	V_{mean}[f] kcal/mol	N[g]
					C•CQ							
C•−COOH	P&G[a]	4.92	1.38	1.25	1.17	1.12	1.07	1.04	1.02	1.70	0.91	3
	P&G[b]	5.00	1.26	1.16	1.10	1.07	1.04	1.02	1.01	1.70	0.73	3
	ROT[c]	4.92	1.37	1.24	1.17	1.12	1.07	1.05	1.02			
	ROT[d]	4.97	1.30	1.19	1.13	1.09	1.05	1.03	1.01			
C•C−OOH	P&G[a]	5.41	2.18	2.29	2.32	2.25	2.03	1.81	1.45	15.55	4.48	3
	P&G[b]	5.50	2.21	2.31	2.29	2.20	1.95	1.73	1.40	15.55	4.15	3
	ROT[c]	5.49	2.30	2.32	2.26	2.14	1.83	1.54	0.98			
	ROT[d]	5.42	2.83	2.57	2.34	2.13	1.76	1.46	0.93			
C•CO−OH	P&G[a]	2.92	1.96	2.14	2.16	2.08	1.86	1.66	1.36	0.91	3.95	2
	P&G[b]	3.20	2.07	2.11	2.01	1.88	1.63	1.45	1.23	0.91	3.09	2
	ROT[c]	3.50	1.32	1.35	1.39	1.43	1.48	1.49	1.43			
	ROT[d]	3.57	1.34	1.39	1.44	1.48	1.50	1.47	1.36			
					TS1							
CC•••OOH	P&G[a]	6.03	2.30	2.13	1.93	1.75	1.49	1.35	1.16	13.93	2.53	2
	P&G[b]	5.97	2.31	2.17	1.97	1.79	1.53	1.37	1.18	13.93	2.64	2
	ROT[c]	5.65	3.50	2.87	2.32	1.94	1.45	1.15	0.72			
	ROT[d]	5.41	3.37	2.53	1.85	1.38	0.83	0.55	0.25			
CCO−OH	P&G[a]	1.99	1.26	1.57	1.78	1.91	2.11	2.23	2.22	0.91	11.29	2
	P&G[b]	2.03	1.30	1.61	1.81	1.94	2.14	2.24	2.19			
	ROT[c]	1.71	2.33	2.35	2.29	2.23	2.18	2.14	2.00	0.91	10.59	2
	ROT[d]	1.93	2.09	2.29	2.42	2.46	2.39	2.23	1.83			

[a] Use of Pitzer and Gwinn approximation and rotational barrier based on MP2(full)/6-31g(d) level of theory. [b] Use of Pitzer and Gwinn approximation and rotational barrier based on CBS-Q//MP2(full)/6-31g(d) level of theory. [c] Using direct integration over energy levels of the exact potential energy curve of the rotational barriers which are calculated at MP2(full)/6-31g(d) level of theory. [d] Using direct integration over energy levels of the exact potential energy curve of the rotational barriers which are calculated at CBS-Q//MP2(full)/6-31g(d) level of theory. [e] Reduced moments of inertia are calculated about the rotational bonds based on MP2(full)/6-31g(d) level of theory. [f] Arithmetic mean of rotational barriers. [g] Number of potential maxima.

nation of hindered rotor contributions to $S°_{298}$ (difference within 0.58 cal/mol-K) and $Cp(T)_{298}$ (difference within 1.16 cal/mol-K).

Other Hydroperoxy Alkyl Radicals and TSs. In TSs, −CH3 torsions are approximated by a symmetrical sinusoidal potential. The rotational barrier heights are calculated to be 1.34, 1.71, 1.63, and 2.15 kcal/mol for TS2A, TS2B, TS3A, and TS3B, respectively, at MP2(full)/6-31G(d) level. Rotational barriers about the CO−OH bond in other hydroperoxy alkyl radicals (CC•CQ, C•CQC, C2C•CQ, and C3•CQ) and TSs (TS2A, TS2B, TS3A, and TS3B) use the CBSQM values for torsional barriers of the CO−OH bond in the C•CQ radical and TS1, respectively. Table 6 lists $S°_{298}$ and $Cp(T)$ contributions from hindered rotors which are calculated using the Pitzer and Gwinn approximation for hydroperoxy radicals and TSs (except 2-hydroperoxy-1-ethyl radical and TS1). Rotation barriers used in this study are also listed in Table 6.

Thermodynamic Properties—$\Delta H_f°_{298}$, $S°_{298}$, and Cp (300) to Cp (1500). Enthalpies of formation for species used in the working reactions are adopted from literature data and are listed in Table 1. Table 7 lists reaction enthalpies in Scheme 2 using CBSlqM, CBSlqB, MP4F, and B3LYP311 calculations. The very low, near-zero, $\Delta H_{\text{rxn},298}$ shows the reactions are thermoneutral which suggest good accuracy (cancellation of errors) for the calculated enthalpies. Table 7 lists reaction enthalpies in Scheme 3 at various levels of theory. Enthalpy of reaction IR6 indicates that the bond enthalpy $DH°_{298}$ (QCC−H) is about 1.67 kcal/mol (average value from CBSlqM, CBSlqB, MP4F,

TABLE 6: Internal Rotor Contribution to Entropies and Heat Capacities Obtained Using Pitzer and Gwinn Approximation

	rotors[a]	$S°_{298}$ cal/mol K	C_{p300} cal/mol K	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}	I_r[b] amu-Å^2	V_{mean}[c] kcal/mol	n[d]
CC·CQ												
	C−C.COOH	5.49	1.29	1.18	1.12	1.08	1.04	1.03	1.01	2.83	0.74	3
	CC.−COOH	6.92	1.91	1.63	1.45	1.34	1.20	1.13	1.06	18.52	1.5	3
	CC.C−OOH	5.82	2.23	2.32	2.30	2.21	1.95	1.73	1.40	21.55	4.15	3
	CC.CO−OH	3.20	2.07	2.12	2.02	1.88	1.63	1.45	1.23	0.92	3.09	2
	total int. rotors	**21.43**	**7.50**	**7.24**	**6.88**	**6.50**	**5.82**	**5.34**	**4.70**			
C·CQC												
	C.−C(C)OOH	4.79	1.57	1.39	1.28	1.20	1.12	1.07	1.03	1.72	1.2	3
	C−C(C.)OOH	4.08	2.06	2.20	2.19	2.09	1.85	1.65	1.35	3.06	3.87	3
	C(C.)C−OOH	5.43	2.10	2.22	2.30	2.33	2.23	2.06	1.66	21.67	5.76	3
	C(C.)CO−OH	3.20	2.07	2.11	2.02	1.88	1.63	1.45	1.23	0.92	3.09	2
	total int. rotors	**17.50**	**7.81**	**7.93**	**7.78**	**7.50**	**6.83**	**6.24**	**5.27**			
C2C·CQ												
	C−C.(C)COOH (×2)	10.31	3.66	3.18	2.85	2.64	2.38	2.25	2.11	3.03	1.5	3
	C2C.COOH	6.94	2.21	1.96	1.74	1.58	1.37	1.25	1.11	27.47	2.1	3
	C2C.C−OOH	5.92	2.23	2.32	2.30	2.21	1.96	1.73	1.40	23.91	4.15	3
	C2C.CO−OH	3.20	2.07	2.12	2.02	1.88	1.63	1.45	1.23	0.92	3.09	2
	total int. rotors	**26.37**	**10.17**	**9.57**	**8.91**	**8.30**	**7.33**	**6.68**	**5.85**			
C3·CQ												
	C−C(C.)(C)OOH (×2)	7.71	3.90	4.31	4.46	4.42	4.08	3.66	2.96	3.06	4.7	3
	C.−C(C2)OOH	4.63	1.75	1.55	1.40	1.31	1.18	1.12	1.05	1.73	1.5	3
	C2C(C.)−OOH	5.32	2.05	2.15	2.24	2.30	2.32	2.22	1.85	24.15	7.0	3
	C2C(C.)O−OH	3.19	2.07	2.11	2.01	1.88	1.63	1.45	1.23	0.91	3.09	2
	total int. rotors	**20.85**	**9.77**	**10.12**	**10.12**	**9.91**	**9.21**	**8.46**	**7.09**			
TS2A												
	C−CCQ	5.21	1.77	1.52	1.37	1.27	1.16	1.10	1.04	2.95	1.34	2
	CCC−OOH	6.25	2.32	2.17	1.97	1.79	1.53	1.37	1.18	18.51	2.64	2
	CCCO−OH	2.03	1.30	1.61	1.81	1.95	2.14	2.24	2.19	0.89	10.59	2
	total int. rotors	**13.50**	**5.39**	**5.30**	**5.15**	**5.01**	**4.83**	**4.72**	**4.41**			
TS2B												
	C−C(OOH)C	5.05	1.94	1.70	1.52	1.40	1.24	1.16	1.07	3.03	1.71	3
	CC(C)−OOH	6.30	2.32	2.17	1.97	1.79	1.53	1.37	1.18	19.49	2.64	2
	CC(C)O−OH	2.03	1.30	1.61	1.81	1.95	2.14	2.24	2.19	0.89	10.59	2
	total int. rotors	**13.39**	**5.56**	**5.49**	**5.30**	**5.13**	**4.92**	**4.77**	**4.44**			
TS3A												
	C−C(C)COOH (×2)	10.13	3.79	3.32	2.97	2.73	2.44	2.29	2.13	2.95	1.63	3
	C2CC−OOH	6.37	2.32	2.17	1.97	1.79	1.53	1.37	1.18	20.93	2.64	2
	C2CCO−OH	2.04	1.30	1.61	1.81	1.95	2.15	2.24	2.19	0.90	10.59	2
	total int. rotors	**18.54**	**7.41**	**7.10**	**6.75**	**6.47**	**6.12**	**5.90**	**5.50**			
TS3B												
	C−C(C)2OOH (×2)	9.59	4.19	3.83	3.44	3.13	2.73	2.50	2.23	3.05	2.15	3
	C3C−OOH	6.41	2.32	2.17	1.97	1.79	1.53	1.37	1.18	21.76	2.64	2
	C3CO−OH	2.04	1.30	1.61	1.81	1.95	2.15	2.24	2.19	0.90	10.59	2
	total int. rotors	**18.03**	**7.82**	**7.61**	**7.22**	**6.87**	**6.41**	**6.11**	**5.60**			

[a] Reduced moments of inertia are calculated about the rotational bonds based on MP2(full)/6-31g(d) level of theory. [b] Arithmetic mean of rotational barriers. [c] Number of potential maxima.

and B3LYP311, CBSQ and G2 calculations) higher than D$H°_{298}$ (CH3CH2−H). Bond enthalpy of D$H°_{298}$ (QCC−H) is determined to be 101.1 + 1.67 = 102.77 kcal/mol, using D$H°_{298}$ (CH3CH2−H) = 101.1 kcal/mol.[25] $\Delta H_f°_{298}$ (C•CQ) is determined as 11.12 kcal/mol, using D$H°_{298}$ (QCC−H) = 102.77 kcal/mol and $\Delta H_f°_{298}$ (CCQ) = −39.52 kcal/mol which is derived from reaction IR1 in Scheme 2 at the CBSlqM level.

Enthalpies of formation of other hydroperoxy alkyl radicals can be also determined using D$H°_{298}$ (QCC−H) and $\Delta H_f°_{298}$ of corresponding hydroperoxide alkanes. $\Delta H_f°_{298}$ of alkyl hydroperoxides and hydroperoxy alkyl radicals determined in this work are listed in Table 7, with evaluated literature and our previous work reported by Lay et al.[19] Enthalpies of formation for alkyl hydroperoxides are determined to be $\Delta H_f°_{298}$ (CCQ) = −39.70 ± 0.3 kcal/mol, $\Delta H_f°_{298}$ (CCCQ) = −44.77 ± 0.41 kcal/mol, $\Delta H_f°_{298}$ (CCQC) = −48.99 ± 0.32 kcal/mol, $\Delta H_f°_{298}$ (C_2CCQ) = −51.32 ± 0.38 kcal/mol, and $\Delta H_f°_{298}$ (C_3-CQ) = −57.91 ± 0.57 kcal/mol based on average values from CBSlqM, CBSlqB, MP4F, and B3LYP311 levels. The uncertainties in $\Delta H_f°_{298}$ are estimated as the sum of deviations between various levels of theory and the uncertainties of $\Delta H_f°_{298}$ of reference species in group balance isodesmic reactions. The deviations between various levels of theory (CBSlqM, CBSlqB, MP4F, and B3LYP311 levels) are small and less than 0.58 kcal/mol. Enthalpies of formation of hydroperoxy alkyl radicals are determined to be $\Delta H_f°_{298}$ (C•CQ) = 10.96 ± 1.06 kcal/mol, $\Delta H_f°_{298}$ (CC•CQ) = 2.62 ± 1.29 kcal/mol, $\Delta H_f°_{298}$ (C•CQC) = 0.68 ± 1.54 kcal/mol, $\Delta H_f°_{298}$ (C_2C•CQ) = −7.42 ± 1.25 kcal/mol, and $\Delta H_f°_{298}$ (C_3•CQ) = −6.42 ± 1.28 kcal/mol based on average values from CBSlqM, CBSlqB, MP4F, and B3LYP311 levels.

Thermodynamic parameters of transition states and hydroperoxy alkyl radicals based on CBSlqM and CBSlqB calculations are listed in Table 8, with properties of reactants determined from THERM.[26] MP2(full)/6-31g(d)- and B3LYP/6-31g(d)-determined $S°_{298}$ and $Cp(T)$'s are in agreement; DFT-determined values are consistently higher than values of MP2 (one exception is $S°_{298}$ of C•CQ where MP2-determined entropy is higher than DFT value by 0.04 cal/mol-K). Differences are within 0.6 cal/mol-K ($S°_{298}$ of TS3B) and 1.22 cal/mol-K (Cp(800 K) of C3•CQ) for MP2 and DFT-determined $S°_{298}$ and $Cp(T)$'s, respectively. $S°_{298}$ of hydroperoxy alkyl radicals are determined to be

TABLE 7

	CBS-q	MP2(full)/6-31g(d)	MP4(full)/6-31G(d,p)	CBS-q	B3LYP/6-31g(d)	B3LYP/6-311+g(3df,2p)
	//MP2(full)/6-31G(d)			//B3LYP/6-31G(d)		
Reaction Enthalpies[a] of Group Isodesmic Reactions Used in Scheme 2						
CCQ + COH = +CCOH + COOH	−0.41	0.12	0.23	−0.42	−0.10	−0.32
CCCQ + COH = CCCOH + COOH	0.50	−0.34	−0.46	0.52	−0.74	−0.24
C2CQ + COH = C2COH + COOH	0.19	0.19	0.16	0.30	−0.59	−0.35
C2CCQ + COH = C2CCOH + COOH	−0.15	−0.34	−0.34	−0.03	−0.62	−0.49
C3CQ + COH = C3COH + COOH	−0.42	−0.18	−0.08	−0.30	−1.16	−1.20

	CBS-q	MP2(full)/6-31g(d)	MP4(full)/6-31G(d,p)	CBS-q	B3LYP/6-31g(d)	B3LYP/6-311+g(3df,2p)
	//MP2(full)/6-31G(d)			//B3LYP/6-31G(d)		
Reaction Enthalpies[a] of Group Isodesmic Reactions Used in Scheme 3						
CCQ + C•C = C•CQ + CC[b]	1.64	1.90	1.84	1.79	1.45	1.37
CCCQ + C•CQ = CC•CQ + CCQ	−2.53	−3.08	−3.26	−3.04	−4.79	−4.29
C2CQ + C•CQ = C•CQC + CCQ	−1.88	−2.00	−2.21	0.13	−0.28	−0.03
C2CCQ + C•CQ = C2C•CQ + CCQ	−6.25	−5.78	−6.16	−6.41	−8.89	−7.54
C3CQ + C•CQ = C3•CQ + CCQ	1.10	1.66	1.15	0.52	−0.03	0.49

	CBS-q	MP2(full)/6-31g(d)	MP4(full)/6-31G(d,p)	CBS-q	B3LYP/6-31g(d)	B3LYP/6-311+g(3df,2p)	Lay et al.[c]	literature
	//MP2(full)/6-31G(d)			//B3LYP/6-31G(d)				
Calculated Enthalpies of Formation[a] for Alkyl Hydroperoxides and Alkyl Hydroperoxy Radicals Using Group Isodesmic Reactions in Scheme 2 and Scheme 3								
CCQ	−39.52	−40.05	−40.16	−39.51	−39.83	−39.61	−39.9	−39.71,[d] −38.9,[e] −41.92[j]
CCCQ	−45.19	−44.35	−44.23	−45.21	−43.95	−44.45		
CCQC	−49.11	−49.11	−49.08	−49.22	−48.33	−48.57	−49.0	−49.0,[f] −49.3,[g] −47.5,[h] −43.5,[e] −51.0[j]
C2CCQ	−51.42	−51.23	−51.23	−51.54	−50.95	−51.08		
C3CQ	−57.99	−58.23	−58.33	−58.11	−57.25	−57.21	−58.4	−58.8,[i] −57.1,[f] −57.6,[h] −57.4,[e] −59.63[j]
C•CQ	11.12	10.85	10.69	11.27	10.62	10.77		
CC•CQ	2.96	3.24	3.18	2.43	1.92	1.93		
C•CQC	−0.32	−0.45	−0.62	1.59	2.06	2.07		
C2C•CQ	−6.99	−6.35	−6.72	−7.29	−9.17	−7.95		
C3•CQ	−6.22	−5.91	−6.51	−6.92	−6.60	−6.05		

[a] kcal/mol. [b] Calculated reaction enthalpies are 1.40 kcal/mol and 1.77 kcal/mol based on CBS−Q and G2 calculations. [c] Ref 19. [d] Ref 33. [e] Ref 34. [f] Ref 35. [g] Ref 36. [h] Ref 9. [i] Ref 37. [j] Ref 38.

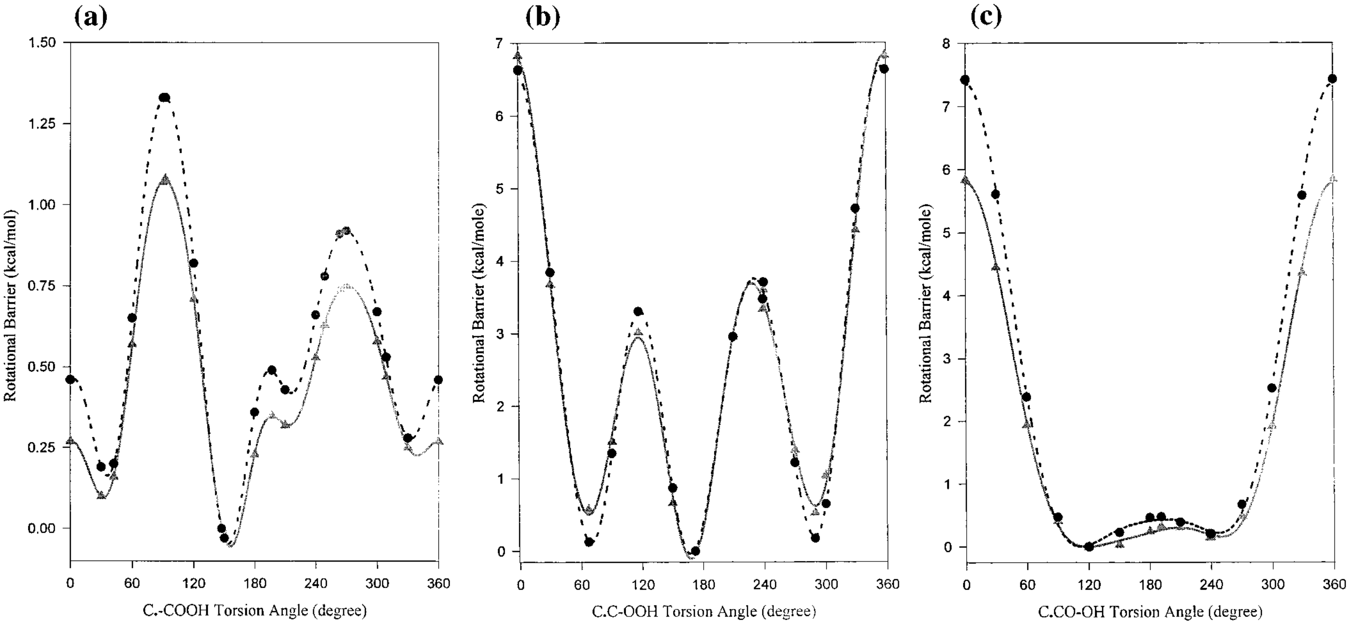


Figure 1. Potential barriers for internal rotations about C•−COOH, C•C−OOH, and C•CO−OH bonds in 2-hydroperoxy-1-ethyl radical (a, b, and c, respectively). Points are calculated values at MP2(full)/6-31g(d) and CBS-Q// MP2(full)/6-31g(d) levels of theory, in circles and triangles, respectively. Lines are results of Fourier expansion equation, F1, with the coefficients listed in the Supporting Information (Table S1).

as follows: $S°_{298}$ (C•CQ) = 82.23 cal/mol-K, $S°_{298}$ (CC•CQ) = 91.39 cal/mol-K, $S°_{298}$ (C•CQC) = 88.15 cal/mol-K, $S°_{298}$ (C_2C•CQ) = 97.93 cal/mol-K, and $S°_{298}$ (C_3•CQ) = 93.02 cal/mol-K based on average values from MP2(full)/6-31g(d) and B3LYP/6-31g(d) calculations. $C_p(300)$ of hydroperoxy alkyl radical are determined to be the following: $C_p(300)$ (C•CQ) = 20.17 cal/mol-K, $C_p(300)$ (CC•CQ) = 24.48 cal/mol-K, $C_p(300)$ (C•CQC) = 26.16 cal/mol-K, $C_p(300)$ (C_2C•CQ) = 30.32 cal/mol-K, and $C_p(300)$ (C_3•CQ) = 32.02 cal/mol-K. Thermodynamic properties are referred to standard state of an ideal gas and pure enantiomer of the most stable conformer.

High-Pressure Rate Constants (k_∞) and Trends. Table 9 lists the total energy, ZPVE, thermal correction to enthalpies, and spin contamination $\langle S^2 \rangle$ of reactants, transition states, and

TABLE 8: Ideal Gas Phase Thermodynamic Properties[a]

species		$H_f^\circ{}_{298}$[b]	$S^\circ{}_{298}$[c]	$C_p(300)$[c]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$
						THERM				
ethylene		12.50	52.30	10.34	12.72	14.86	16.76	19.94	22.37	26.10
propene		4.65	63.81	15.45	19.23	22.72	25.79	30.74	34.49	40.39
isobutene		−3.80	69.99	21.58	26.65	31.30	35.34	41.91	46.89	54.71
						CBS-q//MP2(full)/6-31g(d)				
C•CQ	TVR[d]		68.29	14.62	18.06	21.19	23.84	27.98	31.07	36.07
	internal rotor[e]		13.96	5.47	5.15	4.91	4.7	4.31	3.96	3.3
	total	11.12	82.25	20.09	23.21	26.1	28.54	32.29	35.03	39.37
CC•CQ	TVR		69.9	16.69	21.51	26.11	30.12	36.46	41.18	48.66
	internal rotor		21.43	7.5	7.24	6.88	6.5	5.82	5.34	4.7
	total	2.96	91.33	24.19	28.75	32.99	36.62	42.28	46.52	53.36
CCQC•	TVR		70.6	18.18	23.11	27.56	31.35	37.28	41.71	48.85
	internal rotor		17.5	7.81	7.93	7.78	7.5	6.83	6.24	5.27
	total	−0.32	88.1	25.99	31.04	35.34	38.85	44.11	47.95	54.12
C2C•CQ	TVR		71.41	19.9	26.2	32.17	37.38	45.66	51.83	61.53
	internal rotor		26.37	10.17	9.57	8.91	8.3	7.33	6.68	5.85
	total	−6.99	97.78	30.07	35.77	41.08	45.68	52.99	58.51	67.38
C3•CQ	TVR		71.95	21.77	28.01	33.7	38.59	46.35	52.18	61.54
	internal rotor		20.85	9.77	10.12	10.12	9.91	9.21	8.46	7.09
	total	−6.22	92.8	31.54	38.13	43.82	48.5	55.56	60.64	68.63
TS1	TVR		68.9	14.66	18.1	21.2	23.82	27.89	30.94	35.93
	internal rotor		7.34	5.46	4.82	4.27	3.84	3.22	2.78	2.08
	total	29.57	76.24	20.12	22.92	25.47	27.66	31.11	33.72	38.01
TS2A	TVR		71.24	17.62	22.41	26.87	30.71	36.79	41.35	48.67
	internal rotor		13.5	5.39	5.3	5.15	5.01	4.83	4.72	4.41
	total	20.50	84.74	23.01	27.71	32.02	35.72	41.62	46.07	53.08
TS2B	TVR		70.96	18	22.81	27.22	31.01	36.98	41.47	48.71
	internal rotor		13.39	5.56	5.49	5.3	5.13	4.92	4.77	4.44
	total	19.47	84.35	23.56	28.3	32.52	36.14	41.9	46.24	53.15
TS3A	TVR		72.8	21.03	27.16	32.91	37.91	45.88	51.88	61.44
	internal rotor		18.54	7.41	7.1	6.75	6.47	6.12	5.9	5.5
	total	10.39	91.34	28.44	34.26	39.66	44.38	52	57.78	66.94
TS3B	TVR		72.59	21.75	27.93	33.59	38.48	46.25	52.11	61.51
	internal rotor		18.03	7.82	7.61	7.22	6.87	6.41	6.11	5.6
	total	7.44	90.62	29.57	35.54	40.81	45.35	52.66	58.22	67.11
						CBS-q/B3LYP/6-31g(d)				
C•CQ	TVR		68.25	14.78	18.32	21.49	24.15	28.29	31.37	36.31
	internal rotor		13.96	5.47	5.15	4.91	4.7	4.31	3.96	3.3
	total	11.27	82.21	20.25	23.47	26.40	28.85	32.60	35.33	39.61
CC•CQ	TVR		70.02	17.27	22.31	26.96	30.94	37.19	41.82	49.11
	internal rotor		21.43	7.5	7.24	6.88	6.5	5.82	5.34	4.7
	total	2.43	91.45	24.77	29.55	33.84	37.44	43.01	47.16	53.81
CCQC•	TVR		70.7	18.51	23.54	28.02	31.81	37.72	42.13	49.17
	internal rotor		17.5	7.81	7.93	7.78	7.5	6.83	6.24	5.27
	total	1.59	88.20	26.32	31.47	35.80	39.31	44.55	48.37	54.44
C2C•CQ	TVR		71.7	20.39	26.84	32.87	38.09	46.35	52.47	62.02
	internal rotor		26.37	10.17	9.57	8.91	8.3	7.33	6.68	5.85
	total	−7.29	98.07	30.56	36.41	41.78	46.39	53.68	59.15	67.87
C3•CQ	TVR		72.39	22.72	29.22	34.95	39.79	47.37	53.05	62.12
	internal rotor		20.85	9.77	10.12	10.12	9.91	9.21	8.46	7.09
	total	−6.92	93.24	32.49	39.34	45.07	49.70	56.58	61.51	69.21
TS1	TVR		69.22	15.31	18.87	21.97	24.53	28.48	31.44	36.27
	internal rotor		7.34	5.46	4.82	4.27	3.84	3.22	2.78	2.08
	total	29.12	76.56	20.77	23.69	26.24	28.37	31.70	34.22	38.35
TS2A	TVR		71.54	18.35	23.3	27.79	31.6	37.57	42.03	49.14
	internal rotor		13.5	5.39	5.3	5.15	5.01	4.83	4.72	4.41
	total	19.75	85.04	23.74	28.60	32.94	36.61	42.40	46.75	53.55
TS2B	TVR		71.41	18.87	23.81	28.21	31.93	37.77	42.14	49.16
	internal rotor		13.39	5.56	5.49	5.3	5.13	4.92	4.77	4.44
	total	18.93	84.80	24.43	29.30	33.51	37.06	42.69	46.91	53.60
TS3A	TVR		73.39	21.83	28.16	33.96	38.94	46.81	52.7	62.02
	internal rotor		18.54	7.41	7.1	6.75	6.47	6.12	5.9	5.5
	total	10.52	91.93	29.24	35.26	40.71	45.41	52.93	58.60	67.52
TS3B	TVR		73.15	22.86	29.15	34.79	39.6	47.21	52.93	62.08
	internal rotor		18.03	7.82	7.61	7.22	6.87	6.41	6.11	5.6
	total	7.08	91.18	30.68	36.76	42.01	46.47	53.62	59.04	67.68

[a] Thermodynamic properties are referred to a standard state of an ideal gas of pure enantiomer at 1 atm. [b] In kcal mol^{-1}. [c] In cal mol^{-1} K^{-1}. [d] The sum of contributions from translation, external rotation, vibration, optical isomer, and spin degeneracy. [e] $S^\circ{}_{298}$ and $C_p(T)$ contributions from hindered rotors.

product radicals calculated using MP2(full)/6-31G(d) and B3LYP/6-31G(d) geometries. The ZPVE are scaled by the factor 0.9661 and 0.9804 for MP2(full)/6-31G(d) and B3LYP/6-31g(d) frequencies, respectively. Table 10 lists reaction enthalpies

TABLE 9: Total Energies (0 K, Hartree), Zero-Point Vibrational Energies (ZPVE, kcal/mol), and Thermal Corrections to Enthalpies (H_{thermal}, kcal/mol)

	CBS-q	MP2(full)/6-31g(d)	MP4(full)/6-31g(d,p)	ZPVE	H_{thermal}	spin contamination $\langle S^2 \rangle$	
	//MP2(full)/6-31g(d)					MP2	CBS-q
	Based on MP2(full)/6-31g(d) Geometries						
HO2	−150.7691008	−150.502365	−150.5380066	9.03	2.38		
C2H4	−78.456045	−78.294286	−78.363698	32.69	2.50		
CDCC	−117.7049391	−117.4696584	−117.5715729	51.23	3.14		
C2CDC	−156.9556433	−156.6463965	−156.7808087	69.45	3.90		
TS1	−229.2019201	−228.7666916	−228.872815	43.93	3.88	1.004	0.997
TS2a	−268.4531959	−267.9432248	−268.0822207	62.25	4.80	0.993	0.987
TS2b	−268.4547135	−267.9442604	−268.0831538	62.10	4.72	0.994	0.988
TS3a	−307.7067101	−307.1220775	−307.2938753	80.41	5.66	0.982	0.975
TS3b	−307.7111594	−307.1231334	−307.2948341	80.16	5.50	0.988	0.982
	CBS-q	B31yp/6-31g(d)	B31yp/6-311+g(3df,2p)	ZPVE	H_{thermal}	spin contamination $\langle S^2 \rangle$	
	//B31yp/6-31g(d)					B3LYP	CBS-q
	Based on B3Lyp/6-31g(d) Geometries						
HO2	−150.7692372	−150.8991541	−150.9676579	8.80	2.39		
C2H4	−78.45610003	− 78.5874573	−78.6210637	32.14	2.50		
CDCC	−117.7052425	−117.9075542	−117.9535269	50.24	3.15		
C2CDC	−156.9561062	−157.2272862	−157.285488	68.08	3.92		
TS1	−229.2029457	−229.471956	−229.5712395	42.46	3.95	0.782	1.019
TS2a	−268.454965	−268.7930636	−268.9051628	60.27	4.89	0.779	1.014
TS2b	−268.4562084	−268.7919922	−268.9039991	60.12	4.84	0.781	1.014
TS3a	−307.7073561	−308.113774	−308.2383777	77.92	5.83	0.778	1.011
TS3b	−307.7126306	−308.1107498	−308.2351148	77.63	5.71	0.782	1.014

[a] S^2 values before annihilation. After annihilation values are 0.761, 0.75, 0.761, and 0.763 for MP2, B3LYP, CBSqM, CBSqB.

TABLE 10:

computation level	ethylene CD/H2 (P)	propene CD/H2 (P)	propene CD/C/H (S)	isobutene CD/H2 (P)	isobutene CD/C2 (T)
Reaction Enthalpies for HO_2 Addition to Ethylene, Propene, and Isobutene, at 298 K					
B3LYP/6-31g(d)	9.75	9.12	9.60	8.50	9.99
B3LYP/6-311+g(3df,2p)//B3LYP/6-31g(d)	11.52	10.62	11.15	9.82	11.46
CBS-q//B3LYP/6-31g(d)[a]	13.12	11.60	10.78	10.82	7.38
MP2(full)/6-31g(d)	19.93	19.26	18.39	17.98	16.92
MP4(full)/6-31g(d,p)//MP2(full)/6-31g(d)	19.26	18.35	17.55	16.89	15.88
CBS-q//MP2(full)/6-31g(d)[a]	13.57	12.35	11.32	10.69	7.74

		A (s−1 or cc/mol-s)	E_a (kcal/mol)	T (K)
Experimental Rate[b] Constants for Reactions of HO_2 Addition with Olefins				
ethylene	CD/H2 (P)	3.80×10^{12}	17.85	653−793
(E)-but-2-ene	CD/C/H (S)	4.07×10^{11}	11.95	673−793
2,3-dimethylbut-2-ene	CD/C2 (T)	3.80×10^{11}	8.46	653−793

[a] Choose unit: kcal/mol, include thermal correction and zero-point energy correction. [b] Ref 4a−e.

(energy differences between reactants and TSs) obtained from various levels of theory. Reaction enthalpy ($\Delta H^{\ddagger}_{\text{TS − reactants}}$)$_{298}$ for HO_2 addition to the primary, secondary, and tertiary carbon double bonds are 12.20 (11.85), 11.32 (10.78), and 7.74 (7.38) kcal/mol, respectively, at CBSlqM level. Data in parentheses are calculations at CBSlqB level. The value of 12.20 (11.85) kcal/mol is the average value of HO_2 addition to the primary carbon−carbon double bond of ethylene, propene, and isobutene.

The charge at the carbons where addition is occurring is important to the barrier for HO_2 + olefin. The trend in barrier vs charge at the carbons is often used to estimate barriers for addition reactions.[4,27] In the transition states (TS1, TS2B, and TS3B), CH_3 groups donate electrons (ca. 0.2 Mulliken charge per CH_3, at MP2(full)/6-31g(d) level) to the olefinic carbon (CD/H2, CD/C/H, and CD/C2 carbon atoms), which is undergoing bond formation with HO_2. The Mulliken charges for CD/H2, CD/C/H, and CD/C2 carbon atoms in transition states TS1, TS2B, and TS3B are −0.2913, −0.0917, and +0.0888, respectively. The charge on the oxygen atom in the C- - -O forming bond is ca. −0.15. Partial electron donation from two $-CH_3$ groups in the HO_2, addition to the CD/C2 carbon atom of isobutene results in a lower activation energy than addition to the CD/H2 atom, 7.63 vs 13.49 kcal/mol at CBSlqM level. The Mulliken charge for all species calculated at MP2(full)/6-31g(d) level is presented in the Supporting Information (Table S2).

Table 11 lists rate constants k_∞ determined from TST and fit by three parameters A_∞, n, and E_a over the temperature range 298−2000 K. Calculated rate constants obtained at CBSlqM and CBSlqB levels of theory show similar trends with experimental data (in Table 10b): HO_2 radical addition to the tertiary carbon double bond (HO_2 addition at CD/C2 carbon atom of isobutene) has a lower activation energy than addition to secondary carbon double bond CD/C/H, which is lower than addition to primary double bonds; the values are 12.11(11.56), 11.08(10.34), and 7.63(7.03) kcal/mol, respectively. The E_a's for addition to primary double bonds of ethylene, propene and isobutene also show a respective decreasing trend 13.49(12.89), 12.16(11.20), and 10.70(10.59) kcal/mol, respectively. Values reported by Walker's research group[4a−e] from experiments on overall cyclic ether product formation rates show the E_a for HO_2 addition to carbon double bond CD/H2 (HO_2 + ethylene), CD/C/H (HO_2 + (E)-but-2-ene) and CD/C2 (HO_2 + 2,3-dimeth-

TABLE 11: Rate Constants k_∞ Determined from TST and Reaction Enthalpies

reaction	A (s^{-1} or cm^3/mol−s)	n	E_a (kcal/mol)
	CBSq//MP2(full)/6-31g(d)		
forward			
C2H4+HO2=TS1	4.13E+04	2.3323	13.49
C3H6+HO2=TS2A	2.47E+04	2.1322	12.16
C3H6+HO2=TS2B	7.74E+03	2.2849	11.08
i-C4H8+HO2=TS3A	3.45E+05	1.7648	10.70
i-C4H8+HO2=TS3B	2.78E+04	2.1061	7.63
reverse			
C•CQ=TS1	3.89E+10	0.4809	18.87
CC•CQ=TS2A	7.33E+09	0.6457	17.68
C•CQC=TS2B	3.65E+12	−0.0771	20.32
C2C•CQ=TS3A	2.00E+10	0.5005	17.58
C3•CQ=TS3B	4.89E+13	−0.3253	14.43

reaction	A_{300}	A_{800} (s^{-1} or cm^3/mol−s)	A_{1500}	k_{300}	k_{800} (s^{-1} or cm^3/mol-s)	k_{1500}
forward						
C2H4+HO2=TS1	2.48E+10	2.44E+11	1.06E+12	3.71E+00	5.05E+07	1.15E+10
C3H6+HO2=TS2A	4.72E+09	3.82E+10	1.46E+11	6.52E+00	1.82E+07	2.47E+09
C3H6+HO2=TS2B	3.54E+09	3.32E+10	1.40E+11	3.00E+01	3.13E+07	3.40E+09
i-C4H8+HO2=TS3A	8.12E+09	4.59E+10	1.39E+11	1.31E+02	5.49E+07	3.85E+09
i-C4H8+HO2=TS3B	4.58E+09	3.61E+10	1.36E+11	1.27E+04	2.98E+08	1.05E+10
reverse						
C•CQ=TS1	6.04E+11	9.68E+11	1.31E+12	1.08E−02	6.77E+06	2.33E+09
CC•CQ=TS2A	2.91E+11	5.49E+11	8.24E+11	3.81E−02	8.09E+06	2.18E+09
C•CQC=TS2B	2.35E+12	2.18E+12	2.08E+12	3.69E−03	6.12E+06	2.27E+09
C2C•CQ=TS3A	3.47E+11	5.67E+11	7.77E+11	5.40E−02	8.92E+06	2.13E+09
C3•CQ=TS3B	7.65E+12	5.56E+12	4.53E+12	2.36E+02	6.36E+08	3.58E+10

reaction	A (s^{-1} or cm^3/mol−s)	n	E_a (kcal/mol)
	CBSq//B3LYP/6-31g(d)		
forward			
C2H4+HO2=TS1	6.97E+03	2.6280	12.89
C3H6+HO2=TS2A	2.30E+03	2.5130	11.20
C3H6+HO2=TS2B	7.40E+02	2.6762	10.34
i-C4H8+HO2=TS3A	2.62E+04	2.1984	10.59
i-C4H8+HO2=TS3B	1.59E+03	2.5839	7.03
reverse			
C•CQ=TS1	1.80E+10	0.6306	18.21
CC•CQ=TS2A	6.52E+09	0.6781	17.45
C•CQC=TS2B	1.35E+12	0.1047	17.79
C2C•CQ=TS3A	1.15E+10	0.6102	17.97
C3•CQ=TS3B	6.02E+13	−0.3446	14.79

reaction	A_{300}	A_{800} (s^{-1} or cm^3/mol−s)	A1500	k_{300}	k_{800} (s^{-1} or cm^3/mol−s)	k_{1500}
forward						
C2H4+HO2=TS1	2.25E+10	2.97E+11	1.55E+12	9.23E+00	8.95E+07	2.05E+10
C3H6+HO2=TS2A	3.86E+09	4.54E+10	2.20E+11	2.66E+01	3.95E+07	5.14E+09
C3H6+HO2=TS2B	3.15E+09	4.35E+10	2.34E+11	9.24E+01	6.51E+07	7.28E+09
i-C4H8+HO2=TS3A	7.31E+09	6.32E+10	2.52E+11	1.41E+02	8.09E+07	7.21E+09
i-C4H8+HO2=TS3B	4.01E+09	5.06E+10	2.57E+11	3.05E+04	6.09E+08	2.43E+10
reverse						
C•CQ=TS1	6.56E+11	1.22E+12	1.81E+12	3.53E−02	1.29E+07	4.02E+09
CC•CQ=TS2A	3.12E+11	6.06E+11	9.28E+11	6.03E−02	1.04E+07	2.66E+09
C•CQC=TS2B	2.46E+12	2.72E+12	2.91E+12	2.67E−01	3.75E+07	7.43E+09
C2C•CQ=TS3A	3.74E+11	6.81E+11	9.99E+11	3.04E−02	8.40E+06	2.41E+09
C3•CQ=TS3B	8.43E+12	6.01E+12	4.84E+12	1.41E+02	5.47E+08	3.39E+10

ylbut-2-ene) to be 17.85, 11.95, and 8.46 kcal/mol, respectively. These values from cyclic ether formation result from a kinetic analysis which often incorporates equilibrium and thermochemical properties significantly different from data in this study or our previously published evaluations.[16, 19, 28]

Comparison of calculated A_∞ factors for HO_2 radical addition to the primary, secondary, and tertiary carbon double bonds indicates they are all similar, within 1 order of magnitude. Calculated values (listed in Table 11) are lower by factors of 0.11−0.18 than experimental data, 1.92×10^{12}, 2.04×10^{11}, 1.90×10^{11} cm^3/mol-s (653 to 793 K) for addition to CD/H2, CD/C/H and CD/C2, respectively. The experimental A factors have been divided by two from reported values for steric effect adjustment. Experimental and calculated A factors both show that HO_2 addition at CD/C/H and CD/C2 carbons have similar A factors, which are lower by a factor of 10 than addition at CD/H2. Reaction of HO_2 radical addition to tertiary carbon double bond has higher rate constant than HO_2 radical addition to primary and secondary, resulting from the lower E_a and similar A_∞ factor.

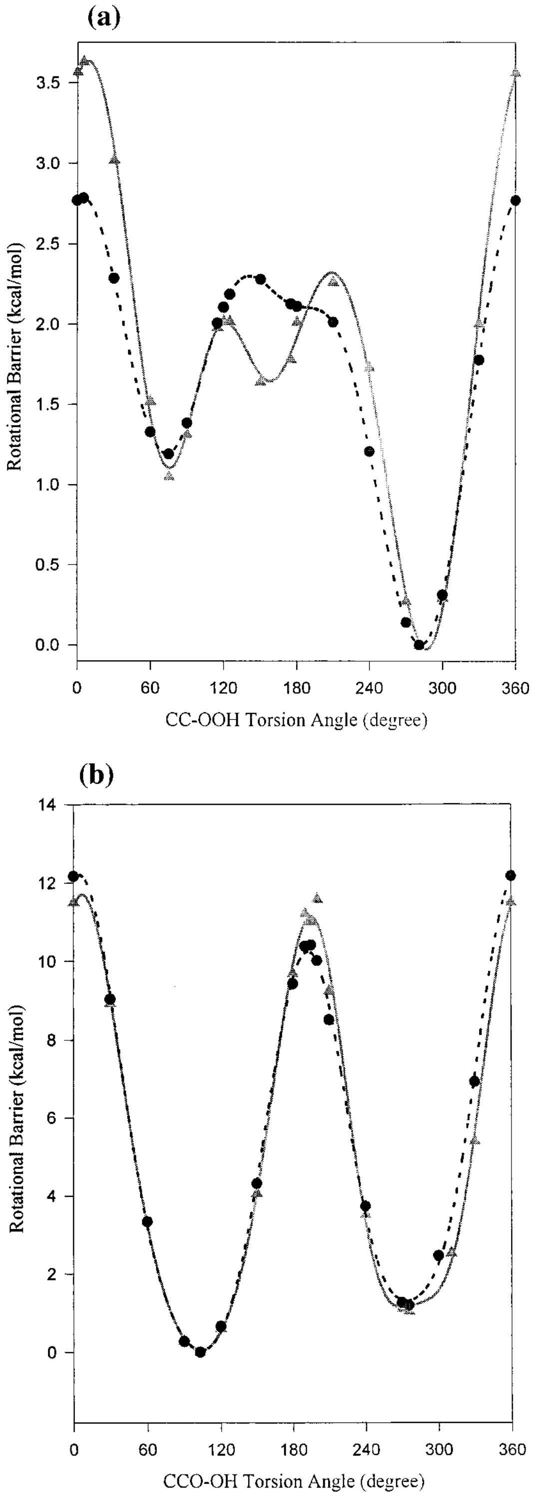


Figure 2. Potential barriers for internal rotations about CC−OOH and CCO−OH bonds in TS1 (a and c, respectively). Points are calculated values at MP2(full)/6-31g(d) and CBS-Q// MP2(full)/6-31g(d) levels of theory, in circles and triangles, respectively. Lines are results of Fourier expansion equation, F1, with the coefficients listed in the Supporting Information (Table S1).

Comparison with Experimental Work. We have analyzed data reported on two systems, *tert*-butyl radical + O_2[29] and allylic isobutenyl radical + O_2[30] where HO_2 + olefin reactions play an important role; our modeling shows very good agreement with the reported data.[31,32] Figure 3 shows a comparison of our calculation with experimental data[31] for loss of *tert*-butyl precursor, 2,2,3,3-tetramethylbutane (C_3CCC_3), production of isobutene and 2,2-dimethyloxirane from the *tert*-butyl radical + O_2 reaction system. Figure 4 shows a comparison of our calculation with experimental data[32] for production of 2,5 dimethylhexa-1,5-diene, methacrolein, isobutene oxides, and acetone from the allylic isobutenyl radical + O_2 reaction system for condition of 0−210 s, 743 K, and 60 Torr.

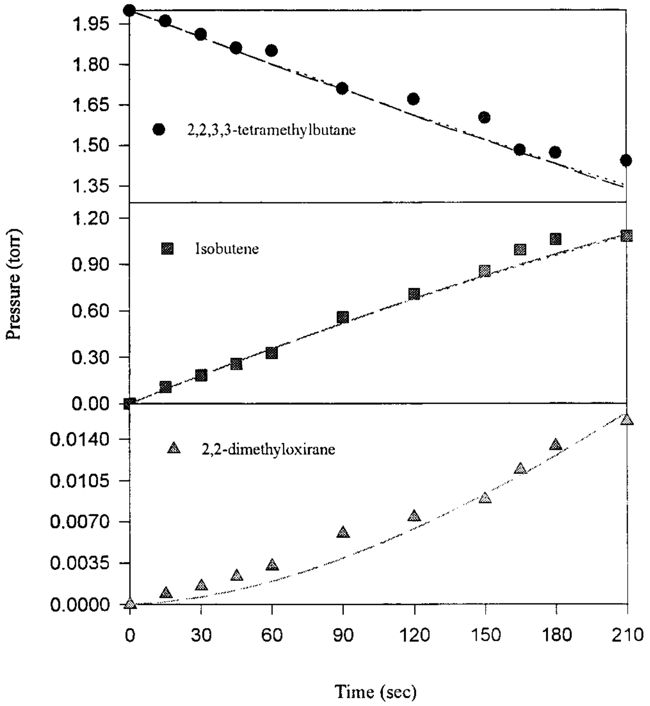


Figure 3. Comparison of model prediction[29] and experimental data[31] for loss of *tert*-butyl precursor, 2,2,3,3-tetramethylbutane (C_3CCC_3), production of isobutene and 2,2-dimethyloxirane from *tert*-butyl radical + O_2 reaction system.

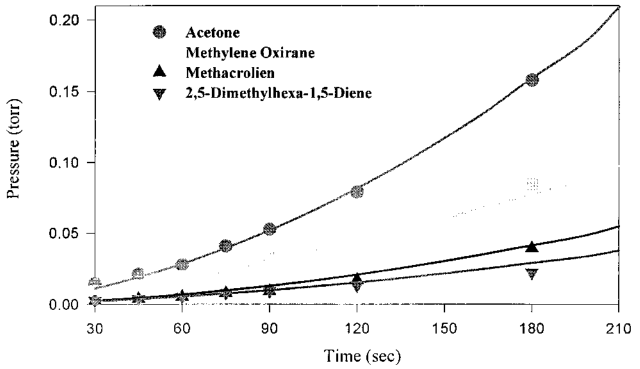


Figure 4. Comparison of model prediction[30] with experimental data[32] for productions of 2,5 dimethylhexa-1,5-diene, methacrolein, isobutene oxides (methylene oxirane + 2,2-dimethyloxirane), and acetone from isobutane oxidation reaction system.

Sensitivity analysis indicates that the cyclic oxides (oxiranes) formed in these two systems result from further reaction of the corresponding hydroperoxy alkyl radical. Furthermore, the important formation path of this hydroperoxy alkyl radical is via HO_2 addition to olefin. The agreement of our modeling results on the oxirane formation profiles supports the kinetic analysis presented in this study.

Oxirane product formation from HO_2 addition to olefin is not a single, direct reaction (see Scheme 1). The reaction system includes multiple reaction channels and products, with paths from both chemical activation and reaction of stabilized adducts important to product formation. The kinetic data derived from the experimental values are from these relatively complex kinetic systems. The experimental rate constants (listed in Table 10) are obtained from research group of Walker.[4a−e] The experimental values result from studies on thermal reactions of radical precursor species in H_2/O_2/inert atmospheres using flow reactors (both KCl and boric acid coated)—at slow flow—up to several minute reaction times. The analysis involves profiles of stable species vs time and assumptions on reaction paths and thermodynamic properties. Accurate thermodynamic properties are important because equilibrium relationships are assumed in deriving the reported kinetic parameters. In addition, it has recently been shown that HO_2 + olefin are a direct product set from molecule elimination of peroxy radicals formed in alkyl radical + O_2 reaction systems, where some previous mechanisms postulated these products occurred via isomerization (H shift) and then either oxirane formation or elimination to HO_2 + olefin. The direct HO_2 elimination was not fully understood in the early analysis of the $C_3C.$ + O_2 reaction system.

Summary

Thermodynamic properties of product radicals and transition states are calculated for HO_2 addition to primary, secondary, and tertiary carbon−carbon double bond of ethylene, propene, and isobutene using ab initio and density functional calculations. $\Delta H_f{}^\circ_{298}$ for the hydroperoxy alkyl radicals, C•CQ, CC•CQ, C•CQC, C_2C•CQ, and C_3•CQ, are estimated using total energies derived from CBSlqM, CBSlqB, MP4F, and B3LYP311 calculations and group balance isodesmic reactions with ZPVE and thermal correction to 298.15K. $\Delta H_f{}^\circ_{298}$ are determined to be $\Delta H_f{}^\circ_{298}$ (C•CQ) = 10.96 ± 1.06 kcal/mol, $\Delta H_f{}^\circ_{298}$ (CC•CQ) = 2.62 ± 1.29 kcal/mol, $\Delta H_f{}^\circ_{298}$ (C•CQC) = 0.68 ± 1.54 kcal/mol, $\Delta H_f{}^\circ_{298}$ (C_2C•CQ) = −7.24 ± 1.25 kcal/mol, and $\Delta H_f{}^\circ_{298}$ (C_3•CQ) = −6.42 ± 1.28 kcal/mol.

S°_{298} and $Cp(T)$ ($300 \leq T/\mathrm{K} \leq 1500$) contributions from vibrational, translational, and external rotational are calculated using the rigid rotor harmonic oscillator approximation based on geometric parameters and vibrational frequencies obtained at MP2(full)/6-31G(d) and B3LYP/6-31G(d) levels of theory. Contributions from hindered rotors of S°_{298} and $Cp(T)$ for C•CQ radical and TS1 are calculated by summation over the energy levels obtained by direct diagonalization of the Hamiltonian matrix of hindered internal rotations, while contributions for other radicals and TSs are calculated by the Pitzer and Gwinn approximation method.

Activation energy based on CBSlqM and CBSlqB calculations show similar trends with experimental data. Calculated E_a's for HO_2 radical addition to the tertiary, secondary, and primary carbon double bond are 12.11(11.56), 11.08(10.34), and 7.63(7.03) kcal/mol, respectively. The Arrhenius preexponential factor, A_{800}, calculated from TST along with MP2- and DFT-determined entropy, 2.44×10^{11} (2.97×10^{11}), 3.32×10^{10} (4.35×10^{10}), and 3.61×10^{10} (5.06×10^{10}) cm^3/mol-s for addition to CD/H2, CD/C/H, and CD/C2 carbon−carbon double bonds, respectively, are also in agreement with experiment. Data in parentheses are calculations at the CBSlqB level.

The high-pressure limit rate constants are (based on CBSlqM calculations) as follows: $k_{1,\infty}(HO_2 + C{=}C \Rightarrow C{\bullet}CQ) = 4.13 \times 10^4\ T^{2.232} \exp(-13.49\ \mathrm{kcal\ mol^{-1}}/RT)$ cm^3/mol-s; $k_{2,\infty}(HO_2 + C{=}CC \Rightarrow CC{\bullet}CQ) = 2.47 \times 10^4\ T^{2.132} \exp(-12.16\ \mathrm{kcal\ mol^{-1}}/RT)$ cm^3/mol-s; $k_{3,\infty}(HO_2 + C{=}CC \Rightarrow C{\bullet}CQC) = 7.74 \times 10^3\ T^{2.285} \exp(-11.08\ \mathrm{kcal\ mol^{-1}}/RT)$ cm^3/mol-s; $k_{4,\infty}(HO_2 + C_2C{=}C \Rightarrow C_2C{\bullet}CQ) = 3.45 \times 10^5\ T^{1.765} \exp(-10.70\ \mathrm{kcal\ mol^{-1}}/RT)$ cm^3/mol-s; $k_{5,\infty}(HO_2 + C_2C{=}C \Rightarrow C_3{\bullet}CQ) = 2.78 \times 10^4\ T^{2.106} \exp(-7.63\ \mathrm{kcal\ mol^{-1}}/RT)$ cm^3/mol-s.

Reverse (hydroperoxide alkyl radical unimolecular dissociation) rate constants are also reported: $k_{-1,\infty} = 3.89 \times 10^{10}\ T^{0.481} \exp(-18.87\ \mathrm{kcal\ mol^{-1}}/RT)$ cm^3/mol-s; $k_{-2,\infty} = 7.33 \times 10^9\ T^{0.646} \exp(-17.68\ \mathrm{kcal\ mol^{-1}}/RT)$ cm^3/mol-s; $k_{-3,\infty} = 3.65 \times 10^{12}\ T^{0.08} \exp(-20.32\ \mathrm{kcal\ mol^{-1}}/RT)$ cm^3/mol-s; $k_{-4,\infty} = 2.0 \times 10^{10}\ T^{0.501} \exp(-17.58\ \mathrm{kcal\ mol^{-1}}/RT)$ cm^3/mol-s; $k_{-5,\infty} = 4.89 \times 10^{13}\ T^{-0.325} \exp(-14.43\ \mathrm{kcal\ mol^{-1}}/\mathrm{RT})$ cm^3/mol-s.

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Supporting Information Available: Coefficients of Truncated Fourier Series Representation Expansions for Internal Rotation Potentials (Table S1); the Mulliken charge for all species calculated at MP2(full)/6-31g(d) level (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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