J. Phys. Chem. A **2004,** *108,* 8353−8366

Thermochemical Properties, Rotation Barriers, Bond Energies, and Group Additivity for Vinyl, Phenyl, Ethynyl, and Allyl Peroxides

Nadia Sebbar,[†] Joseph W. Bozzelli,*[,‡] and Henning Bockhorn[†]

Institut für Technische Chemie and Polymerchemie, Karlsruhe, Universität Karlsruhe (TH), Kaiserstrasse 12, 76128 Karlsruhe, Germany, and Department of Chemical Engineering, Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, New Jersey 07102

Received: September 15, 2003; In Final Form: June 28, 2004

Peroxides have relatively low stability and are often difficult to obtain at needed purity for experimental studies. This study uses computational chemistry to estimate thermochemical properties of peroxides and compares the values to properties of corresponding hydroperoxides. The combined thermochemical properties are utilized to develop groups for use in group additivity. Structures, enthalpy ($\Delta_f H^\circ_{298}$), entropy (S°_{298}), and heat capacity ($C_p(T)$) are determined for several vinyl, allyl, ethynyl, and phenyl peroxides using the density functional B3LYP/6-311G(d,p) calculations. Enthalpies of formation ($\Delta_f H^\circ_{298}$) are determined at the B3LYP/6-311G(d,p) level using four to six isodesmic working reactions. Entropy (S) and heat capacity ($C_p(T)$) values from vibration, translational, and external rotational contributions are calculated using the rigid-rotor-harmonic-oscillator approximation based on the vibration frequencies and structures obtained from the density functional studies. Contribution to $\Delta_f H(T)$, S, and $C_p(T)$ from analysis on the internal rotors is included. $\Delta_f H^\circ_{298}$ for vinyl-methyl peroxide, $CH_2{=}CHOOCH_3$, is -10.04 ± 0.66 kcal mol^{-1} and for allyl-methyl peroxide, $CH_2{=}CHCH_2OOCH_3$, is -12.08 ± 1.05 kcal mol^{-1}. Methyl-substituted vinyl peroxide values are $CH_2{=}C(CH_3)OOCH_3 = -20.79 \pm 0.42$, $CH_3CH{=}C(CH_3)OOCH_3 = -29.58 \pm 0.32$, and $CH_3(CH_3)C{=}CHOOCH_3 = -30.60 \pm 0.90$ kcal mol^{-1}. The cis conformation of $CH_3CH{=}CHOOCH_3$, -21.27 ± 0.47 kcal mol^{-1}, is more stable than the trans form, -19.95 ± 0.67 kcal mol^{-1}. Enthalpies for ethynyl peroxides are 41.31 ± 0.72 kcal mol^{-1} for $HC{\equiv}COOCH_3$ and 29.51 ± 0.27 kcal mol^{-1} for $CH_3C{\equiv}COOCH_3$. The calculated $\Delta_f H^\circ_{298}$ for phenyl peroxide, $C_6H_5OOCH_3$, is -2.19 ± 0.52 kcal mol^{-1}. The resulting peroxide enthalpies allow determination of the RO−OC, ROO−C bond energies. The vinyl, phenyl and ethynyl peroxides are unstable and rapidly dissociate via cleaving of the weak RO−OR′ peroxide bond with formation of a strong carbonyl bond. Enthalpy of formation was also calculated for CH_3OOCH_3 (-30.77 ± 0.64 kcal mol^{-1}) and $CH_3CH_2OOCH_3$ (-39.0 ± 0.24 kcal mol^{-1}) due to the need for these enthalpy values in the working reaction analysis. Thermodynamic properties for the oxygenated carbon groups O/C$_d$/O, O/C$_b$/O, C$_t$/O, O/C$_t$/O, and O/C/C$_t$ were also determined. The agreement between group additivity and calculated enthalpies and heat capacities for the different classes of molecules studied supports the group additivity principal for these systems.

Introduction

Peroxides and peroxy species are important intermediates in photochemical oxidation of hydrocarbons in the atmosphere,[1−4] in polymer initiators, and in thermal oxidation of hydrocarbons. Reactions of peroxides also control the chemistry of intermediate-temperature (below 750 K) hydrocarbon self-ignition. Reactions of ozone with olefins lead to vinyl peroxide formation, where the vinyl peroxide is estimated to undergo rapid unimolecular dissociation to a ketenyl radical plus OH. The reaction scheme in Figure 1 represents a simplified mechanism for the 2-butene + O_3 reaction, showing the formation of vinylic peroxy species as intermediates.

Martinez and Herron[5] estimated the limited stability of $CH_2{=}C(CH_3)OOH$, which they determined was formed in ozonolysis of tetramethyl-ethylene, possibly formed by reaction through a $(CH_3)_2C{\cdot}COO{\cdot}$ intermediate. Olzman et al.[6] have shown that reaction of ozone with substituted olefins forms vinyl hydroperoxides, where the vinyl hydroperoxide undergoes rapid cleavage of the weak peroxide bond to form a OH radical plus a ketenyl radical.

There are a limited number of recent experimental studies on peroxides, primarily those using flow reactors with photoionization, mass spectrometric detection in David Gutman's research group (reviewed and summarized by Knyazev and Slagle[7]), and two studies involving negative ion chemistry from Clifford et al.[8] and Blanksby et al.[9]

There are a larger number of computational chemistry or evaluation studies on peroxy and hydroperoxy alkyl radicals.[10−14] Bozzelli's research group[3,4,15−20] has reported enthalpies from use of isodesmic reactions and entropies and heat capacity values from use of statistical mechanics and analysis of internal rotors. They have also determined group additivity (GA) contributions. Sebbar et al.[3,4] have used the B3LYP method and isodesmic reactions to estimate thermodynamic data on a number of vinyl hydroperoxide and peroxy, as well as allyl and phenyl, hydroperoxides. Hadad's group has performed several studies[21] on

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* Corresponding Author. Phone: + 973-596 3459. Fax: + 973-596 3586. E-mail: bozzelli@njit.edu.

[†] Universität Karlsruhe (TH).

[‡] New Jersey Institute of Technology.

10.1021/jp031067m CCC: $27.50

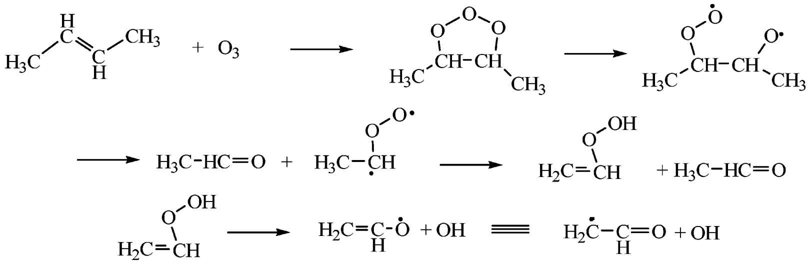

Figure 1. Schematic representation of the mechanism for the ozonolysis of 2-butene.

phenyl peroxy species, but only Gibbs energies are reported. Jonsson and co-workers[22,23] have also reported enthalpy values from semiempirical and a number of higher level ab initio calculations. Sheng et al.[14,24] report data on the ethyl peroxy and 2-hydroperoxide ethyl radicals and on the stable ethylhydroperoxide. Sumathi and Green[25] have reported results from ab initio molecular orbital calculations at the Hartree−Fock level for S and $C_p(T)$ and complete basis set (CBS-Q−atomization reaction) level for enthalpies on methyl, ethyl, isopropyl, and tertbutyl hydroperoxides and corresponding methylperoxides.

There is little or no thermochemical property data available for unsaturated alkylperoxy and peroxide species. Peroxides are often impure and/or unstable, and therefore difficult to isolate and characterize by experimental methods. There are no experimental data on the vinyl, phenyl, ethynyl, or allylic unsaturated peroxides that we are aware of. Experimental studies on vinyl radical[26] and allyl radical[27] reactions with O_2 to form the corresponding peroxy radical are reported by David Gutman's research group. Phenyl-peroxy radical was reported as a major product for phenyl radical reaction with O_2 by M. C. Lin's group at ambient temperatures.[28] Sebbar et al. have published enthalpy, entropy, and heat capacity values on a number of unsaturated hydroperoxides.[3,4] This study reports bond energies, enthalpy, entropy, heat capacity, internal rotation potential, and structure data for a series of unsaturated peroxides. Thermochemical property groups are developed for use in group additivity. Comparisons of data are made with values of corresponding hydroperoxides previous published.[3]

Overall the vinyl, phenyl, and ethynyl−alkyl peroxides do not exist as stable species under atmospheric conditions and time scales of seconds. Determination of the enthalpies of formation provides analysis of the relative bond strengths in these species and subsequent information concerning the reactions of stable peroxide radicals, which are important in both combustion and atmospheric chemistry of hydrocarbons. Reactions of peroxide species and corresponding radicals are important to chain branching in combustion and oxidation that controls ignition in new generation, high-compression nonspark ignition engines. The unsaturated vinyl, phenyl, and ethynyl peroxides and hydroperoxides are also products from reactions of peroxide alkyl radicals.

Computational Methods and Accuracy

All of the calculations are performed using the Gaussian 98 program suite.[29] Structural parameters for all molecules are optimized at the B3LYP/6-311G(d,p) level of theory. Harmonic vibration frequencies and zero-point vibration energies (ZPVE) are computed at the same level. The optimized geometry parameters are used to obtain total electronic energies.[30−32] The CBS/QB3 composite calculation method uses this level for structure calculation based on studies showing it results in improved accuracy.[33]

1. Accuracy of Density Functional Theory for Estimation of Peroxides. Chen and Bozzelli[34] have used density functional calculations for oxygenated hydroperoxides and peroxy radical species; they show that two different levels of B3LYP calculations, combined with use of isodesmic reaction analysis, result in good agreement with MP2, MP4 ab initio, and CBSlq composite methods. B3LYP/6-311G(d,p) was also shown by Mebel et al.[35] to give similar enthalpies to values calculated by the G2M composite method on a number of unsaturated peroxide and peroxy species. The B3LYP/6-31G(d,p) is reported to yield accurate geometries and reasonable energies when used with isodesmic or homodesmic working reactions.[36−39]

Sebbar et al.[3] report density functional calculations for enthalpy of 1-methyl vinyl hydroperoxide ($CH_2{=}C(CH_3)OOH$), −21.8 kcal mol^{-1}, which is in agreement with the value of Olzman and co-workers (−19.6 kcal mol^{-1}).[6] Schlegel and co-workers[40] report the calculation on O−O bond energy for $CH_2{=}C(CH_3)OOH$ to be 22.7 kcal mol^{-1} by using G2MP2 ab initio method, while Sebbar et al.[3] reported 21.2 kcal mol^{-1}. Lee and Bozzelli[41] have determined the value of ketenyl radical $HC^{\bullet}{=}C{=}O$ to be 42.0 kcal mol^{-1} using CBS-QCI/APNO method, while Sebbar et al.[3] have found 40.4 kcal mol^{-1} with the density functional method.

We further justify the use of B3LYP/6-311G(d,p) as a calculation method for these peroxy/peroxide molecules and radicals through a number of comparisons with higher-level calculations and recent experimental data illustrated in Table 1. Calculation of the enthalpies of methyl and propyl hydroperoxides (CH_3OOH, $CH_3CH_2CH_2OOH$), as well as three radicals, $CH_3OO^{\bullet}$, $CH_3CH_2OO^{\bullet}$, and $CH_2^{\bullet}CH_2OOH$ are included in Table 2 to provide comparison of results with literature values. This is achieved by combination of the DFT calculation data with isodesmic work reactions with similar bonds on both sides of the reaction for effective cancellation of errors. Ethylhydroperoxide serves as comparison as well, where DFT results in −39.28 kcal mol^{-1},[3] which is in good agreement with the recent experimental studies of Blanksby et al.,[9] −39.5 kcal mol^{-1}. The use of group additivity parameters[42] results in −39.9 kcal mol^{-1}. These data are in good agreement with CBS-q//MP2(full)/6-31G(d) (−39.52 kcal mol^{-1}),[16] MP2//MP2(full)/6-31G(d) (−40.05 kcal mol^{-1}),[16] MP4SDTQ/6-31G*//MP2/6-31G* (−39.9 kcal mol^{-1}),[42] CBS-Q//B3LYP/6-31G(d,p) (−39.9 kcal mol^{-1}),[24] and G2 (−40.1 kcal mol^{-1})[24] calculations. GA and CBSQ−atomization reaction values from ref 25 show −38.9 and −38.78 kcal mol^{-1} respectively. There is approximately a 1 kcal mol^{-1} difference between values recommended in ref 25 and the G2 calculations that we select as most accurate. This further appears in the enthalpies of dimethyl and ethyl methyl peroxides, which are used as reference species in the working reactions.

The data in Tables 1 and 2 illustrate good agreement through a range of peroxy and peroxide species with a number of high-level calculation methods and values reported in recent experimental studies. From 43 literature values listed, enthalpy values

TABLE 1: Comparison of Enthalpies of Formation ($\Delta_f H^\circ_{298}$, kcal mol^{-1}) of Some Peroxides Determined by Different Methods

species	value	method
CH_3OOH	−31.8 ± 0.94[19,42]	MP2//MP2(full)/6-31G(d)
	−30.67[24]	CBS-APNO
	−30.9 ± 0.7[9]	CBS-APNO
	−33[79]	MM and ab initio calculation
	−31.3[90]	heat of equilibrium measurement
	−30.75[25]	CBS-Q
	−31.36 ± 0.81[a]	*B3LYP/6-311G(d,p)*
CH_3CH_2OOH	−39.52[16]	CBS-q//MP2(full)/6-31G(d)
	−40.05[16]	MP2//MP2(full)/6-31G(d)
	−39.9[42]	MP4SDTQ/6-31G*//MP2/6-31G*
	−39.9 ± 1.5[24]	CBS-Q//B3LYP/6-31G(d,p)
	−40.1 ± 1.8[24]	G2
	−39.5 ± 0.7[9]	derived from experiment
	−40[79]	MM and ab initio calculation
	−38.78[25]	CBS-Q
	−39.28 ± 0.01[3]	*B3LYP/6-311G(d,p)*
$CH_3CH_2CH_2OOH$	−45.19[16]	CBS-q//MP2(full)/6-31G(d)
	−44.35[16]	MP2//MP2(full)/6-31G(d)
	44.05 ± 0.14[a]	*B3LYP/6-311G(d,p)*
$CH_2{=}C(CH_3)OOH$	−24.38[20]	CBS-4//MP2(full)/6-31G(d)
	−24.51[20]	CBS-q//MP2(full)/6-31G(d)
	−24.52[20]	MP2//MP2(full)/6-31G(d)
	−19.6[6]	CCSD(T)
	−21.8 ± 0.06[a]	*B3LYP/6-311G(d,p)*
$CH_2{=}C(CH_3)OOCH_3$	−19.94[20]	CBS-4//MP2(full)/6-31G(d)
	−20.14[20]	CBS-q//MP2(full)/6-31G(d)
	−19.61[20]	MP2//MP2(full)/6-31G(d)
	−20.79 ± 0.42[a]	*B3LYP/6-311G(d,p)*
$CH_3OO^\bullet$	1.2[24]	CBS-APNO
	2.24[78]	G2
	2.7 ± 0.8[81]	experiment $CH_3 + O_2 \leftrightarrow CH_3OO$
	2.9 ± 1.5[82]	experiment $CH_3 + O_2 \leftrightarrow CH_3OO$
	2.15 ± 1.22[7]	experiment $CH_3 + O_2 \leftrightarrow CH_3OO$
	2.07 ± 0.7[9]	CBS/APNO
	2.02 ± 0.1[a]	*B3LYP/6-311G(d,p)*
$CH_3CH_2OO^\bullet$	−6.7[24]	CBS-Q//B3LYP/6-31G(d,p)
	−6.8[24]	G2
	−6.5 ± 2.4[7]	experiment $CH_3CH_2 + O_2 \leftrightarrow CH_3CH_2OO$
	−6.8 ± 0.7[9]	CBS/APNO
	−6.8 ± 2.3[9]	negative-ion/acidity/CBS
	−5.75 ± 0.1[a]	*B3LYP/6-311G(d,p)*
$CH_2^\bullet CH_2OOH$	11.12[16]	CBS-q//MP2(full)/6-31G(d)
	10.85[16]	MP2//MP2(full)/6-31G(d)
	11.2[24]	CBS-Q//B3LYP/6-31G(d,p)
	10.5[24]	G2
	11.34 ± 1[a]	*B3LYP/6-311G(d,p)*
$CH_2{=}CHOO^\bullet$	24.45[35]	G2M(RCC,MP2)
	24.34 ± 0.42[3]	*B3LYP/6-311G(d,p)*
$CH_2{=}C(CH_3)COO^\bullet$	11.34[20]	CBS-4//MP2(full)/6-31G(d)
	11.06[20]	CBS-q//MP2(full)/6-31G(d)
	12.25[20]	MP2//MP2(full)/6-31G(d)
	10.91 ± 0.34[3]	*B3LYP/6-311G(d,p)*
$HC^\bullet{=}C{=}O$	41.98[41]	CBS-QCI/APNO
	40.40[3]	*B3LYP/6-311G(d,p)*

[a] This work. Units: kcal mol^{-1}.

for 34 species agree within less than 1 kcal mol^{-1}, 5 agree within 1.5 kcal mol^{-1}, and 4 values have deviations near 2.5 kcal mol^{-1}.

2. Enthalpies of Formation ($\Delta_f H^\circ_{298}$). Energies from the B3LYP/6-311G(d,p) level are used with a series of working (isodesmic) reactions having bond conservation to estimate the enthalpy of formation ($\Delta_f H^\circ_{298}$) for the vinyl, allyl, ethynyl, and phenyl peroxides. The total energies are corrected by zero-point vibration energies (ZPVE), which are scaled by 0.97 as recommended by Scott and Radom.[43] Thermal correction, 0−298.15 K, is calculated to estimate $\Delta_f H^\circ_{298}$ at the 298.15 K.[44]

The method of isodesmic reactions utilizes a similarity in the bonding environments for reactant and product sets in a work reaction to effect a cancellation of systematic errors in the ab initio or density functional calculations.[24,44,45,46] The basic requirement of an isodesmic reaction is that the number of each type of bond is conserved in the reaction. In addition to bond balance, we try to use working reactions with group balance for maximum cancellation of error. A number of the work reactions in this study do not conserve group balance, but they do conserve a number of the groups and thus have better cancellation of errors than a conventional isodesmic reaction.

3. Entropy (S°_{f298}), Heat Capacities $C_{p,f298}(T)$, and Hindered Rotation Contribution to Thermodynamic Parameters. Entropies, S°_{f298}, and heat capacities are calculated using the rigid-rotor-harmonic-oscillator approximation based on frequencies and moments of inertia of the optimized B3LYP/6-311G(d,p) structures. The SMCPS code (statistical mechanics for heat capacity and entropy) is used to calculate $H - H_0$, C_p, S, and zero-point vibration energy (ZPVE) of molecular species from the calculated moments of inertia for translation, external rotation, and scaled vibration frequencies and vibration contributions to S°_{f298} and $C_{p,f298}(T)$. Symmetry, number of optical isomers, and unpaired electrons are included.[47]

Potential barriers for internal rotations about the C_d−O, O−O, OO−CH_3, and C_d−C internal rotations for vinyl, allyl, ethynyl, and phenyl peroxides are computed at the B3LYP/6-311G(d,p) calculation level in 15° intervals of the corresponding dihedral starting with the lowest energy conformer; the remaining structure is allowed to optimize at each point. Frequencies calculated by the Gaussian code are examined by viewing the vibration mode movement; the contributions from frequencies corresponding to internal rotations are excluded from the entropy and heat capacity and replaced with a more accurate estimate of S and $C_p(T)$ from the internal rotor contributions.

A technique for the calculation of the thermodynamic functions from hindered rotations with arbitrary potentials is used to calculate hindered internal contributions to S°_{f298} and $C_{p,f298}(T)$.[17,18,48] This technique employs expansion of the hindrance potential in the Fourier series, calculation of the Hamiltonian matrix based on wave functions of a free rotor, and subsequent calculation of the internal rotation energy levels by direct diagonalization of the Hamiltonian matrix. Contributions to entropy and heat capacity from internal rotations are determined from a partition function obtained by integration over these energy levels. The energy level distribution is calculated from the structure of each rotor and the respective intramolecular rotation potential energy. The analysis includes contributions to enthalpy, entropy, and heat capacity as a function of temperature from conformers that result from individual internal rotors and optical isomers (RO−OR) of the peroxide.

A truncated Fourier series is used to represent the torsion potential calculated at the discrete torsion angles.

$$V(\Phi) = a_0 + \sum a_i \cos(i\Phi) + \sum b_i \sin(i\Phi) \qquad \text{(I)}$$

where $i = 1-7$.

The values of the coefficients (a_0, a_i, and a_b) are calculated to provide the minimum and maximum of the torsion potentials with allowance of shift of the theoretical extreme angular positions. A FORTRAN program, Rotator,[48−50] calculates the

TABLE 2: Calculated $\Delta_f H^\circ_{298}$ in kcal mol^{-1} for Peroxides vs Reaction

reactions series	$\Delta_f H^\circ_{298}$	therm[a]
$CH_3OOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_4$	−31.54	
$CH_3OOH + CH_3CH_2OH \rightarrow CH_3CH_2OOH + CH_3OH$	−32.23	
$CH_3OOH + CH_3CH_2OCH_3 \rightarrow CH_3CH_2OOH + CH_3OCH_3$	−32.4	
average	**−31.72 ± 1.02**	−31.8/−30.75[b]
$CH_3CH_2CH_2OOH + CH_3OH \rightarrow CH_3CH_2CH_2OH + CH_3OOH$	−44.15	
$CH_3CH_2CH_2OOH + CH_3CH_3 \rightarrow CH_3CH_2CH_3 + CH_3CH_2OOH$	−44.39	
$CH_3CH_2CH_2OOH + CH_3CH_2OH \rightarrow CH_3CH_2CH_2OH + CH_3CH_2OOH$	−44.58	
average	**−44.37 ± 0.2**	−45.03
$CH_3OO^{\bullet} + CH_3CH_3 \rightarrow CH_3CH_2OO^{\bullet} + CH_4$	1.95	
$CH_3OO^{\bullet} + CH_3CH_2OCH_3 \rightarrow CH_3CH_2OO^{\bullet} + CH_3OCH_3$	2.09	
average	**2.02 ± 0.1**	2.40
$CH_3CH_2OO^{\bullet} + CH_3OH \rightarrow CH_3CH_2OH + CH_3OO^{\bullet}$	−5.87	
$CH_3CH_2OO^{\bullet} + CH_3OOH \rightarrow CH_3CH_2OOH + CH_3OO^{\bullet}$	−6.3	
$CH_3CH_2OO^{\bullet} + CH_3OCH_3 \rightarrow CH_3CH_2OCH_3 + CH_3OO^{\bullet}$	−5.69	
average	**−5.95 ± 0.31**	−5.90
$CH_2^{\bullet}CH_2OOH + CH_3OH \rightarrow CH_3CH_2OOH + CH_2^{\bullet}OH$	11.21	
$CH_2^{\bullet}CH_2OOH + CH_3CH_2OH \rightarrow CH_3CH_2OOH + CH_2^{\bullet}CH_2OH$	11.39	
$CH_2^{\bullet}CH_2OOH + CH_4 \rightarrow CH_2^{\bullet}CH_3 + CH_3OOH$	10.19	
average	**10.93 ± 0.67**	8.90

[a] Values are from group additivity unless noted otherwise. [b] Value from ref 25.

TABLE 3: Calculated $\Delta_f H^\circ_{298}$ (kcal mol^{-1}) for Alkyl Peroxides Used in Reference Reactions and Comparison with Literature

reactions series	$\Delta_f H^\circ_{298}$	error limit[a]	therm[b]
$CH_3CH_2OOCH_3 + CH_4 \rightarrow CH_3CH_3 + CH_3OOCH_3$	−39.29	±0.92	
$CH_3CH_2OOCH_3 + CH_3OOH \rightarrow CH_3CH_2OOH + CH_3OOCH_3$	−39.09	±3.0	
$CH_3CH_2OOCH_3 + CH_3OO^{\bullet} \rightarrow CH_3CH_2OO^{\bullet} + CH_3OOCH_3$	−39.28	±4.29	
$CH_3CH_2OOCH_3 + CH_3O^{\bullet} \rightarrow CH_3CH_2O^{\bullet} + CH_3OOCH_3$	−38.91	±2.12	
$CH_3CH_2OOCH_3 + HOOH \rightarrow CH_3CH_2OOH + CH_3OOH$	−38.71	±3.12	
average	**−39.0 ± 0.24**		−39.3[b]/−37.02[c]
$CH_3OOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OCH_3 + CH_3OOH$	−30.18	±2.45	
$CH_3OOCH_3 + CH_3OH \rightarrow CH_3OOH + CH_3OCH_3$	−30.17	±2.26	
$CH_3OOCH_3 + HOOH \rightarrow CH_3OOH + CH_3OOH$	−30.62	±3.03	
$CH_3OOCH_3 + CH_3CH_2O^{\bullet} \rightarrow CH_3OO^{\bullet} + CH_3CH_2OCH_3$	−30.98	±2.90	
$CH_3OOCH_3 + CH_3O^{\bullet} \rightarrow CH_3OO^{\bullet} + CH_3OCH_3$	−31.90	±3.47	
$CH_3OOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OOH + CH_3OCH_3$	−30.79	±2.82	
average	**−30.77 ± 0.64**		−31[b]/−31[d]/−29.17[c]

[a] Reported errors for each of the standard species (when available), and 0.11 estimate in thermal energy for each species in the work reaction (four species, 0.44 total[43]). [b] Values are from group additivity unless noted otherwise. [c] Value from ref 25. [d] Value from ref 42.

reduced mass of the internal rotor from the Gaussian structure, the energy levels, and the partition coefficient from the energy levels.

Lay et al.[48] have shown that inclusion of internal rotor contributions can affect entropy values by 1 cal mol^{-1} K^{-1} per rotor or more. Van Speybroeck et al.[51] have shown differences in kinetic preexponential factors up to 1 order of magnitude between use of torsion frequency versus more accurate internal rotor contribution. In a further, higher level study, Van Speybroeck et al.[52] have performed coupled internal rotor analysis, and their data show that it compared reasonable well with an uncoupled internal rotor analysis, similar to that used in this study.

Results and Discussion

1. Geometries and Vibration Frequencies. Optimized geometries and vibration frequencies at the density functional B3LYP/6-311G(d,p) calculation level for the vinyl, allyl, and ethynyl peroxides and for phenyl peroxide are listed in Table SM 1 and 2 of the Supporting Information. The C_d−OO and O−O bond distances in vinyl, ethynyl, and phenyl hydroperoxides are listed and discussed in an early study[3] and have values and trends similar to these peroxides.

2. Enthalpies of Formation, $\Delta_f H^\circ_{298}$. For each species, four to six isodesmic reactions are used to determine $\Delta_f H^\circ_{298}$ of the target vinyl peroxides: $CH_2{=}CHOOCH_3$, *trans*-$CH_3CH{=}CHOOCH_3$, *cis*-$CH_3CH{=}CHOOCH_3$, $CH_3(CH_3)C{=}CHOOCH_3$, $CH_2{=}C(CH_3)OOCH_3$ and $CH_3CH{=}C(CH_3)OOCH_3$, phenyl peroxide ($C_6H_5OOCH_3$), allyl peroxide ($CH_2{=}CHCH_2OOCH_3$), and ethynyl peroxide ($CH{\equiv}COOCH_3$, $CH_3{-}C{\equiv}COOCH_3$).

$\Delta_f H^\circ_{298}$ values of the target peroxides are estimated using isodesmic reaction schemes, calculated $\Delta H^\circ_{rxn,298}$ for each reaction, and evaluated literature thermodynamic properties for the reference species in the reactions.

The enthalpies of reactions ($\Delta H^\circ_{rxn,298}$) are estimated using total energies obtained by the density functional calculations with zero-point energies (ZPVE) and thermal corrections to 298.15 K taken into account.

Reference Alkyl Peroxide Species. Examination of the isodesmic reactions used to determine $\Delta_f H^\circ_{298}$ on the target peroxides illustrates that accurate enthalpy on $CH_3CH_2OOCH_3$ is needed for use as reference species. The isodesmic reactions used to determine the enthalpy of $CH_3CH_2OOCH_3$ are listed in Table 3, and our recommended value is −39 kcal mol^{-1}; the values estimated with group additivity (−39.3) are also in good agreement. A value of −37.0 kcal mol^{-1} is reported in ref 25.

CH_3OOCH_3 was also calculated with isodesmic reactions (see Table 3). The enthalpy determined for CH_3OOCH_3 is −30.77 kcal mol^{-1}. Lay and Bozzelli[42] and Carballeira et al.[53] reported −31.0 kcal mol^{-1}. The value obtained with group additivity using the O/C/O group developed by Lay and Bozzelli is −31 kcal mol^{-1} as well. In a recent study, Sumathi and Green[25] have

TABLE 4: Enthalpies of Formation for Stable Species Used in Work Reactions

species	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	source
CH_4	-17.89 ± 0.07	ref 59
CH_3CH_3	-20.24 ± 0.12	ref 57
$CH_2{=}CH_2$	12.55 ± 0.1	ref 57
$CH_3CH{=}CH_2$	4.71 ± 0.16	ref 65
$CH_3(CH_3)C{=}CH_2$	-4.29 ± 0.26	ref 63
$HC{\equiv}CH$	54.19 ± 0.19	ref 59
$HC{\equiv}COH$	20.22^a	ref 3
$HC{\equiv}COOH$	42.25 ± 0.13	ref 3
$HC{\equiv}COCH_3$	26.08^a	ref 3
$CH_3C{\equiv}CH$	44.32 ± 0.21	ref 67
$CH_3C{\equiv}COH$	9.84^a	ref 3
$CH_3C{\equiv}COOH$	30.26 ± 0.13	ref 3
$CH_3C{\equiv}COCH_3$	15.93^a	ref 3
C_6H_6	19.81 ± 0.13	ref 64
CH_3CH_2OOH	-39.9 ± 1.5	ref 24
CH_3OOH	-31.8 ± 0.94	ref 18
CH_3OH	-48.08 ± 0.05	ref 57
CH_3CH_2OH	-56.12 ± 0.2	ref 57
CH_3OCH_3	-43.99 ± 0.12	ref 60
CH_3OOCH_3	-31^a	ref 42
$CH_3CH_2OCH_3$	-51.73 ± 0.16	ref 61
$CH_2{=}CHOCH_3$	$-24.54/-23.48$	therm/ref 72
$CH_2{=}CHOOH$	-9.63 ± 0.08	ref 3
$CH_2{=}CHCH_2OH$	-29.55 ± 0.35	ref 66
$CH_2{=}CHCH_2OOH$	-13.59 ± 0.14	ref 3
$CH_2{=}CHCH_2OCH_3$	-25.68^a	ref 3
$CH_2{=}C(CH_3)OH$	$-42.06/-42.1^a$	ref 3/ref 58
$CH_2{=}C(CH_3)OCH_3$	-32.55^a	ref 3
$CH_2{=}C(CH_3)OOH$	-21.80 ± 0.06	ref 3
Syn-$CH_2{=}CHOH$	-30.59 ± 0.55	ref 58
cis-$CH_3CH{=}CHOH$	$-38.84/-41.6^a$	ref 3/ref 62
cis-$CH_3CH{=}CHOOH$	21.66 ± 0.07	ref 3
cis-$CH_3CH{=}CHOCH_3$	-36.24^a	ref 3
trans-$CH_3CH{=}CHOH$	$-38.85/-40.4^a$	ref 3/ref 62
trans-$CH_3CH{=}CHOOH$	-20.44 ± 0.08	ref 3
trans-$CH_3CH{=}CHOCH_3$	-34.33^a	ref 3
trans-$CH_3CH{=}C(CH_3)OH$	$-47.65/-50.7^a$	ref 3/ref 69
$CH_3(CH_3)C{=}CHOH$	-49.31^a	ref 3
$CH_3(CH_3)C{=}CHOCH_3$	-43.72^a	ref 3
$CH_3(CH_3)C{=}COOH$	-30.79 ± 0.06	ref 3
$CH_3CH{=}C(CH_3)OH$	-51.1^a	ref 74
$CH_3CH{=}C(CH_3)OOH$	-30.03 ± 0.23	ref 3
C_6H_5OH	-24.06 ± 0.28	ref 3
C_6H_5OOH	-2.68 ± 0.49	ref 3
$C_6H_5OCH_3$	-17.27 ± 0.93	ref 60
$HOOH$	-32.53^a	ref 59

[a] Error not provided.

TABLE 5: Enthalpy of Formation for Radicals Used in Work Reactions

species	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	source^a
$CH_3^{\bullet}$	34.82 ± 0.2	ref 70
$CH_3O^{\bullet}$	4.10 ± 1.0	ref 71
$C_2H_5O^{\bullet}$	$-2.03 \pm 0.39/-3.90 \pm 1.27$	ref 3/ref 72
$CH_3OO^{\bullet}$	2.15 ± 1.22	ref 7
$C_2H_5OO^{\bullet}$	-6.5 ± 2.36	ref 71
$CH_2{=}CHOO^{\bullet}$	$24.45 \pm 1.15/24.34 \pm 0.42$	ref 35/ref 3
$CH_2{=}CHCH_2OO^{\bullet}$	21.15	ref 71
trans-$CH_3{-}CH{=}CHOO^{\bullet}$	13.38 ± 0.88	ref 3
cis-$CH_3{-}CH{=}CHOO^{\bullet}$	12.73 ± 1.49	ref 3
$CH_3(CH_3)C{=}CHOO^{\bullet}$	2.12 ± 0.35	ref 3
$CH_2{=}C(CH_3)OO^{\bullet}$	10.91 ± 0.34	ref 3
$CH_3CH{=}C(CH_3)OO^{\bullet}$	4.15 ± 1.39	ref 3
$CH{\equiv}COO^{\bullet}$	84.11 ± 0.36	ref 3
$CH_3C{\equiv}COO^{\bullet}$	70.70 ± 0.35	ref 3
$C_6H_5OO^{\bullet}$	31.28 ± 0.48	ref 7
$H^{\bullet}$	52.10 ± 0.001	ref 59
$HO^{\bullet}$	8.96 ± 0.09	ref 68
$HOO^{\bullet}$	3.25 ± 0.5	ref 73
$CH_2{=}CHO^{\bullet}$	4.44 ± 0.31	ref 3
$CH_2{=}CHCH_2O^{\bullet}$	23.48 ± 0.31	ref 3
trans-$CH_3{-}CH{=}CHO^{\bullet}$	-8.17 ± 0.31	ref 3
cis-$CH_3{-}CH{=}CHO^{\bullet}$	-8.90 ± 0.31	ref 3
$CH_3(CH_3)C{=}CHO^{\bullet}$	-23.12 ± 0.31	ref 3
$CH_2{=}C(CH_3)O^{\bullet}$	-9.61 ± 0.31	ref 3
$CH_3CH{=}C(CH_3)O^{\bullet}$	-18.92 ± 0.31	ref 3
$CH{\equiv}CO^{\bullet}$	40.40 ± 0.31	ref 3
$CH_3C{\equiv}CO^{\bullet}$	29.13 ± 0.32	ref 3
$C_6H_5O^{\bullet}$	$12.94 \pm 0.56/$	ref 3
$CH_2{=}CH^{\bullet}$	71.71 ± 0.4	ref 3
$CH_2{=}CHCH_2^{\bullet}$	39.13 ± 0.13	ref 3
trans-$CH_3{-}CH{=}CH^{\bullet}$	64.3 ± 0.12	ref 3
cis-$CH_3{-}CH{=}CH^{\bullet}$	63.66 ± 0.12	ref 3
$CH_3(CH_3)C{=}CH^{\bullet}$	53.92 ± 0.13	ref 3
$CH_2{=}C(CH_3)^{\bullet}$	58.89 ± 0.12	ref 3
$CH_3CH{=}C(CH_3)^{\bullet}$	53.64 ± 0.13	ref 3
$CH{\equiv}C^{\bullet}$	$133 \pm 2.0/135.6 \pm 0.2$	ref 71/ref 85
$CH_3C{\equiv}C^{\bullet}$	128.59 ± 0.13	ref 3
$C_6H_5^{\bullet}$	$81.4 \pm 0.16/81 \pm 2.0$	ref 3/ref 71

[a] The first reference of the pair is used in this study.

developed groups for alcohols, O/C/H, and for hydro and alkyl peroxides, O/H/O and O/C/O, using enthalpy values from CBS-Q calculations with heats of atomization and multivariate linear regression. The use of the two groups from Sumanthi and Green for the calculations of enthalpy values on species in this study consistently results in differences (higher values) in $\Delta_f H^\circ_{298}$ of about 1 kcal mol^{-1} relative to data in this work. The GA values of Sumathi and Green[25] result in enthalpy for CH_3OOCH_3 of -29.1 kcal mol^{-1}. We discussed this difference above (Accuracy of Density Functional Theory for Estimation of Peroxides section) and select values in this study from the combined accuracy of our hydroperoxide and peroxide values previously discussed and listed in Table 1.

Literature enthalpy values for standard reference species in the isodesmic work reactions are listed in Tables 4 and 5.

Enthalpy of Formation Data. $\Delta_f H^\circ_{298}$ of each peroxides is obtained from each of the isodesmic reactions illustrated in Table 6 with the arithmetic mean over the work reactions for the species reported as the enthalpy of formation, $\Delta_f H^\circ_{298}$, in kcal mol^{-1}. The $\Delta_f H^\circ_{298}$ values for many species show good precision through the different work reactions. This is partially attributed to our choice of working reactions and the corresponding error cancellation. The low errors shown in Table 6 for the working reaction sets demonstrates internal consistency and precision in the standard species enthalpy values but only suggests reasonable absolute accuracy. $\Delta_f H^\circ_{298}$ of each peroxide was also estimated by use of the group additivity. The values determined with GA (Table 6) are in good agreement with the DFT values.

The overall accuracy on an absolute scale is more difficult to assess. It is controlled by (i) the choice of the working chemical reactions used to cancel calculation errors, (ii) accuracy of standard or reference species $H_f(298)$ values, (iii) the level of sophistication (method and basis set) applied to calculate the electronic energy, and (iv) the uncertainty of the ZPVE and thermal corrections. Error limits are assigned as the sum of the following error bounds: standard deviation of the three working reactions, reported errors for each of the standard species, and 0.11 estimates in thermal energy for each species in the work reaction (four species, 0.44 total).[43]

3. Bond Energies. Bond energies for the $C_d{-}OOC$, $C_dO{-}OC$, and $C_dOO{-}C$ bonds are reported and compared with previously determined $C_d{-}OOH$, $C_dO{-}OH$, and $C_dOO{-}H$ bond energies,[3] as well as with dimethyl peroxide, methyl hydroperoxide, ethyl methylperoxide, and ethyl hydroperoxide.

The bond energies require knowledge of the enthalpy of formation of the two radicals formed by the bond cleavage reaction. Values for these radical are listed in Table 5, along

TABLE 6: Calculated $\Delta_f H^\circ_{298}$ for Vinyl and Ethynyl Peroxides vs Reaction[a]

reactions series	$\Delta_f H^\circ_{298}$	error limits[b]	therm
$CH_2{=}CHOOCH_3 + CH_3OH \rightarrow CH_3OOCH_3 + CH_2{=}CHOH$	−9.56	±1.70	
$CH_2{=}CHOOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OOCH_3 + CH_2{=}CHOH$	−10.08	±2.14	
$CH_2{=}CHOOCH_3 + CH_3OOH \rightarrow CH_3OOCH_3 + CH_2{=}CHOOH$	−9.60	±2.12	
$CH_2{=}CHOOCH_3 + CH_3CH_3 \rightarrow CH_3CH_2OOCH_3 + CH_2{=}CH_2$	−11.17	±1.61	
$CH_2{=}CHOOCH_3 + CH_3OO^\bullet \rightarrow CH_3OOCH_3 + CH_2{=}CHOO^\bullet$	−9.83	±3.45	
average	**−10.04 ± 0.66**		−11.91
$trans\text{-}CH_3CH{=}CHOOCH_3 + CH_3OH \rightarrow CH_3OOCH_3 + trans\text{-}CH_3CH{=}CHOH$	−19.87	±1.16	
$trans\text{-}CH_3CH{=}CHOOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OOCH_3 + trans\text{-}CH_3CH{=}CHOH$	−20.39	±1.6	
$trans\text{-}CH_3CH{=}CHOOCH_3 + CH_3OCH_3 \rightarrow CH_3OOCH_3 + trans\text{-}CH_3CH{=}CHOCH_3$	−20.67	±1.23	
$trans\text{-}CH_3CH{=}CHOOCH_3 + CH_3CH_3 \rightarrow CH_3CH_2OOCH_3 + CH_3CH{=}CH_2$	−18.91	±1.68	
$trans\text{-}CH_3CH{=}CHOOCH_3 + CH_3OOH \rightarrow CH_3OOCH_3 + trans\text{-}CH_3CH{=}CHOOH$	−19.91	±2.13	
average	**−19.95 ± 0.67**		−19.78
$cis\text{-}CH_3CH{=}CHOOCH_3 + CH_3OH \rightarrow CH_3OOCH_3 + cis\text{-}CH_3CH{=}CHOH$	−21.14	±0.96	
$cis\text{-}CH_3CH{=}CHOOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OOCH_3 + cis\text{-}CH_3CH{=}CHOH$	−21.66	±1.40	
$cis\text{-}CH_3CH{=}CHOOCH_3 + CH_3OCH_3 \rightarrow CH_3OOCH_3 + cis\text{-}CH_3CH{=}CHOCH_3$	−22.13	±1.04	
$cis\text{-}CH_3CH{=}CHOOCH_3 + CH_3OOH \rightarrow CH_3OOCH_3 + cis\text{-}CH_3CH{=}CHOOH$	−21.16	±1.92	
average	**−21.27** ± 0.47		−21[c]
$CH_3(CH_3)C{=}CHOOCH_3 + CH_3OH \rightarrow CH_3OOCH_3 + CH_3(CH_3)C{=}CHOH$	−30.22	±1.39	
$CH_3(CH_3)C{=}CHOOCH_3 + CH_3OCH_3 \rightarrow CH_3OOCH_3 + CH_3(CH_3)C{=}CHOCH_3$	−31.94	±1.46	
$CH_3(CH_3)C{=}CHOOCH_3 + CH_3CH_3 \rightarrow CH_3CH_2OOCH_3 + CH_3(CH_3)C{=}CH_2$	−29.97	±2.01	
$CH_3(CH_3)C{=}CHOOCH_3 + CH_3OOH \rightarrow CH_3OOCH_3 + CH_3(CH_3)C{=}CHOOH$	−30.28	±2.34	
average	**−30.60 ± 0.90**		−28.23
$CH_3CH{=}C(CH_3)OOCH_3 + CH_3OH \rightarrow CH_3OOCH_3 + CH_3CH{=}C(CH_3)OH$	−29.49	±0.81	
$CH_3CH{=}C(CH_3)OOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OOCH_3 + CH_3CH{=}C(CH_3)OH$	−30.02	±1.25	
$CH_3CH{=}C(CH_3)OOCH_3 + CH_3OOH \rightarrow CH_3OOCH_3 + CH_3CH{=}C(CH_3)OOH$	−29.25	±1.93	
$CH_3CH{=}C(CH_3)OOCH_3 + CH_3CH_2OOH \rightarrow CH_3CH_2OOCH_3 + CH_3CH{=}C(CH_3)OOH$	−29.19	±1.81	
average	**−29.58 ± 0.32**		−30.38
$CH_2{=}C(CH_3)OOCH_3 + CH_3OH \rightarrow CH_3OOCH_3 + CH_2{=}C(CH_3)OH$	−20.99	±0.91	
$CH_2{=}C(CH_3)OOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OOCH_3 + CH_2{=}C(CH_3)OH$	−21.52	±1.35	
$CH_2{=}C(CH_3)OOCH_3 + CH_3OCH_3 \rightarrow CH_3OOCH_3 + CH_2{=}C(CH_3)OCH3$	−20.37	±0.98	
$CH_2{=}C(CH_3)OOCH_3 + CH_3CH_3 \rightarrow CH_3CH_2OOCH_3 + CH_2{=}CHCH_3$	−20.69	±1.43	
$CH_2{=}C(CH_3)OOCH_3 + CH_3OOH \rightarrow CH_3OOCH_3 + CH_2{=}C(CH_3)OOH$	−21.04	±1.86	
average	**−20.79 ± 0.42**		−22.51
$C_6H_5OOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OOCH_3 + C_6H_5OH$	−1.52	±1.70	
$C_6H_5OOCH_3 + CH_3OCH_3 \rightarrow CH_3OOCH_3 + C_6H_5OCH_3$	−2.38	±1.98	
$C_6H_5OOCH_3 + CH_3CH_3 \rightarrow CH_3CH_2OOCH_3 + C_6H_6$	−2.97	±1.47	
$C_6H_5OOCH_3 + CH_3CH_2OOH \rightarrow CH_3CH_2OOCH_3 + C_6H_5OOH$	−1.88	±3.04	
$C_6H_5OOCH_3 + CH_2{=}CH_2 \rightarrow CH_2{=}CHOOCH_3 + C_6H_6$	−2.51	±1.82	
$C_6H_5OOCH_3 + CH_3OOH \rightarrow CH_3OOCH_3 + C_6H_5OOH$	−1.93	±2.36	
average	**−2.19 ± 0.52**		−1.88
$CH_2{=}CHCH_2OOCH_3 + CH_3OH \rightarrow CH_3OOCH_3 + CH_2{=}CHCH_2OH$	−10.70	±1.89	
$CH_2{=}CHCH_2OOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OOCH_3 + CH_2{=}CHCH_2OH$	−11.23	±2.33	
$CH_2{=}CHCH_2OOCH_3 + CH_3OCH_3 \rightarrow CH_3OOCH_3 + CH_2{=}CHCH_2OCH3$	−12.67	±1.61	
$CH_2{=}CHCH_2OOCH_3 + CH_3CH_3 \rightarrow CH_3CH_2OOCH3 + CH_2{=}CHCH_3$	−13.11	±2.06	
$CH_2{=}CHCH_2OOCH_3 + CH_3OOH \rightarrow CH_3OOCH_3 + CH_2{=}CHCH_2OOH$	−12.73	±2.57	
average	**−12.08 ± 1.05**		−12.91
$CH{\equiv}COOCH_3 + CH_3OH \rightarrow CH_3OOCH_3 + CH{\equiv}C{-}OH$	41.89	±1.19	
$CH{\equiv}COOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OOCH_3 + CH{\equiv}CHOH$	41.37	±1.63	
$CH{\equiv}COOCH_3 + CH_3CH_3 \rightarrow CH_3CH_2OOCH_3 + HC{\equiv}CH$	40.06	±1.74	
$CH{\equiv}COOCH_3 + CH_3OOH \rightarrow CH_3OOCH_3 + CH{\equiv}COOH$	41.6	±2.21	
$CH{\equiv}COOCH_3 + CH_3CH_2OOH \rightarrow CH_3CH_2OOCH_3 + CH{\equiv}CHOOH$	41.66	±2.89	
average	**41.31 ± 0.72**		41.45
$CH_3C{\equiv}COOCH_3 + CH_3OH \rightarrow CH_3OOCH_3 + CH_3\text{-}C{\equiv}COH$	29.78	±0.76	
$CH_3C{\equiv}COOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OOCH_3 + CH_3{-}C{\equiv}COH$	29.26	±1.20	
$CH_3C{\equiv}COOCH_3 + CH_3CH_3 \rightarrow CH_3CH_2OOCH_3 + CH_3{-}C{\equiv}CH$	29.31	±1.33	
$CH_3C{\equiv}COOCH_3 + CH_3OOH \rightarrow CH_3OOH + CH_3{-}C{\equiv}COOH$	29.72	±1.78	
average	**29.51 ± 0.27**		31.87

[a] Units of kcal mol^{-1}. [b] Reported errors for each of the standard species (when available), and 0.11 estimate in thermal energy for each species in the work reaction (four species, 0.44 total[43]). [c] Corrected with −1.22 for the cis correction (see text).

with literature references. Literature values have been used whenever possible, but when no literature data were available, calculations were performed to determine enthalpies of the radicals. These $C_d{-}OOC$, $C_dO{-}OC$, and $C_dOO{-}C$ bond energy results are listed in Table 7, along with our estimated error limits. The data show good consistency in the calculated bond energies through a given class of radical and the agreement with literature values when available is also good.

3.1. Discussion on Bond Energies. Methyl Vinyl Peroxides: Effect of Methyl Substitution on Bond Energies. C_d represents C_{vinyl} of the vinyl peroxides that we have studied. Methyl vinyl peroxide, $C{=}COOC$, has the highest $C_dOO{-}C$ bond energy, 69.2 kcal mol^{-1}. Methyl group substitution for a hydrogen atom on either carbon of the vinyl group reduces the $C_dOO{-}C$ bond energies by up to 2.7 kcal mol^{-1}. The $C_dOO{-}C$ bonds in this category remain near constant with small increases from

TABLE 7: Comparison of ROO−H vs ROO−C, RO−OH vs RO−OC, and R−OOH vs R−OOC Bond Energies (298 K; Units, kcal mol^{-1})

species[a]	ROO−H[b]	error limit[c]	ROO−C	error limit[c]	RO−OH[b]	error limit[c]	RO−OC	error limit[c]	R−OOH[b]	error limit[c]	R−OOC	error limit[c]
C═COOX	86.07	±1.23	69.2	±1.28	23.03	±0.30	18.58	±1.97	84.60	±0.63	83.91	±2.01
trans-CC═COOX	85.92	±0.96	68.15	±1.75	21.23	±0.48	15.88	±1.98	87.99	±0.70	86.4	±2.01
cis-CC═COOX	86.49	±1.56	68.82	±2.16	21.72	±0.47	16.47	±1.78	88.57	±0.69	87.08	±1.81
C(C)C═COOX	85.01	±0.41	67.45	±1.45	16.63	±0.46	11.58	±2.21	87.96	±0.69	86.67	±2.25
C═C(C)OOX	84.81	±0.40	66.52	±0.96	21.15	±0.46	15.28	±1.73	83.94	±0.68	81.83	±1.76
CC═C(C)OOX	85.52	±1.29	68.55	±1.91	19.31	±0.63	14.76	±1.63	86.16	±0.86	85.37	±1.67
PhOOX	86.06	±0.97	68.36	±1.17	24.58	±1.14	19.3	±2.05	87.33	±1.15	85.81	±1.9
C≡COOX	93.96	±0.49	77.70	±1.26	7.11	±0.53	3.27	±2.01	94	±0.89	93.92	±3.49
CC≡COOX	92.54	±0.48	76.01	±0.82	7.83	±0.54	3.72	±1.58	101.58	±0.76	101.23	±2.07
C═CCOOX	86.3	±1.22	68.05	±1.25	46.03	±0.54	39.66	±2.36	55.97	±0.77	53.36	±2.4

[a] X = H or CH_3. [b] From ref 3. [c] Sum of standard deviation of in bond dissociation reactions.

C═C(C)OO−C (66.5 kcal mol^{-1}) to C(C)C═COO−C (67.4 kcal mol^{-1}) and CC═C(C)OO−C (68.5 kcal mol^{-1}). *trans*-CC═COO−C and *cis*-CC═COO−C have near identical but slightly higher C_{vinyl}OO−C bond energies: 68.1 and 68.8 kcal mol^{-1}, respectively.

The C_dO−OC bond energy in these unsaturated peroxides is very weak; this results in unstable molecules with lifetimes of less than a second at room temperature. The C_dO−OC bond energy ranges from 11.6 to 18.6 kcal mol^{-1}, and the trends indicate that single methyl substitution on the vinyl carbon decreases the C_dO−OC bond by up to 4 kcal mol^{-1}. The simplest methyl vinyl peroxide C═CO−OC has the highest bond strength at 18.58 kcal mol^{-1}. The bond energy decreases with increasing methyl substitution on the vinyl carbons: the *cis*-CC═CO−OC bond is 16.47 kcal mol^{-1}, slightly higher than *trans*-CC═CO−OC, 15.88 kcal mol^{-1}; C═C(C)O−OC is 15.28 kcal mol^{-1} and CC═C(C)O−OC is 14.76 kcal mol^{-1}. Substitution of two methyl groups for two primary olefin hydrogen atoms results in the weakest C_dO−OC bond determined for C(C)C═COOC at only 11.6 kcal mol^{-1}.

The C═C−OOC bonds are similar in bond strength and range from 84 to 87 kcal mol^{-1}.

Methyl Phenyl Peroxide: $PhOOCH_3$. The PhOO−C bond for the phenyl peroxide is 68.4 kcal mol^{-1}, 1 kcal mol^{-1} lower than the C═COO−C bond in methyl vinyl peroxide, 69.2 kcal mol^{-1}. The PhO−OC bond is also very weak, 19.3 kcal mol^{-1}, only 0.7 kcal mol^{-1} stronger than vinyl peroxide C═COO−C, 18.6 kcal mol^{-1}. The phenyl−OOC bond strength is similar to that on the vinyl peroxides, ∼85 kcal mol^{-1}

Methyl Propenyl (Allyl) Peroxide: $C{=}CCOOCH_3$. The C═CCOO−C bond in allyl methyl peroxide is 68.0 kcal mol^{-1}, similar to the phenyl and the vinyl peroxides above. The C═CCO−OC bond is 39.66 kcal mol^{-1}, about 2 times stronger than the vinyl and phenyl peroxides but similar to the RO−OR bond dimethyl or ethyl methyl (alkyl) peroxides.

Methyl Ethynyl Peroxides: $C{\equiv}COOCH_3$ and $CC{\equiv}COOCH_3$. The C_tOO−C bond strength in ethynyl peroxide is 77.7 kcal mol^{-1}, and in CC═COO−H, it is 76 kcal mol^{-1}, an increase of about 9 kcal mol^{-1} relative to the phenyl and vinyl peroxides. This is similar to differences in bond energies in the corresponding hydroperoxides.

The C≡CO−OC and CC≡CO−OC bond energies in ethynyl peroxides are effectively nonexistent at 3.27 and 3.72 kcal mol^{-1}, respectively; the ethynyl peroxide moiety is unstable. The $HC{\equiv}COOCH_3$ and $CH_3C{\equiv}COOCH_3$ molecules will immediately dissociate to form a ketenyl radical ($C^{\bullet}H{=}C{=}O$ or $CC^{\bullet}{=}C{=}O$ and CH_3O) with bond energies less than 4 kcal mol^{-1}. This instability is similar in the ethynyl hydroperoxide molecules.

TABLE 8: ROO−X[a] and RO−OX Bond Energies (298 K; Units, kcal mol^{-1})

	ROO−H	ROO−C	bond differ[b]	RO−OH	RO−OC	bond differ[c]
HOOX	87.89	69.87	18.02	50.45	44.86	5.59
COOX	86.05	67.97	18.08	44.86	39.2	5.66

[a] X= H or CH_3. [b] Bond difference between O−H and O−C. [c] Bond difference between O−OH and O−OC.

$$HC{\equiv}COOCH_3 \equiv HC{\equiv}CO^{\bullet} + {}^{\bullet}OCH_3 \equiv HC^{\bullet}{=}C{=}O + {}^{\bullet}OCH_3, \quad \Delta H^{\circ}_{rxn,298} = 3.27\ \text{kcal mol}^{-1}$$

$$CH_3C{\equiv}COOCH_3 \equiv CH_3C{\equiv}CO^{\bullet} + {}^{\bullet}OCH_3 \equiv CH_3C^{\bullet}{=}C{=}O + {}^{\bullet}OCH_3, \quad \Delta H^{\circ}_{rxn,298} = 3.72\ \text{kcal mol}^{-1}$$

This low bond strength can be explained by the facile formation of a strong carbonyl bond (ketenyl group) at the expense of cleavage of the weaker (second) Π bond in the ethyne and the ketenyl Π system: $RC{\equiv}COOC \rightarrow RC^{\bullet}{=}C{=}O + {}^{\bullet}OC$.

The ethyne peroxides, CC≡COOC and CCC≡COOC, have RC≡C−OOC bond energies of 94.0 and 100.0 kcal mol^{-1}, respectively, showing a significant difference resulting from the methyl substitution on the primary ethyne carbon. The increase in strength of this bond in these quasi-molecules results from the overlap of the Π electrons on the oxygen with the ethyne Π bonds.

3.2 Comparison of Bond Energies in Hydroperoxides versus Peroxides. Tables 7 and 8 list the RC−OOX, RCO−OX, and RCOO−X (X = CH_3 or H) bond energies for the different peroxides. The C_dOO−C energies for all species listed in Table 7 are lower than the corresponding C_dOO−H bond strengths by ca. 17 kcal mol^{-1}. This is consistent with data for alcohols where carbon−oxygen single bonds are typically ∼13.5 kcal mol^{-1} lower than hydrogen−oxygen bonds.

The bond energy in C_dO−OC is about 5 kcal mol^{-1} weaker than the bond in C_dO−OH, for all peroxides reported in Table 7. This result is consistent with the shorter bond length in the C_dO−OH series versus the C_dO−OC bond lengths. The C_dO−OC bond lengths are listed in Table 9 for comparison of the bond distance with bond energies. Table 9 shows that C_dO−OC bonds are slightly longer than C_dO−OH bonds and, therefore, weaker. These results are in agreement with the HO−OH/HO−OCH_3 and CH_3O−OH/CH_3O−OCH_3 systems. In both cases, the substitution of H by a methyl results in a longer bond and weaker bond energy. The HO−OCH_3 bond is 5.6 kcal mol^{-1}

weaker than the HO−OH bond, and the CH_3O-OCH_3 bond is 5.66 kcal mol^{-1} weaker than CH_3O-OH (Table 8).

The C_d-OOC versus C_d-OOH bond energies show almost no variation in the corresponding vinyl, phenyl, and ethynyl species. Differences between C_d-OOC and C_d-OOH bond energy in vinyl species values vary from 0.7 to 1.5 kcal mol^{-1}. This difference increases slightly, when we consider the allyl hydroperoxide and peroxide, 2.6 kcal mol^{-1}.

The ethynyl species do not exhibit any difference in bond energy between C_t-OOC and C_t-OOH, BE = 94 kcal mol^{-1} for CH≡COOH and 101 kcal mol^{-1} for $CH_3C{\equiv}COOC$. The CH_3-OOH/CH_3-OOCH_3 system shows a bond strength difference of 1.9 kcal mol^{-1} (from Table 8).

4. Chain Branching via Cleavage of the Weak Vinyl and Ethynyl Peroxide Bonds. As discussed in a previous study,[3] the RCO−OH bonds are very weak in the vinyl, phenyl, and ethynyl hydroperoxides. The C═CO−OC bonds are slightly weaker (ca. 1−4 kcal mol^{-1}) in the peroxides of this study relative to the hydroperoxides. The peroxide dissociation energies range from 19.3 to 3.2 kcal mol^{-1}, and these species are unstable to simple dissociation:

$$RC{=}CO{-}OC \rightarrow RC{=}CO^{\bullet} + {}^{\bullet}OC \rightarrow RC^{\bullet}C{=}O + {}^{\bullet}OC$$

Reasons for this low bond strength involve the formation of the strong carbonyl bond relative to loss of a weaker Π bond and the overlap of the Π system.

A chain branching process can result from addition reactions of an alkyl peroxy radical to olefins or acetylenes, where vinyl, phenyl, or acetyl peroxides are formed. The initial radical formed by the addition of the peroxy radical would undergo an addition reaction with molecular oxygen, then undergo molecular elimination of HO_2 to form an unsaturated peroxide. The unsaturated peroxide would then undergo rapid cleavage of the weak peroxide bonds. A mechanism that implements this chain branching results from ROO$^{\bullet}$ addition to olefins is illustrated by

$$CH_3OO^{\bullet} + RC{=}C \rightarrow RC^{\bullet}COOC \qquad \text{addition/stabilization}$$

$$RC^{\bullet}OOC + O_2 \rightarrow RC(OO^{\bullet})COOC \qquad (O_2 \text{ addition})$$

$$RC(OO^{\bullet})COOC \rightarrow HO_2 + RC{=}COOC$$

(HO$_2$ molecular elimination)

$$RC{=}COOC \rightarrow RCO^{\bullet} + {}^{\bullet}OC$$

(cleavage of weak vinyl peroxide bond, chain branching, plus two subsequent, facile eliminations to form carbonyls)

5. Internal Rotation Barriers. Potential barriers versus torsion angle for internal rotation are calculated at the B3LYP/6-31G(d,p) level in the following peroxides: $CH_2{=}CHOOCH_3$, *trans*-$CH_3CH{=}CHOOCH_3$, *cis*-$CH_3CH{=}COOCH_3$, $CH_3(CH_3)C{=}CHOOCH_3$, $CH_3CH{=}C(CH_3)OOCH_3$, $CH_2{=}C(CH_3)OOCH_3$, $CH_2{=}CHCH_2OOCH_3$ and $C_6H_5OOCH_3$. Entropy and heat capacity contributions from the internal rotors in these peroxides are estimated using these potentials, the calculated molecule structure, and methods described in the computation section.

The potential energy as function of dihedral angle is determined by scanning individual torsion angles from 0° to 360° at 15° intervals and allowing the remaining molecular structural parameters to be optimized. Potential energy curves for the C_dOO-C, C_dO-OC, C_d-OOC, and C_d-C rotors are illustrated in Figures 2−9, where points are calculated values and lines are the Fourier expansion fit. Values for the coefficients of the Fourier expansion, a_i and b_i in eq I, are obtained from the fitting program in Sigma Plot, version 2.0, and then used in "Rotator" to calculate the contribution of internal rotors to S°_{298} and $C_p{}^{\circ}(T)$ (0.1 ≤ T ≤ 5000 K). The Rotator program takes into account the entropy of mixing and optical isomer corrections.

TABLE 9: RO−OH and RO−OC Bond Lengths in Å

species[a]	O−OH[b]	O−OC
C═COOX	1.460	1.453
trans-CC═COOX	1.470	1.477
cis-CC═COOX	1.467	1.474
C(C)C═COOX	1.477	1.485
C═C(C)OOX	1.470	1.478
CC═C(C)OOX	1.479	1.488
C≡COOX	1.502	1.533
CC≡COOX	1.513	1.544
PhOOX	1.443	1.452
C═CCOOX	1.454	1.464
HOOX	1.453	1.455
COOX	1.455	1.465

[a] X = H or CH_3. [b] From ref 3.

TABLE 10: Comparison of Maximal Rotational Barriers of ROOH versus ROOC (298 K; Units, kcal mol^{-1})

	C_d-OO	O−O	$C-C_d$	$C(-C)C_d/C_d(-C)O$	OO−C
C═COOC	5.57	9.75			2.97
C═COOH[a]	6.22	5.76			
trans-CC═COOC	3.58	8.90	2.09		2.77
trans-CC═COOH[a]	4.33	5.59	2.04		
cis-CC═COOC	3.65	8.91	1.44		2.80
cis-CC═COOH[a]	3.67	5.45	1.33		
C(C)C═COOC	4.63	8.32		1.82	2.73
C(C)C═COOH[a]	4.40	5.01		1.82	
C═C(C)OOC	5.19	13.11		1.97	2.75
C═C(C)OOH[a]	5.93	6.97		1.89	
CC═C(C)OOC	3.44	10.1	1.48	2.03	2.71
CC═C(C)OOH[a]	3.44	6.24	1.49	2.02	
PhOOC	2.31	9.75			2.84
PhOOH[a]	2.56	6.26			
C═CCOOC	4.69	11.55	2.09		2.91
C═CCOOH[a]	6.49	6.30	6.40		

[a] From ref 3.

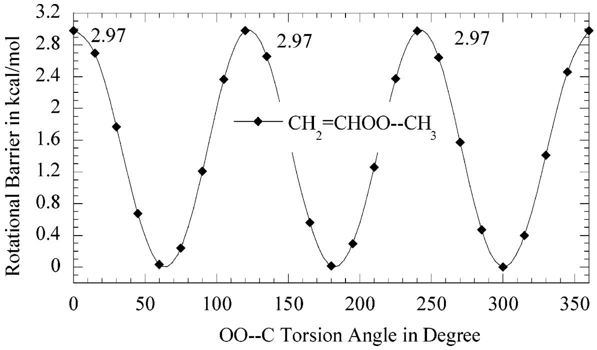

Figure 2. Potential for internal rotation about $CH_2{=}CHOO-CH_3$ bond in vinyl peroxide.

Data on the rotational barriers in the C_d-OOC, C_dO-OC, C_dOO-C, and C_d-C bonds for the peroxides are summarized in Table 10, along with data on the corresponding barriers in hydroperoxides for comparison purposes.

C_dOO-C and Internal Rotor Potentials. A potential energy diagram for internal rotation (ZPVE and thermal corrections included) versus C_dOO-C torsion angle is shown as example in Figure 2 for $CH_2{=}CHOOCH_3$. The C_dOO-CH_3 rotor potentials for the other peroxides are all similar and typical of

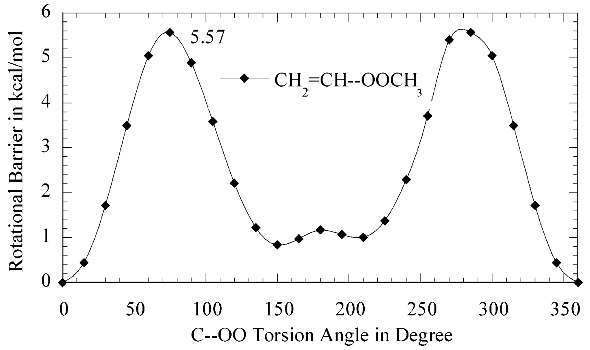

Figure 3. Potential for internal rotation about $CH_2{=}CH{-}OOCH_3$ bond in vinyl peroxide.

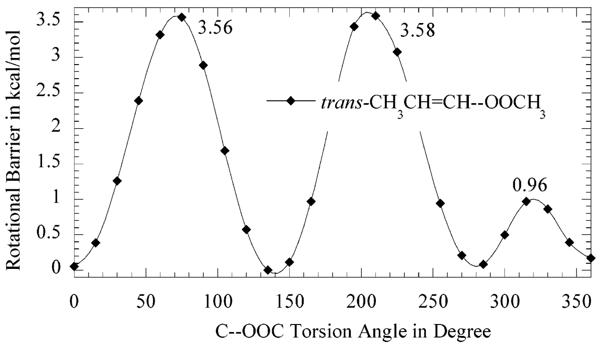

Figure 4. Potential for internal rotation about *trans*-$CH_3CH{=}CH{-}OOCH_3$ bond in vinyl peroxide. Maximum barrier is at dihedral $OOC_dC_d = -65.14°$. Minimum barrier at dihedral $OOC_dC_d = -140.14°$.

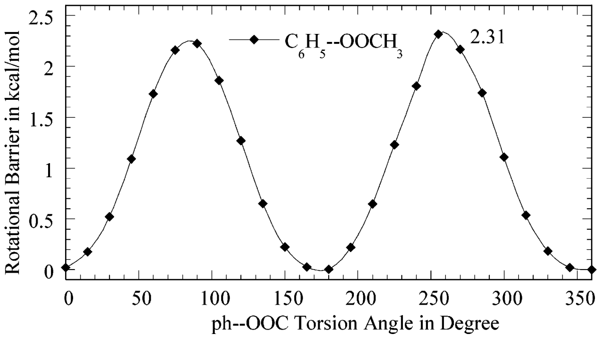

Figure 5. Potential for internal rotation about $C_6H_5{-}OOCH_3$ bond in phenyl peroxide. Maximum barrier is at dihedral $OOC_dC_d = 97.3°$. Minimum barrier at dihedral $OOC_dC_d = 7.3°$.

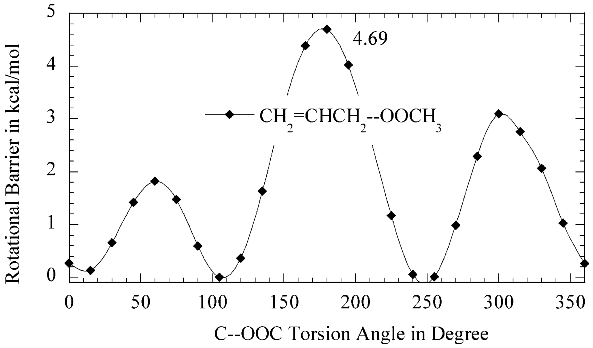

Figure 6. Potential for internal rotations about $CH_2{=}CHCH_2{-}OOCH3$ bond in allyl peroxide.

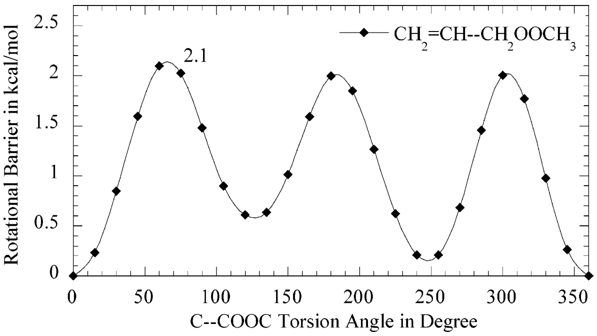

Figure 7. Potential barrier for internal rotation about $CH_2{=}CH{-}CH_2$-$OOCH_3$ bonds in allyl peroxide.

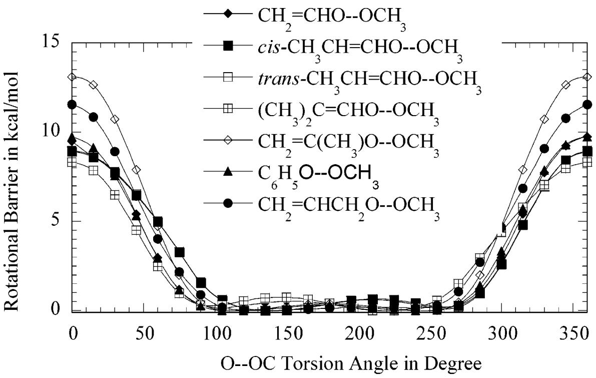

Figure 8. Potential barriers for internal rotations about O−OC bond in studied peroxides.

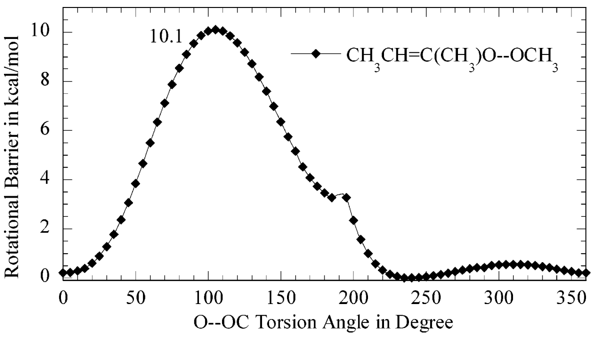

Figure 9. Potential barrier for internal rotation about the O−OC bond in $CH_3CH{=}C(CH_3)O{-}OCH_3$.

alkyl methyl rotations with 3-fold symmetry and barriers ranging between 2.7 and 3.0 kcal mol^{-1}.

C_d−OOC and Internal Rotor Potentials. The rotation barriers about C_d−OOC are similar to or lower than those in C_d−OOH; the barriers vary from 3.4 to 5.5 kcal mol^{-1}. They usually show a 3-fold potential with two higher barriers and one lower, about one-half the higher barrier as shown in Figures 3−6.

C_d−C Rotor Potential. Rotation barriers about $C_d{-}CH_3$ bonds for the peroxides all show the same 3-fold symmetry, because the $RC_dOO{-}CH_3$ rotors all have relatively low barriers, 1.44 and 2.09 kcal mol^{-1} (data listed in Supporting Information).

The C_d−C rotation barrier in the allyl peroxide (Figure 7 and Table 10) is 3-fold symmetric with a barrier of 2.1 kcal mol^{-1}; this is 4.3 kcal mol^{-1} lower than the corresponding rotational barrier for the allyl hydroperoxide. This C=C−COOC barrier is similar to that of the C=C(−C)OOH rotors in the methyl-substituted vinyl hydroperoxides.

C_dO−OC Internal Rotor Potentials. Rotation about C_dO−OC peroxide bonds shows a significant increase relative to the C_dO−OH hydroperoxides, and the potential energy (PE) diagrams in Figures 8 and 9 show a single-fold barrier over 360° rotation. The barrier in $CH_2{=}CHO{-}OCH_3$ is 9.75 kcal mol^{-1}, some 4 kcal mol^{-1} higher than that in the corresponding vinyl hydroperoxide, $CH_2{=}CHO{-}OH$. The $CH_2{=}C(CH_3)O{-}OCH_3$ barrier is 13, some 6.1 kcal mol^{-1} higher than the barrier

TABLE 11: Ideal Gas-Phase Thermodynamic Properties of $CH_2{=}CHOOCH_3$, *trans*-$CH_3CH{=}CHOOCH_3$, *cis*-$CH_3CH{=}CHOOCH_3$, $(CH_3)_2C{=}CHOOCH_3$, $CH_3CH{=}C(CH_3)OOCH_3$, $CH_2{=}C(CH_3)OOCH_3$, $CH_2{=}CHCH_2OOCH_3$, and $C_6H_5OOCH_3$[a]

species			$\Delta_f H^\circ_{298}$[b]	S°_{298}[c]	$C_p(T)$, cal mol^{-1} K^{-1}						
					300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
$CH_2{=}CHOOCH_3$	TVR[f]			65.73	16.70	21.82	26.35	30.13	35.94	40.17	46.65
(2)[d]	I.R.*g*	C=C−OOC		5.38	2.71	2.35	2.18	2.08	1.90	1.75	1.46
(3)[e]		C=CO−OC		6.73	1.32	1.30	1.31	1.33	1.38	1.42	1.45
		C=COO−C		4.42	2.15	2.14	2.01	1.86	1.60	1.43	1.21
	total		**−10.04**	82.26	22.88	27.61	31.85	35.4	40.82	44.77	50.77
trans-$CH_3CH{=}CHOOCH_3$	TVR[f]			68.39	20.45	26.78	32.60	37.56	45.33	51.01	59.70
(2)[d]	I.R.[g]	C−C=COOC		4.88	2.00	1.83	1.65	1.51	1.33	1.22	1.10
(9)[e]		CC=C−OOC		6.76	1.97	1.92	1.85	1.76	1.58	1.45	1.24
		CC=CO−OC		6.66	1.44	1.40	1.41	1.44	1.50	1.55	1.55
		CC=COO−C		4.54	2.13	2.08	1.93	1.78	1.53	1.38	1.18
	total		**−19.95**	91.23	27.99	34.01	39.44	44.05	51.27	56.61	64.77
cis-$CH_3CH{=}CHOOCH_3$	TVR[f]			68.05	20.17	26.64	32.51	37.51	45.29	50.97	59.67
(2)[d]	I.R.[g]	C−C=COOC		5.23	1.77	1.54	1.39	1.29	1.17	1.11	1.05
(9)[e]		CC=C−OOC		7.13	2.28	2.18	2.00	1.83	1.56	1.39	1.19
		CC=CO−OC		6.55	1.47	1.42	1.42	1.44	1.51	1.56	1.55
		CC=COO−C		4.53	2.13	2.09	1.94	1.79	1.54	1.38	1.19
	total		**−21.27**	91.49	27.82	33.87	39.26	43.86	51.07	56.41	64.65
$(CH_3)_2C{=}CHOOCH_3$	TVR[f]			70.25	24.20	31.97	39.09	45.21	54.83	61.91	72.72
(2)[d]	I.R.[g]	(C)C−C=COOC		5.01	1.97	1.75	1.56	1.43	1.26	1.18	1.08
(27)[e]		(C−)CC=COOC		5.01	1.97	1.75	1.56	1.43	1.26	1.18	1.08
		(C)2C=C−OOC		6.72	2.22	2.19	2.16	2.09	1.91	1.72	1.41
		(C)2C=CO−OC		6.69	2.28	2.17	1.99	1.82	1.55	1.39	1.19
		(C)2C=COO−C		4.56	2.13	2.07	1.92	1.77	1.52	1.37	1.18
	total		**−30.60**	98.24	34.77	41.9	48.28	53.75	62.33	68.75	78.66
$CH_3CH{=}C(CH_3)OOCH_3$	TVR[f]			70.43	24.23	32.03	39.17	45.28	54.87	61.92	72.71
(2)[d]	I.R.[g]	C−C=C(C)OOC		5.21	1.77	1.55	1.40	1.30	1.18	1.11	1.05
(27)[e]		CC=C(−C)OOC		4.96	1.93	1.76	1.60	1.47	1.30	1.20	1.09
		CC=C(C)−OOC		6.84	2.66	2.49	2.27	2.05	1.71	1.50	1.24
		CC=C(C)O−OC		6.53	1.47	1.45	1.48	1.51	1.56	1.60	1.59
		CC=C(C)OO−C		4.57	2.13	2.07	1.92	1.76	1.52	1.36	1.17
	total		**−29.58**	98.54	34.19	41.35	47.84	53.37	62.14	68.69	78.85
$CH_2{=}C(CH_3)OOCH_3$	TVR[f]			67.76	20.64	27.18	33.00	37.91	45.53	51.12	59.71
(2)[d]	I.R.[g]	C=C−C(OOC)		4.98	1.93	1.75	1.59	1.46	1.29	1.20	1.09
(9)[e]		C=C(C)−OOC		5.12	3.80	3.64	3.22	2.82	2.24	1.88	1.43
		C=C(C)O−OC		5.29	3.01	2.83	2.51	2.24	1.91	1.75	1.61
		C=C(C)OO−C		4.55	2.13	2.07	1.93	1.77	1.53	1.37	1.18
	total		**−20.79**	87.7	31.51	37.47	42.25	46.2	52.5	57.32	65.02
phenyl-$OOCH_3$	TVR[f]			75.49	27.43	36.96	45.10	51.71	61.47	68.25	78.21
(2)[d]	I.R.[g]	phenyl−OOC		7.37	2.03	1.87	1.70	1.56	1.37	1.25	1.12
(6)[e]		phenylO−OC		6.93	1.30	1.29	1.30	1.33	1.38	1.44	1.47
		phenylOO−C		4.44	2.16	2.15	2.01	1.86	1.60	1.43	1.21
	total		**−2.19**	94.23	32.92	42.27	50.11	56.46	65.82	72.37	82.01
$CH_2{=}CHCH_2OOCH_3$	TVR[f]			69.64	19.68	26.23	32.21	37.28	45.16	50.90	59.64
(2)[d]	I.R.[g]	C=C−COOC		6.64	2.24	1.90	1.66	1.49	1.30	1.19	1.08
(3)[e]		C=CC−OOC		6.76	1.97	1.92	1.85	1.76	1.58	1.45	1.24
		C=CCO−OC		6.66	1.44	1.40	1.41	1.44	1.50	1.55	1.55
		C=CCOO−C		4.54	2.13	2.08	1.93	1.78	1.53	1.38	1.18
	total		**−12.08**	94.24	27.46	33.53	39.06	43.75	51.07	56.47	64.69

[a] *Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm. R−OOC, RO−OC, and ROO−C torsional frequencies are excluded in the calculations of entropies and heat capacities. Instead, a more exact contribution from hindered rotations about C−O and O−O bonds is included.* [b] *$\Delta_f H^\circ_{298}$ in kcal mol^{-1}.* [c] *S°_{298} in cal mol^{-1} K^{-1}.* [d] *Optical isomers number.* [e] *Symmetry number.* [f] *The sum of contributions from translations, external rotations, and vibrations.* [g] *Contribution from internal rotation about the corresponding C−O, O−O, and C−C bonds.*

in the corresponding hydroperoxide $CH_2{=}C(CH_3)O{-}OH$. The $C_dO{-}OH$ rotation barriers in the remaining peroxides are in the range of 8.3−9.7 kcal mol^{-1}, and all are about 3 kcal mol^{-1} higher than the corresponding hydroperoxide (see Table 10 and Figure 8).

The rotational barrier about $C_bO{-}OC$ for phenyl peroxide $C_6H_5OOCH_3$ (Figure 8) is 9.75 kcal mol^{-1}, while the comparable barrier in the phenyl hydroperoxide is only 6.26 kcal mol^{-1}.

Figure 9 shows the potential curve for rotation about the $C_dO{-}OC$ bond in $CH_3CH{=}C(CH_3)O{-}OCH_3$. The rotation barrier is 10.1 kcal mol^{-1}, some 3.8 kcal mol^{-1} higher than that in the corresponding hydroperoxide; this trend is similar to that in phenyl.

Each of these $C_dO{-}OC$ internal rotations have one relatively high barrier, ranging from 8.5 to13 kcal mol^{-1}; the PE curve also shows one very low barrier at a fraction of 1 kcal mol^{-1}. Examination of the vibrational frequency motions suggests that the frequency determined in the B3LYP calculation only represents the low barrier torsion. We use the S and $C_p(T)$ contributions from the internal rotor analysis, and not from the torsion frequency; this is one case where use of the torsion frequency[25] may not be preferred. We hope to analyze this in more detail in future studies. The RO−OC barrier in allyl methyl peroxide $CH_2{=}CHCH_2O{-}OCH_3$ (Figure 8) is also higher, 11.55 kcal mol^{-1}, than that in the hydroperoxide, 6.3 kcal mol^{-1}.

6. Entropy (S°_{f298}) and Heat Capacities ($C_{p,f298}(T)$, 300 ≤ T ≤ 1500 K). S°_{f298} and $C_{p,f298}(T)$ calculation results using

TABLE 12: Groups in Vinyl, Phenyl, and Ethynyl Hydroperoxides and Peroxides

species[a]	C_d/H_2	$C_d/H/O$	$O/C_d/O$[b]	$O/H/O$	C_b/O	C_b/H	$C/C_d/H_3$	$C_d/C/H$	C_d/C_2	$C_d/C/O$
trans-$CH_3CH{=}CHOOH$ (3)		*	*	*			*	*		
cis-$CH_3CH{=}CHOOH$ (3)		*	*	*			*	*		
$(CH_3)_2C{=}CHOOH$ (9)		*	*	*			*		*	
$CH_2{=}C(CH_3)OOH$ (3)	*		*	*			*			*
$CH_3CH{=}C(CH_3)OOH$ (9)			*	*			*	*		*

species[a]	$O/C_b/O$[b]	$O/H/O$	C_b/O	C_b/H
C_6H_5OOH (2)	*	*	*	*

species[a]	C_t/H	$O/C_t/H$	$O/C_t/O$[b]	$O/H/O$	C_t/O[b]	C_t/C	$C/C_t/H_3$	$O/C_t/C$[b]	$C/H_3/O$
$CH{\equiv}COH$ (1)	*	*			*				
$CH_3C{\equiv}COH$ (1)		*			*	*	*		
$CH{\equiv}COCH_3$ (3)	*				*			*	*
$CH_3C{\equiv}COCH_3$ (9)	*				*		*	*	*
$CH{\equiv}COOH$ (1)	*		*	*	*				
$CH_3C{\equiv}COOH$ (3)			*	*	*	*	*		

[a] Symmetry value in parentheses. [b] Group which will be calculated in this work.

TABLE 13: Calculation of $O/C_d/O$, $O/C_b/O$, $O/C_t/O$, C_t/O, and $O/C/C_t$ Groups

	$\Delta_f H^\circ_{298}$[a]	S_{f298}[b]	$C_p(T)$ cal mol^{-1} K^{-1} 300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
				C_t/O					
$CH{\equiv}COH$	31.79	2.92	2.39	3.12	3.39	3.55	3.65	3.74	4.08
$CH_3C{\equiv}COH$	30.39	−2.23	1.16	1.87	2.14	2.3	2.41	2.52	1.89
				$O/C/C_t$					
$CH{\equiv}COCH_3$	−21.94	12.14	2.55	2.43	2.71	3.04	3.72	4.15	4.89
$CH_3C{\equiv}COCH_3$	−21.89	7.88	2.52	2.28	2.53	2.84	3.51	3.95	3.82
				$O/C_t/O$					
$CH{\equiv}COOH$	0.43	9.72	1.55	1.8	2.19	2.39	3.01	3.3	3.96
$CH_3C{\equiv}COOH$	−1.98	3.38	0.66	0.81	1.15	1.31	1.88	2.16	1.81
				$O/C_d/O$					
trans-$CH_3CH{=}CHOOH$	−11.13	10.27	3.14	2.95	3.03	3.15	3.74	4.07	4.23
cis-$CH_3CH{=}CHOOH$	−12.35	11.21	2.86	2.96	3.17	3.3	3.71	3.83	3.65
$(CH_3)_2C{=}CHOOH$	−13.03	5.26	1.11	1.05	1.29	1.57	2.33	2.73	3
$CH_2{=}C(CH_3)OOH$	−9.76	7.70	4.95	5.68	5.97	5.9	5.63	5.32	4.92
$CH_3CH{=}C(CH_3)OOH$	−10.12	7.15	3.96	4.29	4.69	4.84	4.95	4.96	5.04
				$O/C_b/O$					
C_6H_5OOH	−1.98	10.7	2.85	2.92	3.02	3.09	3.48	3.66	3.23

[a] $\Delta_f H^\circ_{298}$ in kcal mol^{-1}. [b] S°_{f298} in cal mol^{-1} K^{-1}.

B3LYP/6-311G(d, p) determined geometries and frequencies are summarized in Table 11. TVR represents the sum of the contributions from translations, vibrations, and external rotations for S°_{f298} and$C_{p,f298}(T)$. The torsion frequencies calculated for the internal rotors are not incorporated into TVR. Instead, a contribution from hindered rotations is calculated. I.R. represents the contributions from the internal rotation about C−O, O−O, and C−C bonds for S°_{f298} and $C_{p,f298}(T)$ separately noted in Table 11.

The final standard entropies also include correction terms for rotational conformers. This correction is usually calculated by the following formula for 1 mol of mixture:[54]

$$\Delta S_{\text{mixing}} = -R\sum n_i \ln(n_i)$$

Where n_i is the equilibrium mole fraction of the ith form. ΔS_{mixing} represents the entropy of mixing of rotational conformations or optical conformations. Contributions from rotational conformers of the rotors in the peroxides are included in the entropy by the calculations from the Rotator code. Energy levels for the internal rotor are calculated, and the partition function corresponding to the rotor is determined and used in the calculation of the rotation entropy. ΔS_{mixing} is not separately calculated nor is a correction for the RO−OR optical isomer added, because this would result in a double counting.

In this study, we report entropy and heat capacity values for eight vinyl, phenyl, and allyl peroxides. In previous studies,[3,4] we have reported these thermodynamic properties for the corresponding hydroperoxides. To evaluate relative differences in the contributions to S and C_p at 298 K for the R−OOC and RO−OC rotors with the R−OOH and RO−OH values in corresponding species, we list the difference of the respective internal rotor contributions (R−OOC and RO−OC) and (R−OOH and RO−OH) in Table 11. The values for the R−OOC and RO−OC are higher by 2.7 to 4.9 cal mol^{-1} K^{-1} for the entropy and by 2.5 cal mol^{-1} K^{-1} at 300 K to 13 cal mol^{-1} K^{-1} at 1500 K for the heat capacity than those for the analogue hydroperoxides. The entropy difference between the allyl peroxide and allyl hydroperoxide is higher, 8.7 cal mol^{-1} K^{-1}. Obvious reasons involve the added three atoms and the higher moments of inertia resulting from the added methyl group in place of H atom.

7. Group Additivity Values. Group additivity is a straightforward and reasonably accurate method to estimate thermodynamic properties of hydrocarbons and oxygenated hydrocarbons.[54] It is particularly useful for application to larger molecules and in codes or databases for thermochemical properties and reaction mechanism generation. In this work, we develop a consistent set of peroxy hydrocarbon and acetylene alcohol

TABLE 14: Group Values[a]

			$C_p(T)$						
groups	$\Delta_fH^\circ_{298}$	S°_{f298}	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
				Literature					
C_d/H2[b]	6.26	27.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19
C_d/C/H[c]	8.59	7.97	4.16	5.03	5.81	6.50	7.65	8.45	9.62
C/C_d/H3[c]	−10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C_d/C2[c]	10.34	−12.70	4.10	4.61	4.99	5.26	5.80	6.08	6.36
C_d/H/O[c]	8.60	6.20	4.75	6.46	7.64	8.35	9.10	9.56	10.46
O/H/O[d]	−16.30	27.83	5.21	5.72	6.17	6.66	7.15	7.61	8.43
C_d/C/O[e]	8.20	−12.32	3.59	4.56	5.04	5.30	5.84	6.07	6.16
C_b/O[c]	−0.90	−10.20	3.90	5.30	6.20	6.60	6.90	6.90	7.07
C_b/H[c]	3.30	11.53	3.24	4.40	5.46	6.30	7.54	8.41	9.73
C/H_3/O[c]	−10.00	30.41	6.19	7.84	9.4	10.79	13.03	14.77	17.58
C_t/H[f]	26.93	24.70	5.28	5.99	6.49	6.87	7.47	7.96	8.85
O/C_t/H[c]	−37.90	29.10	4.3	4.4	4.82	5.23	6.02	6.61	7.44
C/C_t/H_3[g]	−10.20	30.41	6.19	7.84	9.4	10.79	13.02	14.77	17.58
C_t/C[c]	27.55	6.35	3.13	3.48	3.81	4.09	4.6	4.92	6.35
				This Work					
O/C/C_t[i]	−21.91	10.01	2.54	2.36	2.62	2.94	3.62	4.05	4.36
C_t/O[i]	30.79	0.35	1.78	2.50	2.77	2.93	3.03	3.13	2.99
O/C_t/O[i]	−0.77	6.55	1.11	1.31	1.67	1.85	2.45	2.73	2.89
O/C_d/O[h]	−11.27	8.53	3.20	3.39	3.63	3.75	4.07	4.18	4.17
O/C_b/O	−1.98	10.7	2.85	2.92	3.02	3.09	3.48	3.66	3.23
cis/CH_3/OOH	−1.22	0.94	−0.28	0.01	0.14	0.15	−0.03	−0.24	−0.58

[a] $\Delta_fH^\circ_{298}$ in kcal mol^{-1}; S°_{f298} and $C_p{}^\circ(T)$ in cal mol^{-1} K^{-1}. [b] Chen, Wong, and Bozzelli.[80] [c] Benson;[54] also used by Holmes[81], Turecek,[58] and Cohen.[82] [d] Lay and Bozzelli.[42] [e] Zhu, Kim, and Bozzelli.[83] [f] Stein and Fahr.[84] [g] Benson[54] assigned C/C/H_3. [h] $\Delta_fH^\circ_{298}$,$C_p{}^\circ(T)$, and S°_{f298} is the average value derived from five hydroperoxides (see text). [i] Each group is the average value derived from two species (see text).

groups derived from the thermodynamic properties data of a set of hydroperoxides, peroxides, ethers, and alcohols determined in this and in a previous study.[3] (The acetylene alcohol and ether groups are used for the C_t/O group in the peroxides). The calculated group values are used to estimate the peroxides species considered in this work. The values determined using group additivity (GA) are compared to the density functional (DFT) calculations of the peroxide species. We note that our pervious attempts to develop a consistent set of groups that replicate the enthalpy values of the methyl-substituted ethene peroxides and hydroperoxides from previous studies, particularly those of Turecek's group, were unsuccessful; they consistently resulted in deviations of up to 8 or 9 kcal mol^{-1}. The overall agreement results more from improvements in several groups, rather than in dramatically improved enthalpies from the calculations.

Groups are identified for the different hydroperoxides, alcohols, and peroxides species considered and listed in Tables 12 and 13. All values are intrinsic, that is, the entropy component excludes contributions to symmetry and optical isomer number in the parent molecule.

An example of group additivity calculation for $\Delta_fH^\circ_{298}$ and $C_{p,f298}(T)$ on the O/C_t/O group is calculated on the basis of the following $\Delta_fH_{(298)}$ terms (eq 1):

$$(CH{\equiv}CHOH) = (C_t/H) + (C_t/O) + (O/C_t/H) \qquad (1)$$

S°_{298} of O/C_t/O is calculated on the basis of entropy groups (eq 2):

$$(CH{\equiv}CHOH) = (C_t/H) + (C_t/O) + (O/C_t/H) + R\ln(OI) - R\ln(\sigma) \quad (2)$$

where $R = 1.987$ cal mol^{-1} K^{-1}, OI stands for the optical isomer number, and σ is the symmetry number.

C_t/O. The group value of C_t/O (Table 13) is determined from ethynyl alcohols, ethynol $HC{\equiv}COH$ and methyl ethynol $CH_3C{\equiv}COH$. Both species were determined in a previous study[3] using DTF calculations and isodesmic reactions. Thermochemical values for the group are summarized in Table 14. $\Delta_fH^\circ_{298}$ for C_t/O is calculated to be 31.79 kcal mol^{-1} from $HC{\equiv}COH$ and 30.39 kcal mol^{-1} from $CH_3C{\equiv}COH$. The recommended value of C_t/O is taken as the average, 30.79 kcal mol^{-1}.

O/C/C_t. The value of the O/C/C_t group is derived from the enthalpy values of $HC{\equiv}COCH_3$ and $CH_3C{\equiv}COCH_3$ obtained by use of DFT calculations and isodesmic reactions[3]. O/C/C_t derived from $HC{\equiv}COCH_3$ and $CH_3C{\equiv}COCH_3$ are −21.94 and −21.89 kcal mol^{-1}, respectively. $\Delta_fH^\circ_{298}$ of the O/C_t/C group is the average, −21.91 kcal mol^{-1}.

O/C_t/O. The O/C_t/O group value is derived from the thermochemical property data of ethynyl hydroperoxides: $HC{\equiv}COOH$ and $CH_3C{\equiv}COOH$. The $\Delta_fH^\circ_{298}$ mean value for O/C_t/O is −0.77 kcal mol^{-1}. This value allows us to evaluate the two ethynyl peroxides considered above in this work. With the above O/C_t/O value, we can estimate enthalpy of $HC{\equiv}COOCH_3$, 41.87 kcal mol^{-1}, and $CH_3C{\equiv}COOCH_3$, 32.27 kcal mol^{-1}, by use of group additivity; these values are in good agreement with the DFT calculation results (41.23 ± 0.70 and 29.51± 0.27 kcal mol^{-1}, respectively). The entropy, S°_{f298}, is calculated from eq 2 and results in 1.99 cal mol^{-1} K^{-1}. The heat capacity, $C_{p,f298}(T)$**,** for a temperature range from 300 to 1500 K of O/C_t/O is determined according to eq 1.

O/C_d/O. The O/C_d/O[4] group is determined using five hydroperoxides[3]: *trans*-$CH_3CH{=}CHOOH$, *cis*-$CH_3CH{=}CHOOH$, $(CH_3)_2C{=}CHOOH$, $CH_3CH{=}C(CH_3)OOH$, and $CH_2{=}C(CH_3)$-OOH. The thermochemical values for groups from the literature and our previous studies are summarized in Table 14. $\Delta_fH^\circ_{298}$ of the O/C_d/O group is calculated to be −11.27 kcal mol^{-1}, taken as the average results from the five hydroperoxides, where the maximum deviation is 1.4 kcal mol^{-1}. This O/C_d/O group is used to estimate the vinyl peroxide species by using group additivity, THERM,[55,56] and we compare data to the DFT calculations in Table 6.

The entropy, S_{298}**,** of the O/C_d/O group is calculated according to eq 2 and with use of the thermochemical data of the above six hydroperoxides. The heat capacity, $C_{p,f298}(T)$, group values are also determined using the above hydroperoxide molecules. The results are given in Table 14 for a temperature range from 300 to 1500K.

Calculated values for the entropy group, S_{298} of the O/C_d/O, show a range from 10.0 to 5.26 cal mol^{-1} K^{-1}. Both *trans*-$CH_3CH{=}CHOOH$ and *cis*-$CH_3CH{=}CHOOH$ have S_{298} group values near 10 cal mol^{-1} K^{-1} ($\pm$0.66). The two species with a methyl (3-fold symmetric, rotation barrier of 1.9 kcal mol^{-1}) on the peroxide carbon, $CH_3CH{=}C(CH_3)OOH$ and $CH_2{=}C(CH_3)OOH$, provide O/C_d/O group values for entropy, S_{298}, of 7.15 and 7.70 cal mol^{-1} K^{-1}, respectively. The O/C_d/O entropy value of $(CH_3)_2C{=}CHOOH$, which contains two methyl rotors on the non-peroxide double-bond carbon has the lowest value, 5.26 cal mol^{-1} K^{-1}. The recommended value of S_{298} for group O/C_d/O is determined as the average value of all six hydroperoxides, 8.53 ± 1.5 cal mol^{-1} K^{-1}. These data suggests that group additivity for entropy may not hold where methyl and peroxide groups are both interacting with the unsaturated bond. It is possible that the C_d/C/O group values for vinyl alcohols need re-evaluation or addition of more cis/trans interaction groups.

O/C_b/O. The group value of O/C_b/O is derived from the thermodynamic property data of phenyl hydroperoxide C_6H_5OOH. The $\Delta_f H^\circ_{298}$ resulting value of the O/C_b/O group is −1.98 kcal/mol. Heat capacity values, $C_{p,f298}(T)$, are also determined using the data of phenyl hydroperoxide and reaction 1, and the results are given is Table 14 for a temperature range from 300 to 1500 K. The entropy, S°_{f298}, for this group is calculated as 10.7 cal mol^{-1} K^{-1}. The use of this group in the determination of phenyl methyl peroxide enthalpy ($C_6H_5OOCH_3$, −1.88 kcal mol^{-1}) is in good agreement with the DFT result for $C_6H_5OOCH_3$, −2.19 ± 0.52 kcal mol^{-1}.

Cis Correction−cis-(CH_3/OOH). A cis correction for $\Delta_f H^\circ_{298}$ is assigned by Benson[54] for the cis olefins as 1 kcal mol^{-1}. In this work, we estimate the value of the (cis-(CH_3/OOH) correction for use in group additivity. The cis correction is determined by comparing enthalpies of the cis form of $CH_3CH{=}CHOOH$ to the trans form. The value given in Table 14 is the difference between group O/C_d/O (trans) and O/C_d/O (cis). The $\Delta_f H^\circ_{298}$ value derived from $CH_3CH{=}CHOOH$ for cis is 1.22 kcal mol^{-1}, which is similar to that of Benson for methyl groups. S°_{f298} and $C_{p,f298}(T)$ values are also determined.

Summary

Thermodynamic properties ($\Delta_f H^\circ_{298}$, S°_{f298}, and $C_{p,f298}(T)$ ($300 \le T \le 1500$ K)) for the vinyl peroxides $CH_2{=}CHOOCH_3$, *trans*-$CH_3CH{=}CHOOCH_3$, *cis*-$CH_3CH{=}CHOOCH_3$, $(CH_3)_2C{=}CHOOCH_3$, $CH_2{=}C(CH_3)OOCH_3$, and $CH_3CH{=}C(CH_3)OOCH_3$ are reported. Values for allyl peroxide $CH_2{=}CHCH_2OOCH_3$, two ethynyl peroxides, $CH{\equiv}COOCH_3$ and $CH_3C{\equiv}COOCH_3$, and phenyl peroxide $C_6H_5OOCH_3$ are also determined. Standard enthalpies of formation, ΔH°_{298}, are calculated using the B3LYP/6-311G(d,p) level of density functional theory and isodesmic reactions. Rotational barrier potentials are reported for internal rotors in vinyl peroxides and methyl-substituted vinyl peroxides, and hindered internal rotor contributions for $\Delta_f H(T)$, S°_{f298}, and $C_{p,f298}(T)$ are calculated.

Comparison of the thermodynamic properties between the peroxides and corresponding hydroperoxides shows uniformity in property trends. A set of oxygenated hydrocarbon groups are determined that result in consistent prediction of thermodynamic properties for the substituted alkyl and vinyl peroxides and hydroperoxides.

The olefinic and acetylene peroxides and hydroperoxides are unstable to cleavage of the very weak (22−3 kcal mol^{-1}) RO−OH or RO−OR peroxide bonds due to formation of strong carbonyl bonds (ca. 20−40 kcal mol^{-1} stronger than the hydrocarbon Π bonds) in the vinyl, phenyl, and acetylenic peroxides and hydroperoxides.

Acknowledgment. We thank Dr. Chad Sheng (NJIT) for use of his SMCPS (statistical mechanics for heat capacity and entropy) computer code.

Supporting Information Available: SM 1 giving the geometry parameters for vinyl, allyl, ethynyl, and phenyl peroxides and SM 2 listing the vibration frequencies calculated for all peroxides at the B3LYP/6-311G(d,p) level of theory based on optimized geometries at the same level of theory and also marking the calculated torsion frequencies, which are identified by viewing the vibration motion and then omitted from the vibration contributions to entropy and heat capacity; SM3 listing the moment of inertia for the studied peroxides; SM4 giving the total energies at 298 K, scaled ZPVE, and thermal corrections to 298.15 K; SM 5−12 listing the total energies and data on the calculated rotation barriers about C_d−OOC, C_dO−OC, C_dOO−C, and C−C_d bonds for each internal rotor for these peroxides; SM 13−16 listing the coefficient of the Fourier expansions components, a_i and b_i in eq I; SM 17 giving the thermochemical properties of vinyl, allyl, ethynyl, and phenyl peroxides over a larger temperature range (0.1−5000 K); SM 18 comparing the heat capacity contributions to the enthalpy, ($H - H_0$ values) for the three rotors in $CH_2{=}CHOOCH_3$ for (i) vibration frequencies omitting the three torsion frequencies, (ii) vibration frequencies with the three torsion frequencies included, and (iii) vibration frequencies without the torsions but including the contributions from the three internal rotors; Figures SM 1−7 showing potential barriers for internal rotations about OO−CH_3 bonds for the studied peroxides; Figures SM 8−13 showing potential barriers for internal rotations about C_d−CH_3 bonds for *trans*-$CH_3{-}CH{=}CHOOCH_3$, *cis*-$CH_3{-}CH{=}CHOOCH_3$, $CH_3({-}CH_3)C{=}CHOOCH_3$, $CH_3{-}CH{=}C(CH_3)OOCH_3$, $CH_3{-}CH{=}C({-}CH_3)OOCH_3$, and $CH_2{=}C({-}CH_3)OOCH_3$; Figures SM 14−17 showing barriers for internal rotations about C−$OOCH_3$ bond for *cis*-$CH_3CH{=}CH{-}OOCH_3$, $CH_3(CH_3)C{=}CH{-}OOCH_3$, $CH_3CH{=}C(CH_3){-}OOCH_3$, and $CH_2{=}C(CH_3){-}OOCH_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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