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Structures, Intramolecular Rotation Barriers, and Thermodynamic Properties (Enthalpies, Entropies and Heat Capacities) of Chlorinated Methyl Hydroperoxides (CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH)

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Chlorinated methyl hydroperoxides are important intermediates in the oxidation, combustion, and atmospheric photochemistry of chlorocarbons. The thermochemical property data on these oxy-chlorocarbon species are important for understanding their stability, reaction paths, and kinetics. Enthalpy, $\Delta H_f{}^{\circ}{}_{298}$, entropy, S°_{298}, and heat capacities, $C_p(T)$ ($300 \leq T/K \leq 1500$), are determined for monochloromethyl hydroperoxide, dichloromethyl hydroperoxide, and trichloromethyl hydroperoxide using density functional B3LYP/6−31 G(d,p), and B3LYP/6-311+G(3df,2p), *ab initio* QCISD(T)/6-31G(d,p), and the composite CBSQ//B3LYP/6-31G(d,p) calculation methods (abbreviated as CBSQ//B3**). The molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) density functional calculation level, with single point calculations for energy at the B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G-(d,p) levels. The vibration frequencies are scaled for zero point energies and for thermal corrections. The enthalpies of formation ($\Delta H_f{}^{\circ}{}_{298}$) are determined at each calculation level using the $\Delta H^{\circ}_{rxn,298}$ with known enthalpies of other reactants and products in each of five different reactions. Standard entropy (S°_{298}) and heat capacity ($C_p(T)$'s, $300 \leq T/K \leq 1500$) from vibrational, 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. Potential barriers for internal rotation are calculated at the B3LYP/6-31G(d,p) level, and hindered internal rotational contributions to entropy and heat capacity are calculated by summation over the energy levels obtained by direct diagonalizations of the Hamiltonian matrix of hindered internal rotations. An evaluation of data from the reactions, several of which are isodesmic, results in $\Delta H_f{}^{\circ}{}_{298}$ values for CH_2ClOOH of -41.41 ± 1.45kcal/mol, $CHCl_2OOH$ of -44.74 ± 3.25 kcal/mol, and CCl_3OOH of -45.63 ± 3.14 kcal/mol. The $\Delta H_f{}^{\circ}{}_{298}$ values suggest that the electronegative Cl(s) on the methyl increase stability and ROO−H bond energy by several kcal/mol relative to CH_3OOH. Groups for use in Benson type additivity estimations are determined for the carbon with oxygen and chlorine(s). The enthalpy values for the $C/Cl/H_2/OO$, $C/Cl_2/H/OO$ and $C/Cl_3/OO$ groups are −17.91, −21.24, and −22.13 kcal/mol respectively with error limits as above. The enthalpy values from reactions that are isodesmic show good agreement at all of the theory levels, suggesting effective cancellation of errors in the reaction sets. CBSQ//B3LYP/6-31G(d,p) calculations are judged to be the most accurate for enthalpies from nonisodesmic reactions, in this study.

Introduction

Alkyl hydroperoxides are important intermediates in low-temperature combustion processes, such as in the initial stages of combustion[1,2] and in the atmospheric photochemical oxidation of hydrocarbons.[3,4] Chlorinated alkyl hydroperoxides serve a similar role in the oxidation of chlorinated hydrocarbons.[5−8] Knowledge of the thermodynamic parameters for these species is central to understanding and predicting their reaction pathways, rate constants, and equilibrium constants. There are no experimental studies of the thermodynamic properties of chlorinated alkyl hydroperoxides; the rapid interconversion of conformers and the instability of alkyl hydroperoxides lead to complexities in studies of these species.

Experimental and theoretical studies on heats of formation ($\Delta H_f{}^{\circ}{}_{298}$) of few chlorinated alkyl hydroperoxides have been reported. Wallington et al.[5−7] calculated structures and vibrational frequencies of CH_3OOH, CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH at the MP2/6-31G(d,p) level, and Catoire et al.[7a] reported $\Delta H_f{}^{\circ}{}_{298}$ of $CHCl_2OOH$ and CCl_3OOH to be -46.3 ± 4, -48.4 ± 4 kcal/mol. Knyazev et al.[8] estimated the enthalpy of formation of chlorinated alkyl hydroperoxides using their experimental data on the peroxy radicals and on an assumed ROO−H bond enthalpy of 87.5 kcal/mol. They reported that enthalpy of formation for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH are -36.59 ± 3.97, -39.96 ± 3.39, -40.37 ± 2.84 kcal/mol, respectively. Lay et al.[9] calculated the internal rotation barriers, vibrational frequencies, and thermodynamic properties of α-chlorinated ethyl hydroperoxides at the HF/6-31G* and MP2/6-31G* calculation levels.

In this work, enthalpy, $\Delta H_f{}^{\circ}{}_{298}$, entropy, S°_{298}, and heat capacities, $C_p(T)$, are determined for the chlorinated methyl hydroperoxides CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH using density functional and *ab initio* calculation methods. The

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enthalpies of formation are evaluated at each calculation level using five different reactions. Contributions to entropy and heat capacity from internal rotation are estimated using direct integration over the energy levels of the intramolecular rotation potential energy curve, with the B3LYP/6-31G(d,p) level calculations for rotation barrier estimations.

Computational Methods

All of the *ab initio* calculations are performed using the Gaussian 94 program suite.[10] The structural parameters are fully optimized at the B3LYP/6−31G(d,p) level of theory. The harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. The optimized geometrical parameters are used to obtain total electronic energies in the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p), and CBSQ//B3LYP/6-31G(d,p) single-point calculations.[11−13]

B3LYP/6-31G(d,p) is chosen because it is commonly used and is reported to yield accurate geometries and reasonable energies.[14,15] Curtiss et al.[16] reported that B3LYP/6-31G(d,p) provides highly accurate structures for compounds with elements up to atomic number 10. Durant[14,17] has compared density functional calculations B3LYP and hybrid (BH and H) with MP2 and Hartree−Fock methods for geometry and vibration frequencies. He reports that these density functional methods provide excellent geometries and vibration frequencies, relative to MP2 at a reduced computational expense. Petersson et al.[18] currently recommends the use of B3LYP for geometry and frequencies in several of his CBS calculation methods. A comparison of calculation results from B3LYP/6-31G(d,p), with the use of working reactions for $\Delta H_{f\,298}^{\circ}$, against data from higher calculation levels will provide some calibration of the B3LYP/6-31G(d,p) values for larger molecules where this may be one of the few available calculation methods (with similar working reactions). B3LYP/6-311+G(3df,2p) is chosen to see if this larger basis set results in an improvement to the above commonly used density functional calculation method.[15] QCISD(T)/6-31G(d,p) is a configuration interaction method, but with a small, economical basis set.[19,20] CBSQ calculation is a high level composite method with an empirical correction reported compared with QCISD(T)/6-311+G(3df,2p).[13,21] CBSQ[22] attempts to approximate the energy of a species at the infinite basis set limit by an extrapolation of the energies of pair natural orbital at the MP2 level. The effects of going from MP2 to QCISD(T) are accounted for with an additivity scheme. The geometry is obtained at the MP2/6-31G level of theory, whereas the ZPE used is the scaled (by 0.9135) HF/6-31G value. For the open-shell systems, there is also a correction for spin contamination in the unrestricted Hartree−Fock wave function. The CBSQ method has been shown to yield reliable $\Delta H_{f\,298}^{\circ}$ values for small molecules.[22] The CBSQ//B3LYP/6-31G(d,p) method differs from CBSQ in that it employs an improved geometry and ZPE. The CBSQ//B3LYP/6-31G(d,p) employs geometry optimized at the B3LYP/6-31G(d,p) level and a ZPE calculation from scaled (by 0.9806)[23] B3LYP/6-31G(d,p) harmonic vibrational frequencies. This is very similar to the CBS−RAD method[24] recommended by the Radom research group but has a QCISD(T) calculation in place of CCSD(T). These calculations are referred to as CBSQ//B3** in the present study.

1. Enthalpies of Formation ($\Delta H_{f\,298}^{\circ}$). Enthalpies of formation ($\Delta H_{f\,298}^{\circ}$) for the chlorinated methyl hydroperoxides are estimated using total energies obtained by the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p), and CBSQ//B3LYP/6-31G(d,p) calculation methods and five reactions, three of which are isodesmic. The total energies are corrected by zero-point vibration energies (ZPVE), which are scaled by 0.9806 as recommended by Scott et al.[23] Thermal correction, 0 K to 298.15 K, is calculated to estimate $\Delta H_{f\,298}^{\circ}$ at 298.15 K.[25]

The method of isodesmic reactions relies on the similarity of the bonding environments in the reactants and products that leads to partial cancellation of systematic errors in the density functional and *ab initio* molecular orbital calculations.[25] The following reactions are selected to determine $\Delta H_{f\,298}^{\circ}$ of each chlorinated methyl hydroperoxide.

$$CH_{3-x}Cl_xOOH + CH_4 \rightarrow CH_3OOH + CH_{4-x}Cl_x \quad (1)$$

$$CH_{3-x}Cl_xOOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CH_{3-x}Cl_x \quad (2)$$

$$CH_{3-x}Cl_xOOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_{4-x}Cl_x \quad (3)$$

$$CH_{3-x}Cl_xOOH + x\,H_2 \rightarrow CH_3OOH + x\,HCl \quad (4)$$

$$CH_{3-x}Cl_xOOH + x\,H_2O \rightarrow CH_3OOH + x\,HOCl \quad (5)$$

The basic requirement of an isodesmic reaction is that the number of each type of bond is conserved in the reaction. Reactions 1, 2, and 3 are isodesmic; reactions 4 and 5 are not. Reactions 4 and 5 have one (two, three) added H_2's (for 4) and H_2O's (for 5) in the reactants and corresponding HCl's and HOCl's in the products, for the respective monochloromethyl-, (dichloromethyl-, trichloromethyl-) hydroperoxides. Density functional and *ab initio* calculations with ZPVE and thermal correction are performed for all four compounds in each reaction, and the enthalpy of reaction $\Delta H_{rxn,298}^{\circ}$ is calculated. Because the enthalpies of formation of the three compounds, have been experimentally determined or theoretically calculated, the unknown enthalpy of the target compound is obtained.

Density functional and *ab initio* calculations at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3** level of theory are performed on the most stable conformer of each compound, and the $\Delta H_{f\,298}^{\circ}$ of this conformer is calculated using isodesmic reactions. $\Delta H_{f\,298}^{\circ}$'s of other conformers, if present, are estimated with the same method. Final $\Delta H_{f\,298}^{\circ}$ values are from a statistical distribution of rotational conformers.

The AM1[26,27] and PM3[28] methods in the MOPAC 6.0[29] package are used to perform the semiempirical MO calculations. The enthalpy of formation of three title molecules are calculated with AM1 and PM3 parameters and compared to those obtained from the density functional and *ab initio* studies. Direct results from the MOPAC calculations, as well as results from reaction analysis with MOPAC data are presented.

2. Entropy (S_{298}°) and Heat Capacities ($C_p(T)$'s, $300 \leq T/K \leq 1500$)) and Hindered Rotation contribution to Thermodynamic Parameters. Entropies S_{298}° and heat capacities ($C_p(T)$'s, $300 \leq T/K \leq 1500$) are calculated using the rigid-rotor-harmonic-oscillator approximation, based on frequencies and moments of inertia of the optimized B3LYP/6-31G(d,p) structures. Contributions to entropy and heat capacity from internal rotation are determined using direct integration over energy levels of the intramolecular rotational potential energy. Potential barriers for internal rotations about the C−O and O−O bonds are determined at the B3LYP/6-31G(d,p) calculation level. A technique for calculation of thermodynamic functions from hindered rotations with arbitrary potentials is used to calculate hindered internal contributions to S°_{298} and $C_p(T)$'s.[9,30,31] This technique employs expansion of the hindrance potential in the Fourier series, calculation of the Hamiltonian matrix on the basis of wave functions of free internal rotation, and subsequent calculation of energy levels by direct diagonalization of the Hamiltonian matrix. In this work, the torsional potential calculated at the discrete torsional angles is represented by a truncated Fourier series.

$$V(\Phi) = a_0 + \sum a_i \cos (i\Phi) + \sum b_i \sin (i\Phi) \qquad i = 1, 2, 3, 4, 5 \quad \text{(F1)}$$

The values of the coefficients a_i and b_i are calculated to provide the minima and maxima of the torsional potentials with allowance of a shift of the theoretical extreme angular positions.

Results and Discussion

1. **Geometries and Vibrational Frequencies.** The fully optimized geometries at the B3LYP/6−31G(d,p) density functional calculation level for the three chlorinated methyl hydroperoxides are presented in Figure 1. The numerical values of the structural parameters including carbon−hydrogen, carbon−chlorine, carbon−oxygen, oxygen−oxygen, and oxygen−hydrogen bond distances along with applicable bond angles are listed in Table 1. The calculation at the B3LYP/6−31 g(d,p) level gives O—O bond length 1.45 Å in all three chlorinated hydroperoxides, which is in good agreement with the experimental data (1.452 Å for H_2O_2) by Khachkuruzov and Przhevalskii[32] using IR spectroscopy. The effects of chlorine α-substitution on molecular geometries can be seen from Table 1. The O—H bond lengths for CH_3OOH, CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH optimized at the B3LYP/6-31G(d,p) are 0.9713, 0.9742, 0.9748, and 0.9752 Å, respectively, they increase with the increased chlorine substitution. The increase in O—H bond length from methyl hydroperoxide to chlorinated hydroperoxides suggests a weaker bond, but in fact, the bond is determined to be ca. 6 kcal/mol stronger (see the bond energy section). The C—O bond length decreases 0.04 Å for the first chloro substitution, then a further decrease of 0.007 Å for the dichloro; but an increase of 0.01 Å (from the dichloro) is calculated for the trichloro. The interaction between the −OOH group and the methyl groups appears to increase with one or more chlorines on the methyl, based on the O—H bond length increase of 0.0029 to 0.0039 Å and the C—O bond length decrease of 0.047 to 0.037 Å.

Several structural parameters for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH calculated at the MP2/6-31G(d,p) level by Wallington et al.[5−7] are also listed in Table 1 for comparison. The bond length and bond angles for the three chlorinated methyl hydroperoxides optimized in this work show good agreement with those estimated at the MP2/6-31G(d,p) level.

As illustrated in Figure 1 and Table 1, the lowest energy conformation for the three title chlorinated hydroperoxides has the peroxy oxygen gauche to the maximum number of chlorine atoms, despite the apparent steric penalty incurred for adopting such a position. This is because the gauche orientation of the peroxy group is consistent with a tendency to minimize the repulsion between nonbonding electron pairs of oxygen atom and chlorine atom and allows for intramolecular interaction between the peroxy hydrogen atom and a chlorine atom on the methyl group. The same phenomena exists in the chlorinated methanols reported by Schneider et al.[7b]

Harmonic vibrational frequencies are calculated for the three chlorinated methyl hydroperoxides at the B3LYP/6-31G(d,p) level of theory on the basis of optimized geometries at the same level of theory. The vibrational frequencies and moments of inertia for the three chlorinated methyl hydroperoxides are given in Tables 2 and 3. In Table 2, the two lowest frequencies (corresponding to torsional motion) are omitted in calculation of entropies S°_{298} and heat capacities $C_p(T)$, but we replace their contributions with values from analysis of the internal rotations (see below). Table 2 also lists comparisons of vibrational

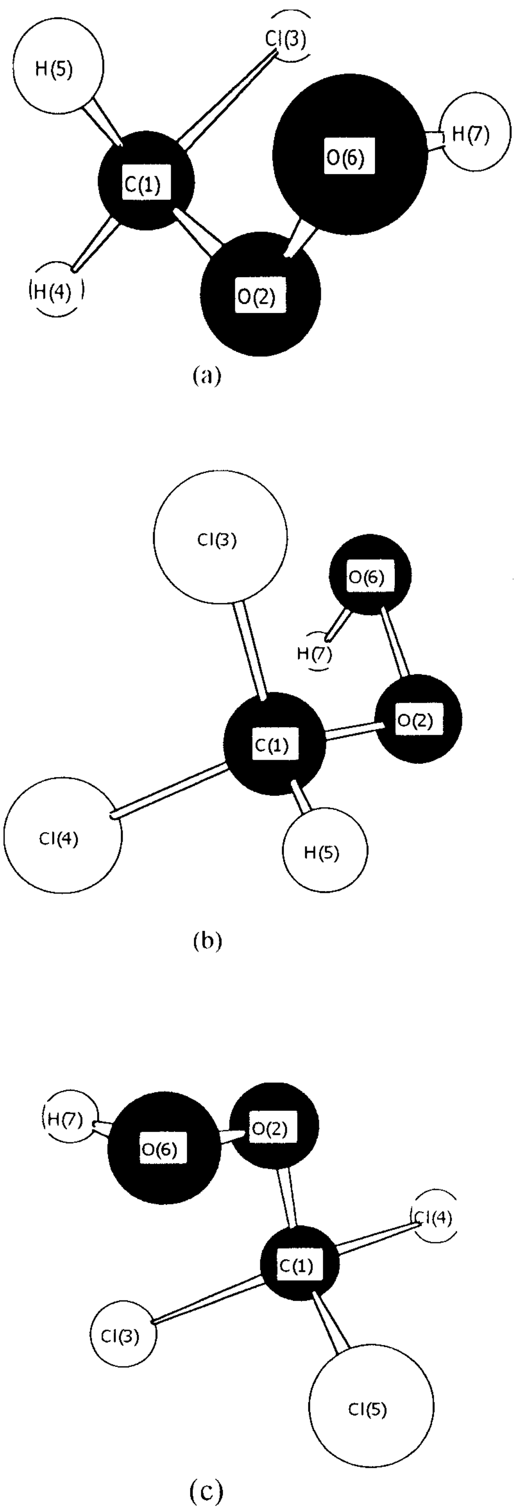

Figure 1. B3LYP/6-31G(d,p) optimized geometries of three chlorinated methyl hydroperoxides: (a) monochloromethyl hydroperoxide; (b) dichloromethyl hydroperoxide; and (c) trichloromethyl hydroperoxide. See Table 1 for structure parameters.

TABLE 1: Geometry Parameters[a] for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH

	CH_3OOH		CH_2ClOOH		$CHCl_2OOH$		CCl_3OOH	
	X_3=X_4=X_5=H		X_3=Cl, X_4=X_5=H		X_3=X_4=Cl, X_5=H		X_3=X_4=X_5=Cl	
parameters	B3LYP[b]	MP2[c]	B3LYP[b]	MP2[c]	B3LYP[b]	MP2[c]	B3LYP[b]	MP2[c]
r (C_1−O_2)	1.4168	1.4187	1.3774	1.3903	1.3702	1.3848	1.3799	1.3950
r (C_1−X_3)	1.0977	1.0895	1.8422	1.7924	1.7967	1.7651	1.8177	1.7794
r (C_1−X_4)	1.0946	1.0872	1.0903	1.0851	1.8200	1.7798	1.7842	1.7589
r (C_1−X_5)	1.0961	1.0883	1.0897	1.0846	1.0893	1.0853	1.7941	1.7640
r (O_2−O_6)	1.4566	1.4684	1.4494	1.4608	1.4456	1.4574	1.4466	1.4580
r (O_6−H_7)	0.9713	0.9691	0.9742	0.9716	0.9748	0.9721	0.9752	0.9726
$\angle$(O_2−C_1−X_3)	111.86	111.02	112.68	112.74	113.97	113.32	111.07	111.99
$\angle$(O_2−C_1−X_4)	104.60	104.34	105.98	104.91	112.10	112.10	103.01	102.33
$\angle$(O_2−C_1−X_5)	111.47	111.41	112.52	111.42	104.75	103.39	112.67	111.00
$\angle$(C_1−O_2−O_6)	106.10	104.54	107.93	106.20	110.37	108.29	109.45	107.59
$\angle$(O_2−O_6−H_7)	99.85	98.42	100.44	99.42	100.41	99.27	100.30	99.16
$\angle$(X_3−C_1−O_2−O_6)	64.08		75.96		−60.84		63.41	
$\angle$(X_4−C_1−O_2−O_6)	−177.25		−167.69		65.28		−178.72	
$\angle$(X_5−C_1−O_2−O_6)	−58.95		−43.54		−178.80		−59.27	
$\angle$(C_1−O_2−O_6−H_7)	−115.10		−95.20		−93.67		−96.31	

[a] Distances in angstroms and angles in degrees. [b] Geometry parameters optimized at the B3LYP/6−31 G(d,p) level of theory. [c] Geometry parameters optimized at the MP2/6−31 G(d,p) level of theory performed by Wallington et al.

TABLE 2: Vibrational Frequencies (cm^{-1}) for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH

species	ν1[b]	ν2[b]	ν3	ν4	ν5	ν6	ν7	ν8	ν9	ν10	ν11	ν12	ν13	ν14	ν15
CH_2ClOOH[a]	151	267	368	497	668	885	1002	1103	1275	1341	1399	1465	3106	3192	3723
CH_2ClOOH[c]	163	275	374	513	759	869	1037	1114	1308	1391	1408	1514	3189	3283	3801
CH_2ClOOH[d]						823		1061			1359				3548
$CHCl_2OOH$[a]	144	225	243	294	402	556	726	771	901	1085	1227	1332	1413	3164	3718
$CHCl_2OOH$[c]	152	240	257	312	414	586	794	827	889	1095	1302	1364	1401	3236	3796
CCl_3OOH[a]	147	201	238	258	276	333	404	436	548	766	857	932	1056	1410	3712
CCl_3OOH[c]	158	211	259	279	291	353	421	457	579	856	899	938	1074	1399	3791

[a] Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d,p) level of theory. [b] R—OOH and RO—OH torsional frequencies; these frequencies are not included in the calculation of entropies S°_{298} and heat capacities $C_p(T)$, see text. [c] Frequencies are calculated at the MP2/6-31G(d,p) level by Wallington et al. [d] Infrared frequencies observed by Wallington et al.

TABLE 3: Moments of Inertia[a] for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH

	I_a[b]	I_b	I_c
CH_2ClOOH	124.2324	523.8976	600.9131
$CHCl_2OOH$	533.0179	638.9753	1000.1587
CCl_3OOH	945.1712	1098.1882	1239.2754

[a] Optimized at the B3LYP/6-31G(d,p) level of theory. [b] Units in amu-Bohr^2.

frequencies calculated at the MP2/6-31G(d,p) level and infrared frequencies observed by Wallington et al.[6−7]

2. Enthalpies of Formation ($\Delta H_f{}^{\circ}{}_{298}$). The enthalpies of formation ($\Delta H_f{}^{\circ}{}_{298}$) are estimated using total energies and calculated $\Delta H^{\circ}_{rxn,298}$ for the listed reactions. Five reaction schemes, three of which are isodesmic, calculated $\Delta H^{\circ}_{rxn,298}$ for each reaction and evaluated literature thermodynamic properties for these reference reactants and products are utilized to estimate $\Delta H_f{}^{\circ}{}_{298}$ of the target chlorinated methyl hydroperoxides. The enthalpies of reaction ($\Delta H^{\circ}_{rxn,298}$) are estimated using total energies obtained by the density functional and *ab initio* calculations. Zero-point energies (ZPVEs) and thermal correction to 298.15 K are taken into account. The total energies at 298 K from B3LYP/6-31G(d,p), B3LYP/6-311+G(3df+2p), QCISD(T)/6-31G(d,p), and CBSQ//B3** calculation levels, scaled ZPVEs, and thermal corrections to 298.15 K are listed in Table 4.

As an example, one reaction used to calculated $\Delta H_f{}^{\circ}{}_{298}$ (CH_2ClOOH) is

$$\Delta H^{\circ}_{rxn,298} = \Delta H_f{}^{\circ}{}_{298}(CH_3OOH) + \Delta H_f{}^{\circ}{}_{298}(CH_3CH_2Cl) - \Delta H_f{}^{\circ}{}_{298}(CH_2ClOOH) - \Delta H_f{}^{\circ}{}_{298}(CH_3CH_3)$$

The reaction enthalpies and $\Delta H_f{}^{\circ}{}_{298}$'s of the three chlorinated methyl hydroperoxides obtained from the use of the reaction schemes are tabulated in Tables 5 and 6. The enthalpies of formation and the uncertainties of the reference species (data from literature), which are used to determined $\Delta H_f{}^{\circ}{}_{298}$ values studied in this work, are also listed in Table 4.

CH_3OOH is an important reference species for above reaction schemes, and it is worth while discussing the selection of its $\Delta H_f{}^{\circ}{}_{298}$ value. The enthalpy of formation for CH_3OOH has been reported to be −31.8 kcal/mol by Lay et al.;[33] −31.71 kcal/mol by Jungkamp et al.;[34] −31.3 kcal/mol by Nangia et al.;[35] −32.2 kcal/mol by Knyazev.[8] Three isodesmic reactions are selected to further estimate $\Delta H_f{}^{\circ}{}_{298}$ for CH_3OOH using the methyl peroxy ($CH_3OO^{\bullet}$) enthalpy value reported by Knyazev et al.[8] The results are shown in Table 7. Because reaction 2 in Table 7 is the best isodesmic reaction and the calculated $\Delta H_f{}^{\circ}{}_{298}$ is close to the value reported by Lay et al.,[33] we select −31.8 kcal/mol as the enthalpy of formation for this important reference species CH_3OOH.

Table 6 shows that the calculated enthalpy of formation is nearly constant, for each chlorohydroperoxide, at the CBSQ//B3** calculation level throughout the five reaction schemes. The CBSQ//B3** calculated $\Delta H_f{}^{\circ}{}_{298}$ averaged over the five respective reactions for CH_2ClOOH is −41.78 ± 0.71 kcal/mol; the $\Delta H_f{}^{\circ}{}_{298}$ for $CHCl_2OOH$ is −45.90 ± 2.00 kcal/mol; the $\Delta H_f{}^{\circ}{}_{298}$ for CCl_3OOH is −47.69 ± 3.40 kcal/mol. These error limits are the calculated deviations from the five reaction schemes and do not include the error from uncertainties in the standard compound values. The calculation results for the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), and QCISD(T)/6-31G(d,p) calculation levels result in uniform $\Delta H_f{}^{\circ}{}_{298}$ values

TABLE 4: Total Energies[a] at 298 K and $\Delta H_f{}^\circ_{298}$ for Species in the Reaction Schemes

	B3LYP/6-31 G(d,p)	B3LYP/6-311+ G(3df,2p)	QCISD(T)/6-31 G(d,p)	CBSQ//B3LYP/6-31 G(d,p)	ZPVE[b]	Therm Corr[c]	$\Delta H_f{}^\circ_{298}$[d]
CH_2ClOOH	−650.405 353 1	−650.513 813 3	−649.349 970 2	−649.751 2186	28.66	3.60	
$CHCl_2OOH$	−1109.999 424 6	−1110.142 232 9	−1108.383 635 9	−1108.906 495 4	22.71	4.19	
CCl_3OOH	−1569.586 841 7	−1569.764 828 2	−1567.412 699 1	−1568.059 090 9	16.23	4.90	
CH_4	−40.476 061 7	−40.488 794 1	−40.341 605 0	−40.405 300 8	27.70	2.39	−17.89[e] ± 0.07
CH_3Cl	−500.071 397 0	−500.117 743 3	−499.373 546 6	−499.556 713 8	23.33	2.49	−19.60[f] ± 0.12
CH_2Cl_2	−959.665 491 3	−959.746 850 6	−958.405 631 2	−958.710 282 1	18.13	2.84	−22.83[e] ± 0.29
$CHCl_3$	−1419.255 437 9	−1419.372 527 8	−1417.435 113 5	−1417.863 764 5	12.23	3.40	−24.20[g] ± 0.31
CH_3OOH	−190.797 370 1	−190.873 332 6	−190.306 013 2	−190.587 220 1	33.68	3.30	−31.8[h] ± 0.94
H_2O	−76.395 006 2	−76.438 518 2	−76.206 908 1	−76.332 953 2	13.15	2.37	−57.80[g] ± 0.1
HOCl	−535.932 086 5	−536.004 360 7	−535.178 477 8	−535.417 512 6	8.07	2.44	−17.80[e] ± 0.5
H_2	−1.165 260 6	−1.166 735 1	−1.151 865 3	−1.1625 320	6.26	2.07	0.00[e] ± 0.0
HCl	−460.790 878 6	−460.828 474 9	−460.214 566 8	−460.343 785 2	4.14	2.07	−22.06[e] ± 0.05
CH_3CH_3	−79.760 847 2	−79.783 602 4	−79.507 639 8	−79.624 778 1	46.10	2.77	−20.24[g] ± 0.12
CH_3CH_2Cl	−539.362 542 1	−539.419 120 2	−538.546 625 0	−538.784 168 6	41.12	3.12	−26.84[f] ± 0.26
CH_3CHCl_2	−998.959 619 9	−999.051 132 0	−997.583 0538	−997.943 266 1	35.45	3.63	−31.09[f] ± 0.67
CH_3CCl_3	−1458.549 738 2	−1458.676 677 9	−1456.614 298 8	−1457.099 632 7	29.21	4.28	−34.01[f] ± 0.41
CH_3CH_2OOH	−230.090 414 4	−230.175 425 7	−229.481 049 7	−229.815 649 6	51.37	3.96	−39.9[h] ± 0.53
HOOH				−151.373 099 8	16.24	2.64	−32.53[e]
$CH_3O^\bullet$				−114.870 211 4	22.49	2.48	4.10 ± 1.0[i]
$HOO^\bullet$				−150.735 417 1	8.68	2.38	3.50 ± 0.5[j]
$CH_3OO^\bullet$				−189.953 104 4	26.48	3.02	2.15 ± 1.22[k]

[a] Total energy calculation based on the geometries optimized at B3LYP/6-31G(d,p) level of theory, ZPVE's and thermal corrections to 298 K are included. Units in Hartree. [b] ZPVE: scaled zero-point energies in kcal/mol. Two hindered rotational frequencies are included in ZPVE, which are scaled by 0.9806 (Scott and Radom). [c] Therm Corr: Thermal corrections in kcal/mol. [d] Units in kcal/mol. The uncertainties are evaluated from ref 36 and 37. [e] Reference 38. [f] Reference 39. [g] Reference 40. [h] Reference 33. [i] Reference 41. [j] Reference 42. [k] Reference 8.

TABLE 5: Reaction Enthalpies[a] at 298K

reaction series	B3LYP/ 6-31G(d,p)	B3LYP/ 6-311+G(3df,2p)	QCISD(T)/ 6-31G(d,p)	CBSQ//B3LYP/ 6-31G(d,p)
1. $\mathit{CH_2ClOOH} + CH_4 \rightarrow CH_3OOH + CH_3Cl$	7.94	7.24	7.54	7.90
$\mathit{CHCl_2OOH} + CH_4 \rightarrow CH_3OOH + CH_2Cl_2$	7.92	6.80	8.53	8.97
$\mathit{CCl_3OOH} + CH_4 \rightarrow CH_3OOH + CHCl_3$	6.34	4.87	8.27	8.41
2. $\mathit{CH_2ClOOH} + CH_3CH_3 \rightarrow CH_3OOH + CH_3CH_2Cl$	3.95	3.11	3.12	2.89
$\mathit{CHCl_2OOH} + CH_3CH_3 \rightarrow CH_3OOH + CH_3CHCl_2$	2.06	0.86	1.39	0.49
$\mathit{CCl_3OOH} + CH_3CH_3 \rightarrow CH_3OOH + CH_3CCl_3$	0.36	−0.99	0.02	−1.87
3. $\mathit{CH_2ClOOH} + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_3Cl$	2.75	2.66	1.89	2.28
$\mathit{CHCl_2OOH} + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_2Cl_2$	2.74	2.23	2.88	3.35
$\mathit{CCl_3OOH} + CH_3CH_3 \rightarrow CH_3CH_2OOH + CHCl_3$	1.15	0.30	2.62	2.80
4. $\mathit{CH_2ClOOH} + H_2 \rightarrow CH_3OOH + HCl$	−11.07	−13.34	−11.76	−10.83
$\mathit{CHCl_2OOH} + 2H_2 \rightarrow CH_3OOH + 2HCl$	−30.86	−34.25	−29.98	−27.13
$\mathit{CCl_3OOH} + 3H_2 \rightarrow CH_3OOH + 3HCl$	−54.83	−58.81	−51.09	−45.11
5. $\mathit{CH_2ClOOH} + H_2O \rightarrow CH_3OOH + HOCl$	44.49	46.84	45.42	49.85
$\mathit{CHCl_2OOH} + 2H_2O \rightarrow CH_3OOH + 2HOCl$	80.25	86.10	84.39	94.23
$\mathit{CCl_3OOH} + 3H_2O \rightarrow CH_3OOH + 3HOCl$	111.84	121.72	120.47	136.92

[a] Reaction enthalpies include thermal correction and zero-point energy. Units in kcal/mol. Reaction series 1, 2, and 3 are isodesmic reaction, 4 and 5 are not. No reaction series conserves groups.

among the three isodesmic reaction schemes. The average $\Delta H_f{}^\circ_{298}$ from three isodesmic reaction schemes at the B3LYP/6-31G(d,p) level are −41.94, −44.87, and −45.13 kcal/mol for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH, respectively. These values are in good agreement (within ± 0.5 kcal/mol) with the average $\Delta H_f{}^\circ_{298}$ from the higher level CBSQ//B3** calculations (see also Table 6). The agreement suggests that the economical calculations at the B3LYP/6-31G(d,p) level, with isodesmic reactions, will be accurate for similar compounds with large numbers of heavy atoms.

Overall, results among the four calculation methods appear quite consistent for the three isodesmic reaction series. The enthalpy values derived between reaction schemes (1) and (3) show deviation within 0.1 kcal/mol at the QCISD(T) and CBSQ//B3** levels. The enthalpy values derived from reaction scheme (2) result in data that is up to 3 kcal/mol different for the trichlorohydroperoxide. This is because the chemical environment in reaction Scheme 2 is slightly different than that of reaction Schemes 1 and 3. In reaction Schemes 1 and 3, the changed environment of the C−Cl bond in CH_3Cl is adjacent to terminal H atoms that are relatively electropositive. The C−Cl bond in CH_2ClOOH is adjacent to one nonterminal −OOH group. In reaction Scheme 2, the changed environment involves a methyl group, not C−H. We suggest that the general environment in reaction Scheme 2 results in a better cancellation of errors than those of reaction Schemes 1 and 3. The consistency of the data across calculation levels supports this postulate.

There is marginal consistency for CH_2ClOOH and $CHCl_2OOH$ across reaction Scheme 4, which is not isodesmic, but uses H_2 and HCl for element balance; enthalpy data here are inconsistent for CCl_3OOH. QCISD values in Scheme 4 are all in good agreement, CBSQ results appear low, and B3LYP/6-311+G(3d,2p) calculation values are high relative to the isodesmic reaction schemes.

Density functional and QCISD calculated enthalpies from reaction Scheme 5, which uses H_2O and HOCl for element balance, are inconsistent with data from the other reaction schemes; CBSQ//B3* values are, however, much better. All of the calculated values, with the exception of CBSQ, are high, and the magnitude of error appears to scale with the coefficient

TABLE 6: Calculated $\Delta H_f^\circ{}_{298}$ for Chlorinated Methyl Hydroperoxides vs Reaction[a]

reaction series	B3LYP/ 6-31G(d,p)	B3LYP/ 6311+G(3df,2p)	QCISD(T)/ 6-31G(d,p)	CBSQ//B3**	error limits[c]
1. $CH_2ClOOH + CH_4 \rightarrow CH_3OOH + CH_3Cl$	−41.45	−39.04	−41.05	−41.41	± 1.13
$CHCl_2OOH + CH_4 \rightarrow CH_3OOH + CH_2Cl_2$	−44.66	−43.54	−45.27	−45.71	± 1.30
$CCl_3OOH + CH_4 \rightarrow CH_3OOH + CHCl_3$	−44.44	−42.98	−46.38	−46.52	± 1.32
2. $CH_2ClOOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CH_2Cl$	−42.35	−41.51	−41.52	−41.29	± 1.32
$CHCl_2OOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CHCl_2$	−44.71	−43.51	−44.04	−43.14	± 1.73
$CCl_3OOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CCl_3$	−45.93	−44.58	−45.59	−43.70	± 1.47
3. $CH_2ClOOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_3Cl$	−42.01	−41.92	−41.15	−41.54	± 0.77
$CHCl_2OOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_2Cl_2$	−45.23	−44.72	−45.37	−45.84	± 0.94
$CCl_3OOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CHCl_3$	−45.01	−44.16	−46.48	−46.66	± 0.96
4. $CH_2ClOOH + H_2 \rightarrow CH_3OOH + HCl$	−42.79	−40.52	−42.10	−43.03	± 0.99
$CHCl_2OOH + 2H_2 \rightarrow CH_3OOH + 2HCl$	−45.06	−41.67	−45.94	−48.79	± 1.04
$CCl_3OOH + 3H_2 \rightarrow CH_3OOH + 3HCl$	−43.15	−39.17	−46.89	−52.87	± 1.09
5. $CH_2ClOOH + H_2O \rightarrow CH_3OOH + HOCl$	−36.29	−38.64	−37.22	−41.65	± 1.54
$CHCl_2OOH + 2H_2O \rightarrow CH_3OOH + 2HOCl$	−32.05	−37.90	−36.19	−46.02	± 2.14
$CCl_3OOH + 3H_2O \rightarrow CH_3OOH + 3HOCl$	−23.64	−33.52	−32.27	−48.72	± 2.74
average value and deviation for CH_2ClOOH[b]:	−41.94±0.45	−40.82 ± 1.56	−41.24 ± 0.25	−41.41 ± 0.13	
average value and deviation for $CHCl_2OOH$[b]:	−44.87±0.32	−43.92 ± 0.69	−44.89 ± 0.74	−44.90 ± 1.52	
average value and deviation for CCl_3OOH[b]:	−45.13±0.75	−43.91 ± 0.83	−46.15 ± 0.49	−45.63 ± 1.67	

[a] Units in kcal/mol. [b] Average enthalpy of formation and deviations between reaction schemes 1, 2 and 3. Uncertainties of reference compound enthalpy not included. [c] Deviations from the uncertainty in reference compound enthalpies. Reaction schemes, 1, 2, and 3 are isodesmic; reaction Schemes 4 and 5 are not isodesmic.

TABLE 7: Reaction Enthalpies and Enthalpies of Formation for Methyl Hydroperoxide[a]

reaction series	$\Delta H^\circ{}_{rxn,298}$ (kcal/mol)	$\Delta H_f^\circ{}_{298}$ (kcal/mol)
1. $CH_3OOH + H_2O \rightarrow HOOH + CH_3OH$	8.05	−30.86
2. $CH_3OOH + HOO^\bullet \rightarrow HOOH + CH_3OO^\bullet$	−2.24	−31.64
3. $CH_3OOH + CH_3O^\bullet \rightarrow CH_3OH + CH_3OO^\bullet$	−18.77	−31.26

[a] Reaction enthalpies and enthalpies of formation are calculated at the CBSQ//B3** level. For the values of reference species, see Table 4.

of H_2O and HOCl, suggesting a significant error in calculation of one or both of these species. The CBSQ data provides support for accuracy of CBSQ/B3** calculation enthalpies using the methods in this study.

There are three conformers of the chloromethyl and dichloromethyl hydroperoxides. The total electronic energies, including ZPVE and thermal correction to 298 K of the CH_2ClOOH, $CHCl_2OOH$ conformers are estimated at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) calculation levels. Energy difference values of the conformers at the above levels are listed in Table 8. $\Delta H_f^\circ{}_{298}$ of the rotational conformers are calculated at the CBSQ//B3LYP** level using three isodesmic reaction schemes. The statistical distribution and overall $\Delta H_f^\circ{}_{298}$ of three chlorinated methyl hydroperoxides are also listed in Table 8. The energy difference values of the conformers at the B3LYP/6-311+G(3df,2p), QCISD(T) and CBSQ//B3** levels show similar values. The energy difference values at the CBSQ//B3** calculation level are used to calculate the statistical distribution of rotation conformers.

The accuracy of the enthalpies of formation obtained theoretically is controlled by several factors: the level of sophistication (method + basis set) applied to calculate the electronic energy, the reliability of the enthalpies of formation of the reference compounds, the uncertainty in the thermal corrections, and the choice of the working chemical reaction used in the cancellation of calculation errors. The maximum uncertainty in enthalpy values for the reference compounds is listed in Table 6, with individual compound uncertainties in Table 4. The summed uncertainty in enthalpy on the standards in the working reactions as well as averaged deviations in enthalpies from the all of the calculation levels in the isodesmic reaction schemes are within the error limits of CBSQ//B3** values. The ZPVE and thermal correction in data of Table 4 have small contributions to the error on a relative base. Scott and Radom report errors after scaling (0.9806) for B3LYP/6-31G(d,p) of 0.1 kcal/mol for ZPVE in their study of 39 molecules, incorporating 1066 known vibrations. They also report errors of ca. 0.01 kcal/mol for thermal correction from 0 to 298 K in density function theory.[23] These reported error values are likely smaller than in this study; but we assume that they are nonrandom, that they are canceled in the isodesmic reactions to a significant extent. The overall average (using the three isodesmic reactions based on all the four calculation level) $\Delta H_f^\circ{}_{298}$ of CH_2ClOOH, $CHCl_2OOH$, CCl_3OOH are −41.35 ± 2.14 kcal/mol, −44.65 ± 2.63 kcal/mol, −45.20 ± 2.71 kcal/mol, respectively. The $\Delta H_f^\circ{}_{298}$ from

TABLE 8: Enthalpy and Energy Difference of the Conformers, Relative Fraction, and Overall $\Delta H_f^\circ{}_{298}$ for Chlorinated Methyl Hydroperoxides

	ΔE of conformers (kcal/mol)						
	B3LYP/ 6-31G(d,p)	B3LYP/ 6-311+G(3df,2p)	QCISD(T)/ 6-31G(d,p)	CBSQ//B3LYP/ 6-31G(d,p)	$\Delta H_f^\circ{}_{298}$ [d] (kcal/mol)	relative fraction	final $\Delta H_f^\circ{}_{298}$ (kcal/mol)
$CH_2ClOOH(2)$[a]					−41.41	0.4998	
$CH_2ClOOH(1)$[b]	5.65	4.92	4.32	4.36	−37.05	0.003	−41.41 ± 1.45
$CHCl_2OOH(1)$[a]					−44.90	0.6018	
$CHCl_2OOH(1)$[b]	0.33	0.16	−0.01	0.29	−44.61	0.3687	
$CHCl_2OOH(1)$[c]	2.34	1.90	1.75	1.79	−43.11	0.0293	−44.74 ± 3.25
CCl_3OOH					−45.63	1.0000	−45.63 ± 3.14

[a] The OH−H anti conformer in CH_2ClOOH and $CHCl_2OOH$. Units in hartree. [b] The OH−Cl anti conformer in CH_2ClOOH and $CHCl_2OOH$. [c] The OH−Cl anti conformer in $CHCl_2OOH$. [d] Enthalpy of formation at 298 K calculated at the CBSQ//B3LYP/6-31G(d,p) level.

TABLE 9: ROO—H, RO—OH, and R—OOH Bond Energy Calculation

reaction series	bond energy (kcal/mol)
ROO—H	
$CH_3OOH \rightarrow CH_3OO^\bullet + H$	86.05
$CH_2ClOOH \rightarrow CH_2ClOO^\bullet + H$	92.28
$CHCl_2OOH \rightarrow CHCl_2OO^\bullet + H$	92.22
$CCl_3OOH \rightarrow CCl_3OO^\bullet + H$	92.21
RO—OH	
$CH_3OOH \rightarrow CH_3O^\bullet + OH$	45.33
$CH_2ClOOH \rightarrow CH_2ClO^\bullet + OH$	46.37
$CHCl_2OOH \rightarrow CHCl_2O^\bullet + OH$	48.58
$CCl_3OOH \rightarrow CCl_3O^\bullet + OH$	47.05
R—OOH	
$CH_3OOH \rightarrow CH_3 + OOH$	70.12
$CH_2ClOOH \rightarrow CH_2Cl + OOH$	72.94
$CHCl_2OOH \rightarrow CHCl_2 + OOH$	71.71
$CCl_3OOH \rightarrow CCl_3 + OOH$	67.61

TABLE 10: Enthalpies of Formation, Chloro-peroxy, Chloro-oxy and Chlor*o*-methyl Radicals

species	$\Delta H_f{}^\circ{}_{298}$ (kcal/mol)	source
$CH_2ClOO^\bullet$	−1.22	ref 8
$CHCl_2OO^\bullet$	−4.59	ref 8
$CCl_3OO^\bullet$	−5.00	ref 8
$CH_2ClO^\bullet$	−4.46	ref 43
$CHCl_2O^\bullet$	−5.56	ref 43
$CCl_3O^\bullet$	−7.49	ref 43
CH_3	34.82	ref 38
CH_2Cl	28.04	ref 44
$CHCl_2$	23.50	ref 45
CCl_3	19.00	ref 38
H	52.10	ref 38
OH	9.43	ref 46

the CBSQ//B3** calculation level (using the three isodesmic reactions) for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH are −41.40 ± 1.45 kcal/mol, −44.71 ± 3.25 kcal/mol, and −45.63 ± 3.14 kcal/mol, respectively. The error limits of $\Delta H_f{}^\circ{}_{298}$ of three chlorinated methyl hydroperoxides are obtained by adding the errors inherent in the present computational approach and the uncertainties in the experimental heats of formation.

3. **Bond Energies.** The ROO—H, RO—OH, and R—OOH bond energies are estimated using the $\Delta H_f{}^\circ{}_{298}$ from the CBSQ//B3** calculation level for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH, respectively; these results are presented in Table 9, with enthalpies of the peroxy and alkoxy radicals in Table 10. The ROO—H bond energies for three chlorinated hydroperoxides are each increased ca. 6 kcal/mol, relative to that of methyl hydroperoxide. The RO—OH bond energies increase from 45.3 in CH_3O—OH to 48.6 in $CHCl_2O$—OH, then decrease to 47 kcal/mol in CCl_3O—OH. The CX_3—OOH bond energies increase from 70.1 in CH_3—OOH to 73 in CH_2Cl—OOH and then decrease to 67.6 in CCl_3—OOH.

The increase in O—H bond energies may result from interaction between the electronegative chlorine on the methyl and electropositive peroxy hydrogen, as well as the increased electronegativity of the Cl(s) on the methyl further attracting the hydrogen's electron through the peroxy hydrogen bonding. The distances between a peroxy hydrogen atom and a chlorine atom on the methyl group are close enough for some electrostatic interaction (2.8 Å[47a]) and are less than the sum of the van der Waals radii of H and Cl (3.0 Å[47b]): 2.974, 2.851, and 2.828 Å for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH, respectively. Recent evaluations[48a] suggest significant hydrogen bonding interactions occur between C—Cl···H bonds.

There is uncertainty in the dissociation energy of a hydrogen or halogen atom from the alpha carbon of an alkyl hydroperoxide. The formation of an alkyl-radical on the alpha carbon of CH_3OOH ($\Delta H_f{}^\circ{}_{298} = -31.8$), for example, from an abstraction or simple dissociation results in $C^\bullet H_2OOH$. Estimating a C—H bond energy of 100 kcal/mol results in an estimated $\Delta H_f{}^\circ{}_{298}$ for this radical of ca. 16 kcal/mol. This radical, however, immediately dissociates to low energy products $CH_2O + OH$, which have a sum enthalpy of −16.5 kcal/mol. The dissociation to lower enthalpy products results from cleavage of a weak O—O bond; with formation of a strong double bond in the carbonyl moiety. A very different estimated bond energy of ca. 67 kcal/mol; results if one assumes the abstraction or dissociation transition state sees full energy of the final products. Methyl hypochlorites or other oxygen halogens will exhibit the same phenomena. Higher level calculations, e.g., CBSlq and CBSQ, suggest no barrier for $C^\bullet H_2OOH \rightarrow CH_2O + OH$[54] or $C^\bullet H_2OCl \rightarrow CH_2O + Cl$.

4. **Semiempirical Data.** A comparison of enthalpies of formation calculated using density functional and *ab initio* theory

TABLE 11: Reaction Enthalpies and Enthalpies of Formation for Chlorinated Methyl Hydroperoxides Using Semi-empirical AM1 and PM3 Methods

	$\Delta H_{rxn,\,298}{}^a$		$\Delta H_f{}^\circ{}_{298}{}^b$	
reaction series	AM1	PM3	AM1	PM3
1. $CH_2ClOOH + CH_4 \rightarrow CH_3OOH + CH_3Cl$	−2.889	3.084	−30.62	−36.59
$CHCl_2OOH + CH_4 \rightarrow CH_3OOH + CH_2Cl_2$	−9.259	4.747	−27.48	−41.48
$CCl_3OOH + CH_4 \rightarrow CH_3OOH + CHCl_3$	−16.882	3.360	−21.22	−41.47
2. $CH_2ClOOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CH_2Cl$	−1.469	0.822	−36.93	−39.22
$CHCl_2OOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CHCl_2$	−5.880	0.480	−36.81	−43.17
$CCl_3OOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CCl_3$	−11.176	−2.559	−34.43	−43.05
3. $CH_2ClOOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_3Cl$	−0.828	2.558	−38.47	−41.86
$CHCl_2OOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_2Cl_2$	−7.198	4.221	−35.33	−46.75
$CCl_3OOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CHCl_3$	−14.821	2.834	−29.08	−46.73
4. $CH_2ClOOH + H_2 \rightarrow CH_3OOH + HCl$	−12.145	−2.250	−41.72	−51.61
$CHCl_2OOH + 2H_2 \rightarrow CH_3OOH + 2HCl$	−31.041	−5.122	−44.89	−70.80
$CCl_3OOH + 3H_2 \rightarrow CH_3OOH + 3HCl$	−54.945	−9.775	−43.04	−88.21
5. $CH_2ClOOH + H_2O \rightarrow CH_3OOH + HOCl$	44.763	23.884	−36.56	−15.68
$CHCl_2OOH + 2H_2O \rightarrow CH_3OOH + 2HOCl$	82.775	47.146	−34.58	1.05
$CCl_3OOH + 3H_2O \rightarrow CH_3OOH + 3HOCl$	115.779	68.627	−27.58	19.57
$\Delta H_f{}^\circ{}_{298}$ of CH_2ClOOH^c:			−38.659	−41.890
$\Delta H_f{}^\circ{}_{298}$ of $CHCl_2OOH^c$:			−39.190	−46.016
$\Delta H_f{}^\circ{}_{298}$ of CCl_3OOH^c:			−34.713	−48.361

[a] Reaction enthalpies at 298 K calculated by five reaction schemes. Units in kcal/mol. [b] Enthalpies of formation at 298 K calculated by five reaction schemes. Units in kcal/mol. [c] Enthalpies of formation at 298 K calculated by MOPAC program directly.

TABLE 12: Total Energy and Internal Rotation Barriers about C−O Bond of Chlorinated Methyl Hydroperoxides

CH_2ClOOH			$CHCl_2OOH$			CCl_3OOH		
torsion angle	total energy[a]	rotational barrier[b]	torsion angle	total energy[a]	rotational barrier[b]	torsion angle	total energy[a]	rotational barrier[b]
0.0	−650.437 283 1	12.22	0.0	−1110.029 303 9	8.15	0.0	−1569.609 497 1	6.91
15.0	−650.439 168 3	11.03	6.7	−1110.028 998 3	8.34	2.1	−1569.609 468 9	6.92
30.0	−650.4439082	8.06	15.0	−1110.0294478	8.06	15.0	−1569.6105499	6.24
45.0	−650.449 927 3	4.28	30.0	−1110.032 310 2	6.26	30.0	−1569.613 958 5	4.11
60.0	−650.454 850 3	1.19	45.0	−1110.036 669 1	3.53	45.0	−1569.618 027 8	1.55
75.0	−650.456 742 7	0.01	60.0	−1110.040 476 7	1.14	60.0	−1569.620 403 2	0.06
76.0	−650.456 750 6	0.00	73.8	−1110.041 734 7	0.35	63.4	−1569.620 501 2	0.00
90.0	−650.455 611 0	0.72	75.0	−1110.041 724 8	0.35	75.0	−1569.619 428 1	0.67
105.0	−650.452 765 7	2.50	90.0	−1110.040 528 3	1.11	90.0	−1569.615 776 1	2.97
120.0	−650.449 706 5	4.42	105.0	−1110.038 539 4	2.35	105.0	−1569.611 744 3	5.50
135.0	−650.447 585 9	5.75	120.0	−1110.037 193 5	3.20	120.0	−1569.609 555 9	6.87
150.0	−650.446 890 7	6.19	128.0	−1110.037 028 5	3.30	123.4	−1569.609 468 8	6.92
150.6	−650.446 889 4	6.19	135.0	−1110.037 160 0	3.22	135.0	−1569.610 453 0	6.31
165.0	−650.447 213 5	5.98	150.0	−1110.037 979 2	2.71	150.0	−1569.614 050 4	4.05
180.0	−650.447 557 6	5.77	162.8	−1110.038 455 1	2.41	165.0	−1569.618 345 9	1.35
181.2	−650.447 558 8	5.77	165.0	−1110.038 439 0	2.42	180.0	−1569.620 484 3	0.01
195.0	−650.447 215 5	5.98	180.0	−1110.036 275 4	3.77	181.3	−1569.620 501 2	0.00
210.0	−650.446 468 0	6.45	195.0	−1110.033 751 5	5.36	195.0	−1569.618 909 8	1.00
220.0	−650.446 234 7	6.60	210.0	−1110.029 689 5	7.91	210.0	−1569.614 841 4	3.55
225.0	−650.446 311 3	6.55	225.0	−1110.027 314 1	9.40	225.0	−1569.610 943 3	6.00
240.0	−650.447 500 2	5.80	229.1	−1110.027 184 1	9.48	239.5	−1569.609 468 9	6.92
255.0	−650.452 765 7	2.50	240.0	−1110.028 079 8	8.92	240.0	−1569.609 470 9	6.92
270.0	−650.455 610 5	0.72	255.0	−1110.031 800 7	6.58	255.0	−1569.611 126 3	5.88
283.8	−650.456 751 0	0.00	270.0	−1110.036 726 4	3.49	270.0	−1569.614 872 7	3.53
285.0	−650.456 742 7	0.01	285.0	−1110.040 823 5	0.92	285.0	−1569.618 728 4	1.11
300.0	−650.454 850 3	1.19	299.0	−1110.042 290 1	0.00	300.0	−1569.620 495 8	0.00
315.0	−650.449 927 3	4.28	300.0	−1110.0422 80 9	0.01	300.7	−1569.620 500 8	0.00
330.0	−650.443 908 2	8.06	315.0	−1110.040 436 5	1.16	315.0	−1569.618 970 5	0.96
345.0	−650.439 168 2	11.03	330.0	−1110.036 289 1	3.77	330.0	−1569.615 154 7	3.35
359.1	−650.437 276 4	12.22	345.0	−1110.0319 42 4	6.49	345.0	−1569.611 319 9	5.76
360.0	−650.437 283 1	12.22	360.0	−1110.029 303 9	8.15	360.0	−1569.609 496 6	6.91

[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree. [b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

with the semiempirical MO methods, AM1 and PM3, is also performed. The results listed in Table 11 indicate that the PM3 method with isodesmic reaction schemes or the direct output values from MOPAC PM3 provide reasonable enthalpies of formation for the three chlorinated methyl hydroperoxides.

5. **Rotational Barriers.** The potential barriers for internal rotations of CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH are calculated at the B3LYP/6-31G(d,p) level. The potential energy as function of dihedral angle is determined by scanning the torsion angles from 0° to 360° at 15° intervals and allowing the remaining molecular structural parameters to be optimized.

Rotations about the C−O and O−O bonds in the three chlorinated methyl hydroperoxides show potentials consisting of three minima and three maxima. The geometries at the points of these minima and maxima are fully optimized at the B3LYP/6-31G(d,p) level. The barriers for internal rotations are calculated from the differences between the total energy of each structure and that of the global equilibrium. The total energies and calculated rotation barriers about C−O and O−O bonds for each rotational structure of three chlorinated methyl hydroperoxides are listed in Tables 12 and 13. Potential energy vs torsion angle diagrams for internal rotations about C−O and O−O bonds of the three chlorinated methyl hydroperoxides are shown in Figures 2, 3, 4, and 5. The points are the calculated values at the B3LYP/6-31G(d,p) level. The lines are the results of the Fourier expansion F1. The values of the coefficients of the Fourier expansion, a_i and b_i in equation F1, are listed in Table 14.

Figure 2 shows the potential curve for rotational barriers about the C−O bond in chloromethyl hydroperoxide. The OH−H anti conformer is most stable because it has only one nonbonding electron pair close to the Cl atom. The highest rotational barrier is 12.22 kcal/mol, corresponding to the OH−Cl eclipsed structure. The OH−Cl anti conformer, has an energy 5.77 kcal/mol above the lowest minimum and is only slightly lower, by 0.42 and 0.83 kcal/mol, than the two adjacent rotational maxima at 150° and 220° from the OH−Cl eclipsed structure. These three structures have similar energy because they all have two nonbonding electron pairs close to the Cl atom.

Figure 3 shows the calculated potential curve for rotational barriers about the C−O bond in dichloromethyl hydroperoxide. One of the two OH−Cl eclipsed structures is shown with a slightly higher energy, 9.48 versus 8.34 kcal/mol. This results from the rotation about the O−O bond, and the higher energy corresponds to the structure that has the peroxy H oriented toward the H atom in the methyl group. The third maximum that corresponds to the OH−H eclipsed structure is significantly lower, only 3.30 kcal/mol, due to intramolecular CH···O interaction[48b,48c] between the H atom in the methyl group and the O atom in the O−H bond. The nonbonded interatomic distance from the peroxy oxygen to hydrogen in the methyl group is 2.244 Å. Of the three minima, the energy of the OH−H anti conformer is 0.35 kcal/mol lower than that of a nonsymmetric OH−Cl anti conformer. This is because the interatomic distance between the peroxy H atom and the Cl atom in the symmetric OH−H anti conformer, 2.851 Å, is shorter than that of the nonsymmetric OH−Cl anti conformer, 2.907 Å. In contrast, the third minimum corresponding to a nonsymmetric structure with the O−OH bond positioned between the C−H and the C−Cl bonds is 2.06 kcal/mol higher than that of the second minimum due to the peroxy H oriented toward the H atom in the methyl group.

TABLE 13: Total Energy and Internal Rotation Barriers about O−O Bond of Chlorinated Methyl Hydroperoxides

CH_2ClOOH			$CHCl_2OOH$			CCl_3OOH		
torsion angle	total energy[a]	rotational barrier[b]	torsion angle	total energy[a]	rotational barrier[b]	torsion angle	total energy[a]	rotational barrier[b]
0.0	−650.444 919 9	7.42	0.0	−1110.028 452 8	8.33	0.0	−1569.611 763 6	5.48
10.6	−650.444 575 7	7.64	10.0	−1110.028 093 1	8.56	15.0	−1569.612 505 3	5.02
15.0	−650.444 633 3	7.60	15.0	−1110.028 171 1	8.51	30.0	−1569.614 402 7	3.83
30.0	−650.445 550 5	7.03	30.0	−1110.029 265 5	7.82	45.0	−1569.616 683 3	2.40
45.0	−650.447 168 1	6.01	45.0	−1110.031 210 0	6.60	60.0	−1569.618 624 4	1.18
60.0	−650.448 957 5	4.89	60.0	−1110.033 412 7	5.22	75.0	−1569.619 883 0	0.39
75.0	−650.450 568 6	3.88	75.0	−1110.035 450 0	3.94	90.0	−1569.620 450 5	0.03
90.0	−650.451 811 0	3.10	90.0	−1110.037 034 0	2.95	96.4	−1569.620 501 1	0.00
105.0	−650.452 627 0	2.59	105.0	−1110.038 015 3	2.33	105.0	−1569.620 414 7	0.05
120.0	−650.453 059 5	2.32	120.0	−1110.038 419 8	2.08	120.0	−1569.619 926 3	0.36
135.0	−650.453 232 8	2.21	126.9	−1110.038 455 5	2.06	135.0	−1569.619 202 3	0.82
150.0	−650.453 293 6	2.17	135.0	−1110.038 417 2	2.08	150.0	−1569.618 457 7	1.28
165.0	−650.453 385 9	2.11	150.0	−1110.038 242 3	2.19	165.0	−1569.617 901 1	1.63
180.0	−650.453 617 2	1.97	165.0	−1110.038 111 2	2.27	180.0	−1569.617 695 8	1.76
195.0	−650.454 042 9	1.70	167.8	−1110.038 107 0	2.28	180.1	−1569.617 695 8	1.76
210.0	−650.454 659 0	1.31	180.0	−1110.038 201 9	2.22	195.0	−1569.617 901 4	1.63
225.0	−650.455 396 1	0.85	195.0	−1110.038 603 1	1.97	210.0	−1569.618 457 7	1.28
240.0	−650.456 135 6	0.39	210.0	−1110.039 303 2	1.53	225.0	−1569.619 202 2	0.82
255.0	−650.456 650 2	0.06	225.0	−1110.040 182 7	0.97	240.0	−1569.619 926 1	0.36
264.3	−650.456 750 5	0.00	240.0	−1110.041 040 2	0.44	255.0	−1569.620 414 8	0.05
270.0	−650.456 708 4	0.03	255.0	−1110.041 624 7	0.07	263.7	−1569.620 501 2	0.00
285.0	−650.456 126 8	0.39	263.9	−1110.041 734 9	0.00	270.0	−1569.620 450 5	0.03
300.0	−650.454 678 1	1.30	270.0	−1110.041 672 9	0.04	285.0	−1569.619 882 8	0.39
315.0	−650.452 283 4	2.80	285.0	−1110.040 920 7	0.51	300.0	−1569.618 624 7	1.18
330.0	−650.449 322 5	4.66	300.0	−1110.039 166 5	1.61	315.0	−1569.616 683 8	2.40
345.0	−650.446 602 4	6.37	315.0	−1110.036 428 3	3.33	330.0	−1569.614 402 8	3.83
360.0	−650.444 919 9	7.42	330.0	−1110.033 178 6	5.37	345.0	−1569.612 505 6	5.02
			345.0	−1110.030 256 4	7.20	360.0	−1569.611 764 5	5.48
			360.0	−1110.028 453 6	8.33	360.0	−1569.611 764 1	5.48

[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree. [b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

TABLE 14: Coefficients of Truncated Fourier Series Representation Expansions for Internal Rotation Potentials[a]

species	a_0	a_1	a_2	a_3	a_4	a_5
$CH_2Cl-OOH$	5.031	0.954	4.143	2.290	−0.200	−0.006
$CHCl_2-OOH$	4.173	−0.220	1.786	2.603	−0.130	0.056
CCl_3-OOH	3.513	−0.016	0.169	3.431	−0.177	−0.021
$CH_2ClO-OH$	3.048	2.384	1.567	0.328	0.080	0.018
$CHCl_2O-OH$	3.317	2.747	1.890	0.300	0.069	0.013
CCl_3O-OH	1.717	1.491	1.793	0.347	0.111	0.025

	b_1	b_2	b_3	b_4	b_5
$CH_2Cl-OOH$	−0.165	−0.174	−0.560	−0.072	−0.128
$CHCl_2-OOH$	−1.288	2.110	−0.057	0.126	0.025
CCl_3-OOH	0.008	0.053	0.303	0.024	0.002
$CH_2ClO-OH$	1.577	0.457	0.024	−0.021	−0.015
$CHCl_2O-OH$	1.504	0.542	0.035	−0.025	−0.012
CCl_3O-OH	0.000	0.000	0.000	0.000	0.000

[a] Units in kcal/mol. Values of rotation barriers calculated at B3LYP/6-31G(d,p) level are used to calculate the coefficients.

Figure 4 shows the calculated symmetric rotational barriers about the C−O bond for trichloromethyl hydroperoxide. The rotational barrier is 6.92 kcal/mol, corresponding to the OH−Cl eclipsed structure, above the stable OH−Cl gauche staggered conformer.

Figure 5 shows calculated rotational barriers about the O−O bond of the three chlorinated methyl hydroperoxides. The HO−OCX$_3$ (X =H, Cl) eclipsed structures for three chlorinated methyl hydroperoxides correspond to the highest rotational barriers, because the four nonbonding electron pairs on the peroxy oxygen atoms eclipse each other. Although the conformers with the four nonbonding electron pairs on peroxy oxygen atoms are staggered, with respect to each other, they correspond to the most stable conformers. The rotational barrier about the O−O bond of dichloromethyl hydroperoxide is 0.92 kcal/mol higher than that of chloromethyl hydroperoxide. This is due to the fact the OH is affected by the repulsion from two Cl atoms in $CHCl_2OOH$ and from one Cl atom in CH_2ClOOH. For their HO−OCX$_3$ eclipsed structures, the nonbonded interatomic distance between H(5) in the methyl group and peroxy O(6) in $CHCl_2OOH$ is longer than that of CH_2ClOOH, 2.608 Å versus 2.448 Å, this may be another reason for the higher barrier for $CHCl_2OOH$. For the three HO−OCX$_3$ eclipsed structures, the interatomic distances between the peroxy H atom and the Cl (7) atoms are 2.911, 2.624, and 2.361 Å for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH respectively; it decreases with the increased chlorine substitution. For CCl_3OOH, three chlorine atoms on the methyl group result in symmetric rotation barriers about the O−O bond, and its barriers about the CO−O torsion are the lowest among the three chlorinated methyl hydroperoxides.

6. Entropy (S°_{298}) and Heat Capacity ($C_p(T)$'s ($300 \leq T/K \leq 1500$)). S°_{298} and $C_p(T)$'s calculation results using B3LYP/6-31G(d,p) determined geometries and frequencies are summarized in Table 15. TVR represents the sum of the contributions from translations, external rotations and vibrations for S°_{298} and $C_p(T)$'s. The torsion frequencies calculated for the internal rotors are not included in TVR. Instead, a more exact contribution from hindered rotations is calculated. I.R., represents the contributions from the internal rotation about C−O and O−O bonds for S°_{298} and $C_p(T)$'s. The final standard entropies also include correction terms for rotational conformers. This correction is calculated by the following formula for 1 mole of mixture:[49]

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

where n_i is the equilibrium mole fraction of the ith form. ΔS_{mixing}

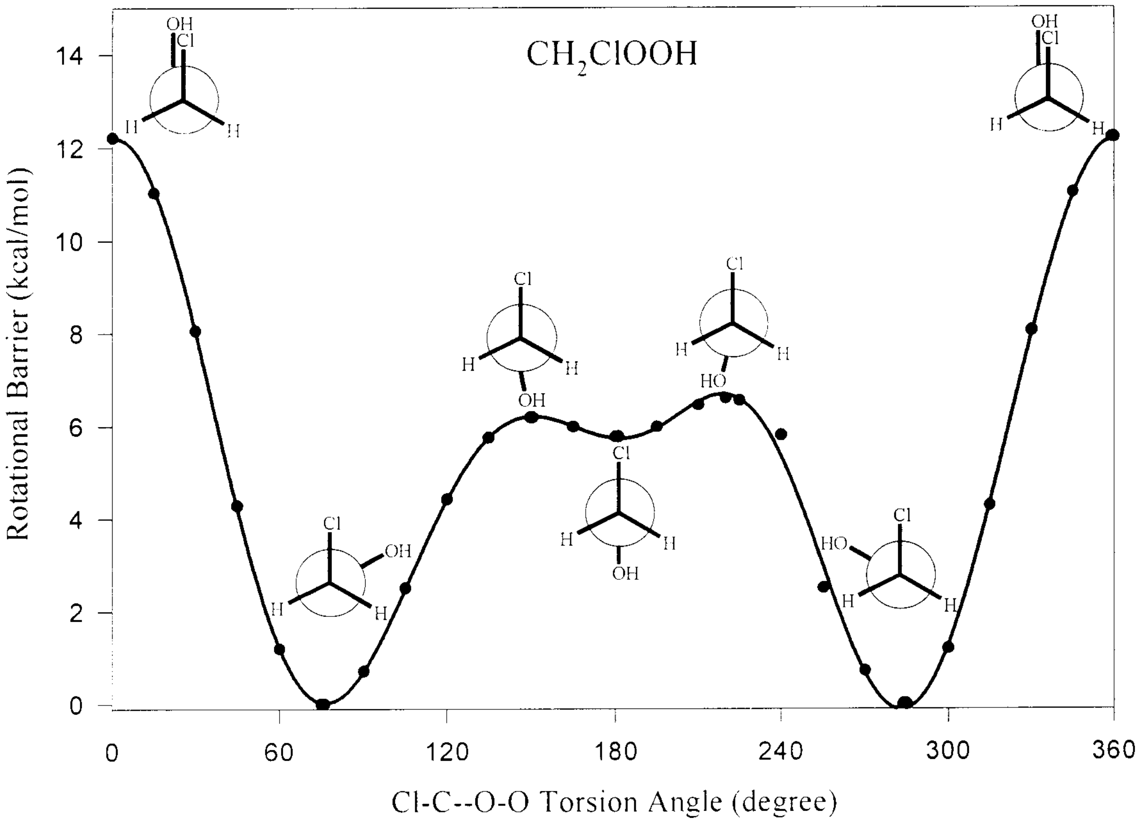

Figure 2. Potential barriers for internal rotation about the C—O bond of CH_2ClOOH. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Line is Fourier expansion, F1, with the coefficients listed in Table 14. The geometries at the points of minima and maxima are fully optimized except the points of C—O—O—H dihedral angles at 0° and 150°, at which C—O—O—H dihedral angles are frozen.

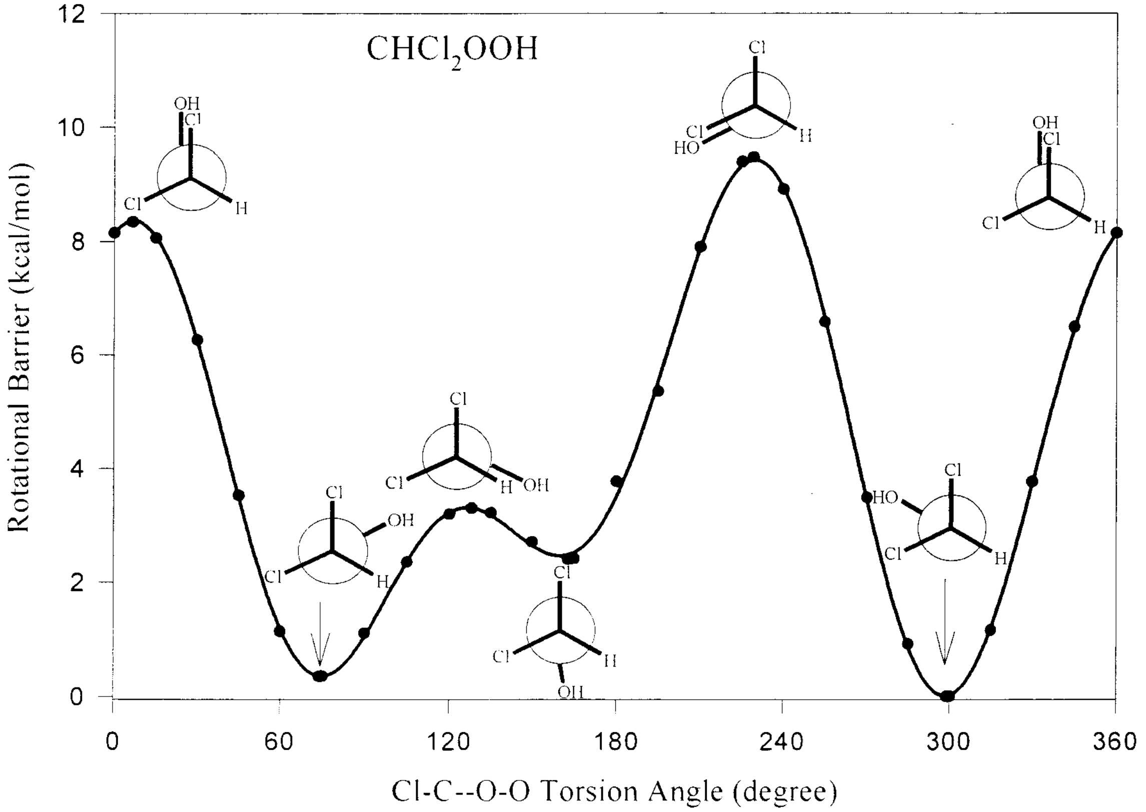

Figure 3. Potential barriers for internal rotation about the C—O bond of $CHCl_2OOH$. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Line is Fourier expansion, F1, with the coefficients listed in Table 14. The geometries at the points of minima and maxima are fully optimized.

represents the entropy of mixing of rotational conformations or optical conformations.

S°_{298} and $C_p(T)$'s values are also listed with R—OOH and RO—OH hindered torsional rotation treated as vibrations for

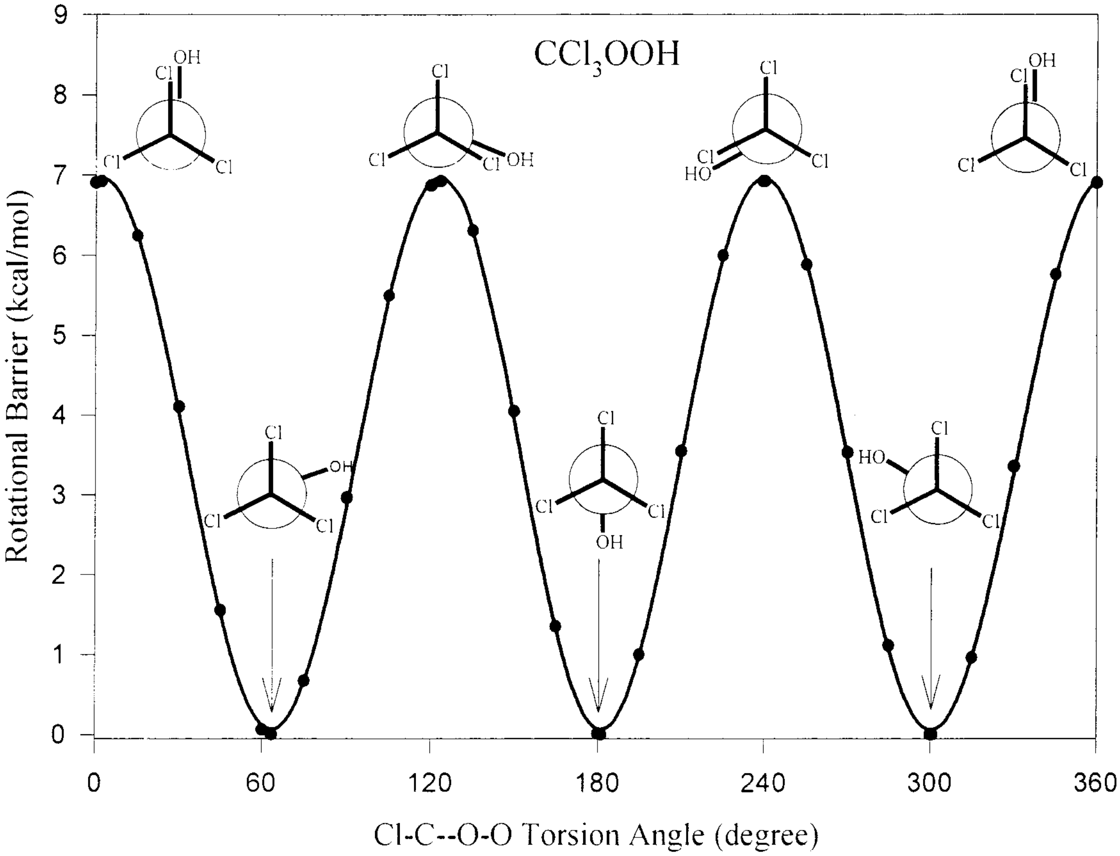

Figure 4. Potential barriers for internal rotation about the C—O bond of CCl_3OOH. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Line is Fourier expansions, F1, with the coefficients listed in Table 14. The geometries at the points of minima and maxima are fully optimized except C—O—O—H dihedral angles are frozen at the three maxima.

TABLE 15: Ideal Gas-Phase Thermodynamic Properties of Chlorinated Methyl Hydroperoxides[a]

species and symmetry No.		$\Delta H_f°_{298}$[b]	$S°_{298}$[c]	Cp300[c]	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500
CH_2ClOOH	TVR[d]		68.16	13.34	16.16	18.60	20.59	23.54	25.65	28.92
(1)	I.R,[e]		6.84	4.63	4.74	4.72	4.67	4.44	4.09	3.16
	total[f]	−41.41 ± 1.45	76.39	17.97	20.90	23.32	25.26	27.98	29.74	32.08
	total[g]		72.44	16.98	19.94	22.45	24.47	27.47	29.59	32.88
	Knyazev et al.[i]	−36.59 ± 3.97								
$CHCl_2OOH$	TVR[d]		74.38	16.76	19.70	22.00	23.75	26.19	27.82	30.24
(1)	I.R.[e]		7.11	5.37	5.39	5.08	4.70	4.06	3.57	2.73
	total[f]	−44.74 ± 3.25	83.03	22.13	25.09	27.08	28.45	30.25	31.39	32.97
	total[g]		79.05	20.47	23.52	25.88	27.66	30.13	31.77	34.21
	Catoire et al.[h]	− 46.3 ± 4								
	Knyazev et al.[i]	−39.96 ± 3.39								
CCl_3OOH	TVR[d]		78.01	21.02	23.90	25.89	27.29	29.07	30.15	31.65
(3)	I.R.[e]		8.90	3.87	3.85	3.79	3.70	3.45	3.12	2.39
	total[f]	−45.63 ± 3.14	86.91	24.89	27.75	29.68	30.99	32.52	33.27	34.04
	total[g]		82.85	24.76	27.74	29.78	31.21	33.01	34.10	35.61
	Catoire et al.[h]	−48.4 ± 4								
	Knyazev et al.[i]	−40.37 ± 2.84								

[a] Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm. R—OOH and RO—OH torsional frequencies are excluded in the calculations of entropies and heat capacities. Instead, a more exact contribution from hindered rotations about the C—O and O—O bonds is included. [b] Units in kcal/mol. [c] Units in cal/mol.K. [d] The sum of contributions from translations, external rotations, and vibrations. [e] Contribution from internal rotation about the C—O and O—O bonds. [f] Symmetry number is taken into account (−Rln(symmetry number)). [g] Thermodynamic properties in the standard state of an ideal gas at 1 atm. R—OOH and RO—OH torsional frequencies are treated as vibrations in the calculations of entropies and heat capacities. [h] Reference 7a. [i] Reference 8.

comparison in Table 15. The differences in standard entropy between two different methods (internal rotor and vibration) are large, 3.96, 3.95, and 4.06 cal/mol•K for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH, respectively. The differences in heat capacities are relatively small, within 1 cal/mol•K.

Table 15 also lists comparisons with previous literature data. Our results show enthalpy values to be about 4.8 kcal/mol lower than the enthalpy data reported by Knyazev et al.[8] but slightly higher than those reported by Catoire et al.[7a] This discrepancy may be a result of two effects: one is a slightly stronger ROO—H bond energy of the chlorinated hydroperoxides due to the electron withdrawing effects of the Cl(s), and the second is the occurrence of an intramolecular interaction between the peroxy hydrogen atom and a chlorine on the methyl group. Knyazev's

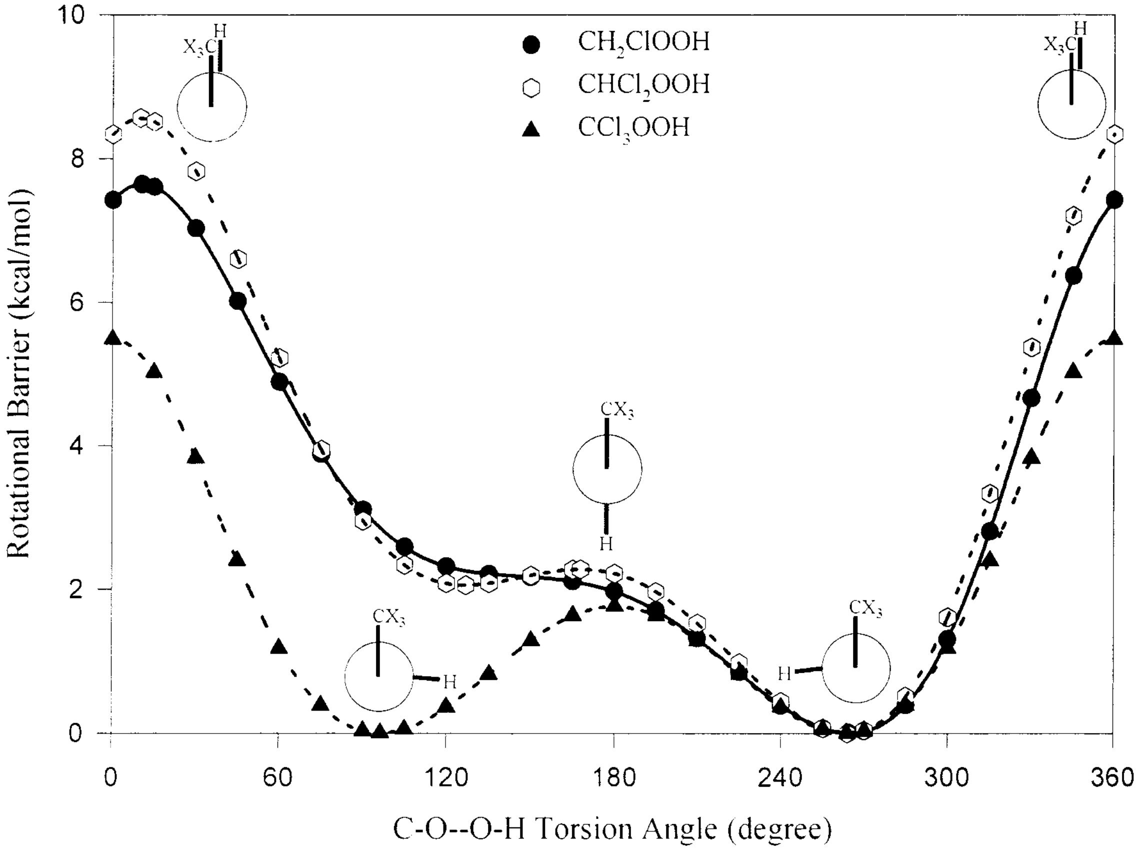

Figure 5. Potential barriers for internal rotation about the O—O bond of the three chlorinated methyl hydroperoxides. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Lines are Fourier expansions, F1, with the coefficients listed in Table 14. The geometries at the points of minima and maxima are fully optimized. X stands for Cl or H atom.

TABLE 16: Group Values

groups	$\Delta H_f{}^\circ{}_{298}$[a]	$S^\circ{}_{298}$[b]	Cp300[b]	Cp400	Cp500	Cp600	Cp800	Cp1000
OO/C/H[c]	−23.50	36.84	9.74	10.47	11.00	11.74	12.19	12.91
C/Cl/H$_2$/OO	−17.91	38.17	8.23	10.43	12.32	13.52	15.79	16.83
C/Cl$_2$/H/OO	−21.24	44.81	12.39	14.62	16.08	16.71	18.06	18.48
C/Cl$_3$/OO	−21.13	50.87	15.15	17.28	18.68	19.25	20.33	20.36

[a] Units in kcal/mol. [b] Units in cal/mol•K. [c] Reference 53.

values are calculated from the experimental heats of formation of the R• (radicals), the values of ΔH°_{298} (R + O_2 = RO_2), and a bond energy DH°_{298}(ROO—H) = 87.5 kcal/mol where this value is assumed to be independent of R.

7. **Group Additivity Values.** Group additivity[49] is a straightforward and reasonably accurate calculation method to estimate thermodynamic properties of hydrocarbons and oxygenated hydrocarbons;[50] modifications have also been reported that make it useful for chlorinated and fluorinated hydrocarbons.[30,31,51,52] In this work, we develop a set of chloro-oxy hydrocarbon groups derived from the thermodynamic property data of chlorinated methyl hydroperoxides. The values are reported for the groups C/Cl/H$_2$/OO, C/Cl$_2$/H/OO, and C/Cl$_3$/OO derived from CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH, respectively. $\Delta H_f{}^\circ{}_{298}$ and C_P's of C/Cl/H$_2$/O are calculated on the basis of

$$(CH_2ClOOH) = (C/Cl/H_2/OO) + (OO/C/H)$$

S°_{298} of C/Cl/H$_2$/O is calculated on the basis of

$$(CH_2ClOOH) = (C/Cl/H_2/OO) + (OO/C/H) + R\ln(\sigma) + OI$$

where R = 1.987 cal/mol•K, σ is symmetry number, and OI stand for optical isomer group. The group values of C/Cl$_2$/H/OO and C/Cl$_3$/OO are estimated in the same manner. The selection of the initial group values is critical to the development of group additivity for accurate property estimation. These criteria are fully discussed in ref 51 and 52. The group values for $\Delta H_f{}^\circ{}_{298}$, S°_{298}, and $C_p(T)$ of OO/C/H are taken from the existing literature value.[53] The carbon−chlorine−oxygen group values are derived in this work are listed in Table 16. Table 16 shows that group value for heat of formation decrease with increased number of chlorine atoms but not in a linear progression. The carbon−chlorine−oxygen group value for entropies and heat capacities below 1500 K increase with degree of chlorine substitution as expected for the increased mass and lower vibrational frequencies.

Summary

The thermodynamic properties of three chlorinated methyl hydroperoxides are calculated using density functional and *ab initio* methods with five reaction schemes for cancellation of errors in energy. The standard enthalpies of formation, $\Delta H_f{}^\circ{}_{298}$'s are calculated using only isodesmic reaction schemes based on the B3LYP/6-31G(d, p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p), and CBSQ//B3LYP/6-31G(d,p) calculation levels and include the statistical distribution of rotational conformers. The CBSQ//B3** calculation values of $\Delta H_{f}{}^{\circ}_{298}$ do not show the large deviations for nonisodesmic reactions that are observed in the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), and QCISD(T)/6-31G(d,p) calculations. CX_3OO-H bond energies are increased ca. 6 kcal/mol compared that in CH_3-$OO-H$. The entropies S°_{298} and heat capacities ($C_p(T)$'s ($300 \leq T/K \leq 1500$)) are determined with B3LYP/6-31G(d,p) optimized geometries, and frequencies, and the entropy correction for mixing of rotational conformers is included. Enthalpy, entropy, and $C_p(T)$ properties are determined for C/Cl/H_2/OO, C/Cl_2/H/OO, and C/Cl_3/OO chloro-peroxy group for use in group additivity. Intramolecular torsion potentials are also determined.

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