

Structures, Rotational Barriers, and Thermochemical Properties of β -Chlorinated Ethyl Hydroperoxides

Hongyan Sun and Joseph W. Bozzelli*

Department of Chemistry and Environmental Science, New Jersey Institute of Technology,
Newark, New Jersey 07102

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Structures, internal rotational barriers, and thermochemical properties of 2-chloroethyl hydroperoxide, 2,2-dichloroethyl hydroperoxide, and 2,2,2-trichloroethyl hydroperoxide are computed by ab initio and density functional calculations. Molecular structures and vibrational frequencies are determined at the B3LYP/6-31G(d,p) density functional level, with single-point calculations for the energy at the B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p), and CBSQ//B3LYP/6-31G(d,p) levels. The S°_{298} and $C_p(T)$ values ($0 \leq T/K \leq 5000$) from vibrational, translational, and external rotational contributions are calculated using statistical mechanics based on the vibrational frequencies and structures obtained from the density functional study. Potential barriers for the internal rotations are calculated at the B3LYP/6-31G(d,p) level, and all minima and maxima on the torsional potentials are fully optimized. The hindered rotational contributions to S°_{298} and $C_p(T)$ are calculated by using direct integration over energy levels of the internal rotational potentials. The enthalpies of formation are calculated using isodesmic reactions, and the recommended $\Delta H_f^{\circ}_{298}$ values for $\text{CH}_2\text{ClCH}_2\text{OOH}$, $\text{CHCl}_2\text{CH}_2\text{OOH}$, and $\text{CCl}_3\text{CH}_2\text{OOH}$ are -45.47 ± 1.20 , -48.92 ± 1.50 , and -50.21 ± 1.36 kcal/mol, respectively. Interaction terms for a peroxy group with chlorine(s) on a β carbon are developed for the group additivity approach. Bond energies calculated from the enthalpies of β -chlorinated ethyl hydroperoxides and their corresponding radicals show good agreement with those from our previous studies.

Introduction

The incineration and atmospheric oxidation processes of chlorine-containing organic compounds are of major interest since such compounds can contribute to the transport of chlorine species to the atmosphere and stratosphere. The oxidation of chlorinated hydrocarbon is initiated mainly by the reaction with OH radical to produce chloroalkyl radicals that will react with O_2 to generate peroxy radicals. Chlorinated alkyl peroxy species are also formed in the atmosphere where chlorine atoms can add to olefins and then react with O_2 . Chloroalkyl hydroperoxides are produced in the further reactions of alkylperoxy radicals with the hydroperoxy radical, HO_2 , and are also formed via H-atom abstraction from other hydrocarbon species with weakly bonded hydrogen atoms. Chloroalkyl hydroperoxides are important intermediates in low-temperature oxidation such as in the initial stages of combustion and in the atmospheric photochemical oxidation of chlorohydrocarbons because peroxy radical reactions are the first step in the oxidation processes. Chloroalkyl hydroperoxides are also the logical starting molecules in estimating the thermochemistry of the corresponding chlorinated peroxy radicals.

The thermodynamic properties of chlorinated alkyl hydroperoxides are needed for understanding and predicting the reaction pathways, rate constants, and equilibrium constants in order to assess the impact of chlorocarbon degradation products on the environment. Experimental and theoretical studies on thermodynamic properties of chlorinated methyl hydroperoxides and α -chlorinated ethyl hydroperoxides have been reported,^{1–6} but there are no thermochemical data on β -chlorinated ethyl hydroperoxides in the published literature. While the activation energy for abstraction of H from chlorinated ethane is lower in

the α site than in the β site,⁷ the abstraction of H from chlorinated ethane in the β site is favored by steric factors and is also an important channel. These β site abstraction reactions will lead to the formation of β -chlorinated ethyl hydroperoxides. Enthalpy, $\Delta H_f^{\circ}_{298}$, entropy, S°_{298} , and heat capacities $C_p(T)$ for the β -chlorinated ethyl hydroperoxides ($\text{CH}_2\text{ClCH}_2\text{OOH}$, $\text{CHCl}_2\text{CH}_2\text{OOH}$, and $\text{CCl}_3\text{CH}_2\text{OOH}$) are calculated in this study using density functional and ab initio methods. These parameters are useful in the evaluation of both atmosphere and combustion reaction paths and kinetics of chlorocarbon oxidation processes.

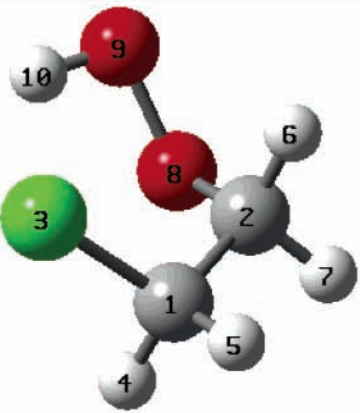
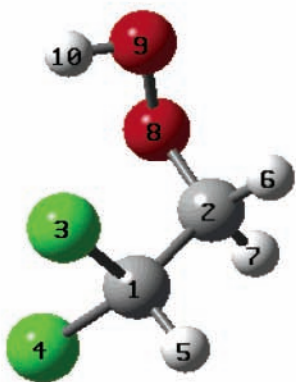
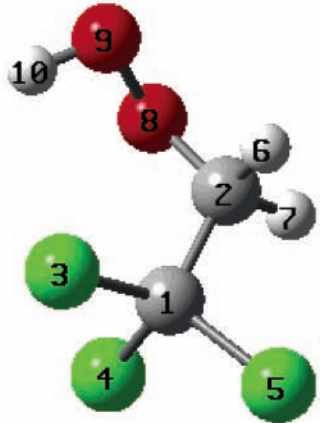
Calculation Methods

All of the density functional and ab initio calculations are performed using the Gaussian-94 program.⁸ The geometry optimization, harmonic vibration frequencies, and zero-point vibrational energies (ZPVE) are computed at the B3LYP/6-31G(d,p) level. The optimized geometry parameters are used to obtain total electronic energies 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) single-point levels of calculation. The selection of this calculation method was fully discussed in the previous studies.^{5,9,10} Total energies are corrected by ZPVE, which are scaled by 0.9806 as recommended by Scott et al.¹¹ Thermal correction is taken into account using the B3LYP structure and vibrations.

The $\Delta H_f^{\circ}_{298}$ are calculated using total energies and isodesmic reactions. Isodesmic reactions are hypothetical reactions where the number of electron pairs and the bonds of the same type are conserved on both sides of the equation, only the relationship among the bonds is altered. Contributions of vibration, translation, and external rotation to entropies and heat capacities are calculated from scaled vibrational frequencies and moments of inertia of the optimized structures. Contributions from hindered

* Corresponding author. E-mail: bozzelli@njit.edu.

TABLE 1: Geometry Parameters Optimized at the B3LYP/6-31G(d,p) Level

Molecule	Bond Length ^a	Bond Angle ^b	Dihedral Angle ^c	Frequencies ^d	Moments of Inertia ^e				
CH₂ClCH₂OOH									
	r21	1.5218	a312	113.14	d4123	118.85	104	902	1405
	r31	1.8220	a412	110.76	d5123	240.70	143	963	1461
	r41	1.0907	a512	110.71	d6213	57.82	261	1067	1480
	r51	1.0919	a621	112.01	d7213	177.20	342	1072	3036
	r62	1.0937	a721	107.27	d8213	292.70	422	1222	3097
	r72	1.0989	a821	113.52	d9821	92.75	508	1282	3114
	r82	1.4213	a982	108.29	d10982	271.05	648	1341	3166
	r98	1.4513	a1098	101.17			845	1389	3720
	r109	0.9735							
							277.36	690.73	904.71
CHCl₂CH₂OOH									
	r21	1.5317	a312	112.52	d4123	124.53	54	674	1307
	r31	1.8100	a412	111.10	d5123	242.41	147	730	1384
	r41	1.7989	a512	109.99	d6213	58.42	197	877	1402
	r51	1.0897	a621	109.31	d7213	176.87	273	952	1455
	r62	1.0948	a721	107.15	d8213	293.52	288	1043	3055
	r72	1.0963	a821	115.21	d9821	89.98	319	1094	3116
	r82	1.4112	a982	108.28	d10982	262.57	469	1252	3143
	r98	1.4524	a1098	100.93			579	1281	3738
	r109	0.9727							
							680.85	994.20	1427.15
CCl₃CH₂OOH									
	r21	1.5458	a312	111.38	d4123	121.03	66	398	1097
	r31	1.8053	a412	110.10	d5123	240.54	150	509	1305
	r41	1.7951	a512	107.39	d6213	60.68	171	565	1378
	r51	1.8035	a621	109.06	d7213	179.55	222	695	1397
	r62	1.0927	a721	106.92	d8213	296.25	256	791	1455
	r72	1.0945	a821	113.89	d9821	93.22	293	889	3077
	r82	1.4071	a982	108.56	d10982	258.09	300	1028	3145
	r98	1.4522	a1098	100.79			329	1059	3740
	r109	0.9726							
							1029.96	1670.23	1794.54

^a Bond length in Å. ^b Bond angle in degree. ^c Dihedral angle in degree. ^d Frequencies in cm⁻¹. ^e Moments of inertia in amu.Bohr².

rotors to S_{298}° and $C_p(T)$ are determined using direct integration over energy levels of the intramolecular rotational potential curves which can be represented by a truncated Fourier series expansion.⁶ The number of optical isomers and the mixing of rotational conformers are also incorporated for calculation of S_{298}° .

Results and Discussion

Geometries. The fully optimized geometric parameters along with vibrational frequencies and moments of inertia calculated at the B3LYP/6-31G(d,p) level for the three chlorinated ethyl hydroperoxides are presented in Table 1. The calculation at the B3LYP/6-31G(d,p) level gives O–O bond length of 1.45 Å in all three chlorinated ethyl hydroperoxides, which is in good

TABLE 2: Effect of β -Chlorine Substitution on Bond Length

species	C–C (Å)	C–O (Å)	O–H (Å)
CH ₃ CH ₂ OOH	1.5227	1.4266	0.9707
CH ₂ ClCH ₂ OOH	1.5218	1.4213	0.9735
CHCl ₂ CH ₂ OOH	1.5317	1.4113	0.9728
CCl ₃ CH ₂ OOH	1.5458	1.4071	0.9727

agreement with the experimental data (1.452 Å for H₂O₂) of Khachkuruzov and Przhhevskii¹² using IR spectroscopy.

Effects of β -chlorine substitution on molecular geometries can be seen from Table 2. The C–C bond lengths for β -chloroethyl hydroperoxides are increased with the increased chlorine substitution, but the C–O bond lengths decrease with

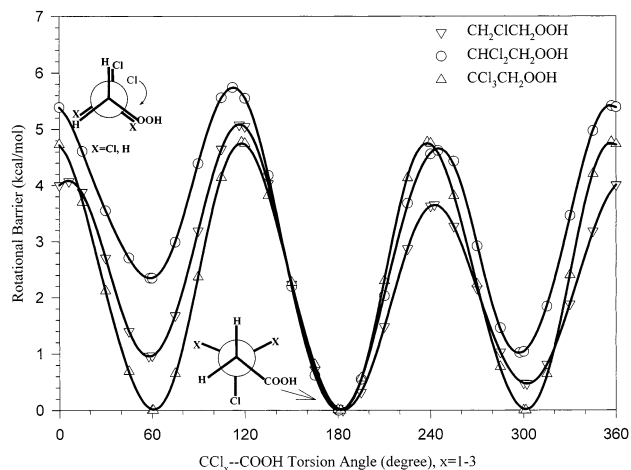


Figure 1. Potential barriers for internal rotation about the C–C bond of $\text{CH}_2\text{ClCH}_2\text{OOH}$, $\text{CHCl}_2\text{CH}_2\text{OOH}$, and $\text{CCl}_3\text{CH}_2\text{OOH}$. Points are calculated values at the B3LYP/6-31G(d,p) level. Lines are Fourier expansion with the coefficients listed in the Supporting Information (Table S2).

the increased chlorine substitution. This is because the Cl atom withdraws the electrons through its inductive effect; the lone pairs from the peroxy oxygen are oriented toward the $-\text{CH}_2-$ group, making the C–O bond length shorter than the normal C–O bond.

As illustrated in Table 1, the lowest energy conformation for the three chlorinated ethyl hydroperoxides has the $-\text{OOH}$ group gauche to the maximum number of chlorine atoms, despite the apparent steric penalty incurred. This is because the gauche orientation of the peroxy group allows for intramolecular interaction between the peroxy H atom and a Cl atom on the chloroethyl group. The interatomic distances between the peroxy H atom and a Cl atom in the chloroethyl group for $\text{CH}_2\text{ClCH}_2\text{OOH}$, $\text{CHCl}_2\text{CH}_2\text{OOH}$, and $\text{CCl}_3\text{CH}_2\text{OOH}$ are 2.642, 2.742, and 2.751 Å, respectively. These distances provide an indication to the degree of intramolecular hydrogen bonding present in these species. Hydrogen bonding can occur when the distance between a hydrogen atom and an electronegative donor is significantly less than the sum of the van der Waals radii. The van der Waals radii are 1.2 and 1.8 Å for H and Cl atoms, respectively.¹³ Due to the intramolecular hydrogen bonding between the peroxy H atom and a Cl atom, the O–H bond lengths for the three β -chloroethyl hydroperoxides increase 0.03 Å relative to normal O–H bond in $\text{CH}_3\text{CH}_2\text{OOH}$. This hydrogen bonding results in an increase in the O–H bond strength by ca. 2 kcal/mol (see Appendix Table A1). Additional chlorine substitutions on the ethyl hydroperoxides slightly decrease the O–H bond lengths 0.007 ~ 0.008 Å, and increase the O–H bond strength by 1.2 kcal/mol. These O–H bond length decreases coincide with the increased interatomic $\text{H}\cdots\text{Cl}$ distances, which are due to the increased repulsion between the electronegative O and Cl atoms.

Rotational Barriers. Potential energy as a function of torsion angle is determined by scanning the dihedral angles from 0° to 360° at 15° increments and allowing the remaining molecular structural parameters to be optimized at the B3LYP/6-31G(d,p) level. The barrier of a given rotation is then calculated as the difference between the highest point on the potential energy surface and the corresponding most stable conformer. The geometries at the points of minima and maxima are fully optimized. The calculated rotational barriers about the C–C, C–O, and O–O bonds of the target three species are shown in Figures 1, 2, and 3, respectively.

The calculated rotational barriers about the C–C bond of the three target species are shown in Figure 1. All three curves show

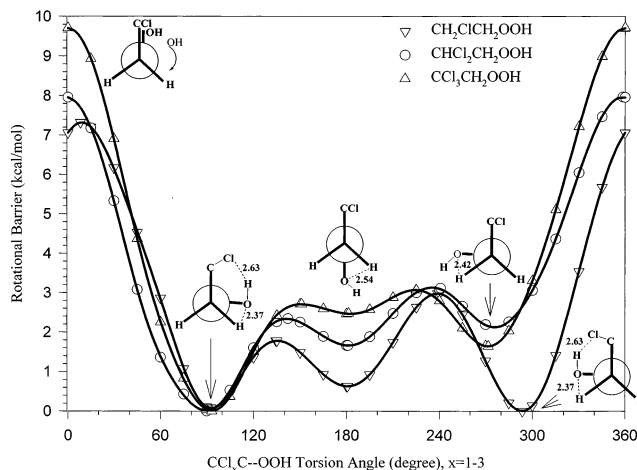


Figure 2. Potential barriers for internal rotation about the C–O bond of $\text{CH}_2\text{ClCH}_2\text{OOH}$, $\text{CHCl}_2\text{CH}_2\text{OOH}$, and $\text{CCl}_3\text{CH}_2\text{OOH}$. Points are calculated values at the B3LYP/6-31G(d,p) level. Lines are Fourier expansion with the coefficients listed in the Supporting Information (Table S2).

three minima and three maxima, with barriers between 4.77 and 5.74 kcal/mol; the curve for $\text{CCl}_3-\text{CH}_2\text{OOH}$ shows 3-fold symmetry. These curves represent typical C–C bond rotational potentials, in which the eclipsed structures are corresponding to the maxima and the staggered structures are corresponding to the minima on the potential curves.

Figure 2 shows the potential curves for rotational barriers about the C–O bond for three chloroethyl hydroperoxides. The conformers with dihedral $\angle\text{C}-\text{C}-\text{O}-\text{O} \approx 90^\circ$ are most stable because of two electrostatic interactions. The first is the $\text{O}\cdots\text{H}$ interaction between the peroxy O atom and the H atom in the $-\text{CH}_2-$ group, and the interatomic distance between them is 2.37 Å, which is significantly less than the sum of the van der Waals radii for O and H atoms (2.70 Å). The second is the $\text{H}\cdots\text{Cl}$ interaction between the peroxy H atom and the Cl atom in the chloroethyl group; the interatomic distance is 2.63 Å, which is less than the sum of the van der Waals radii of H and Cl (3.0 Å).¹³ The conformers with dihedral $\angle\text{C}-\text{C}-\text{O}-\text{O} \approx 180^\circ$ or 270° do not have the second $\text{H}\cdots\text{Cl}$ interactions, so they have 0.63~2.47 kcal/mol higher energy than the lowest energy conformers. The highest rotational barriers about the C–O bond are 7.2 ~ 9.7 kcal/mol, corresponding to the $\text{OH}-\text{CCl}_x$ ($x = 1\sim 3$) eclipsed structures.

Figure 3 shows calculated rotational barriers about the O–O bond of the three chlorinated ethyl hydroperoxides. The $\text{HO}-\text{OCCl}_x$ ($x = 1\sim 3$) eclipsed structures for the three chlorinated ethyl hydroperoxides correspond to the highest rotational barriers, because the four nonbonding electron pairs on peroxy oxygen atoms eclipse to each other. While the conformers with four nonbonding electron pairs on the peroxy oxygen atoms are staggered to each other, and the nearest interatomic distances between the peroxy H atom and the Cl atom correspond to the most stable conformers.

Enthalpy of Formation. The $\Delta H_f^\circ_{298}$ values are calculated using total energies and working isodesmic reactions. The accuracy of the enthalpies of formation obtained theoretically is controlled by several factors: the level of sophistication applied to calculate the electronic energy, the reliability of the $\Delta H_f^\circ_{298}$ of the reference compounds, the uncertainty of the ZPVE values plus the thermal corrections, and the choice of the working isodesmic reactions. The total energies of the three chlorinated hydroperoxides are listed in Supporting Information (Table S1), and the $\Delta H_f^\circ_{298}$ and their uncertainties for standard

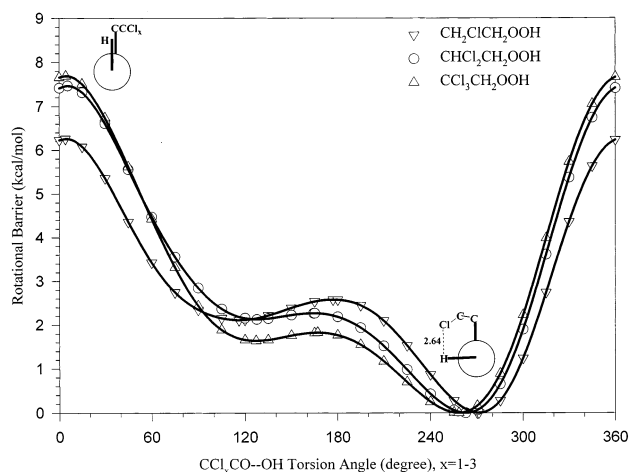


Figure 3. Potential barriers for internal rotation about the O–O bond of $\text{CH}_2\text{ClCH}_2\text{OOH}$, $\text{CHCl}_2\text{CH}_2\text{OOH}$, and $\text{CCl}_3\text{CH}_2\text{OOH}$. Points are calculated values at the B3LYP/6-31G(d,p) level. Lines are Fourier expansion with the coefficients listed in the Supporting Information (Table S2).

species used in the reactions are listed in Table 3. The reaction enthalpies and ΔH_f° values for three target species obtained from three isodesmic reactions are tabulated in Table 4. The results for ΔH_f° values in Table 4 show good consistency for the three chloroethyl hydroperoxides over three isodesmic reactions and the four calculation methods. DFT calculations show good agreement with the high level ab initio calculations, indicating the errors inherent in computations for different types of molecule are canceled to a significant extent, and lead to reliable results.

The calculated ΔH_f° in Table 4 are the enthalpy values for the pure enantiomer of the lowest energy. The recommended ΔH_f° values for $\text{CH}_2\text{ClCH}_2\text{OOH}$, $\text{CHCl}_2\text{CH}_2\text{OOH}$, and $\text{CCl}_3\text{CH}_2\text{OOH}$ are -45.47 ± 1.20 , -48.92 ± 1.50 , and -50.21 ± 1.36 kcal/mol, respectively. Here the statistical distribution of rotational conformers is considered and calculated by $\Delta H_f^\circ_{\text{mix}} = \sum n_i \Delta H_f^\circ_i$, where n_i and $\Delta H_f^\circ_i$ are the Boltzmann equilibrium mole fraction and the enthalpy of formation of the i th conformer

(see entropy and heat capacity section). The error limits of ΔH_f° are calculated by adding the deviations between the working reactions, the errors from ZPVEs and thermal corrections, and the maximum uncertainties in the ΔH_f° of reference species. Manion¹⁹ in an extensive review, compared ab initio calculated values and experimental results on the relative ΔH_f° of the isomeric chlorinated C_2 compounds with two to four chlorine atoms. He reports the theory and experiment are in good agreement with the largest deviation of 0.79 kcal/mol. Based on this comparison, our calculated ΔH_f° values for the three chlorinated ethyl hydroperoxides should have similar accuracy.

Entropy and Heat Capacity. S°_{298} and $C_p(T)$ ($300 \leq T/\text{K} \leq 1500$) calculation results using the geometries and harmonic frequencies determined at the B3LYP/6-31G(d,p) level are summarized in Table 5. The torsion frequencies, corresponding to the C–C, C–O, and O–O bond rotations, are omitted in calculation of S°_{298} and $C_p(T)$, but we replace their contributions with values from analysis of the internal rotations. TVR represent the sum of the contributions from translation, vibration, and external rotation to S°_{298} and $C_p(T)$ obtained by statistical mechanics. I.R. represent the contributions from hindered internal rotations about the C–C, C–O, and O–O bonds to S°_{298} and $C_p(T)$. This calculation is based on an optimized 3D atom coordinate for the lowest energy conformer, the respective connection to atoms of the bond about which rotation is occurring, and the coefficients of the Fourier expansion components from rotational potential curves. The coefficients of the Fourier expansion components are listed in Table S2 (Supporting Information).

The entropy correction for mixing, $\Delta S_{\text{mixing}} = -R \sum n_i \ln(n_i)$, for rotational conformers was included in the entropy calculation²⁰ where n_i is the Boltzmann equilibrium mole fraction of the i th conformer. Here, Boltzmann mole fractions at different temperatures were calculated based on the energy difference for rotational conformers at 0 K. The thermochemical parameters for heat capacity, entropy, and enthalpy corrections ($0 \leq T/\text{K} \leq 5000$) for the three target species in this work are listed in Table 6. The contributions from hindered internal rotations to

TABLE 3: ΔH_f° for Standard Species Used in Isodesmic Reactions^a

species	ΔH_f° (kcal/mol)	ref	species	ΔH_f° (kcal/mol)	ref
CH_4	-17.89 ± 0.07	14	$\text{C}_2\text{H}_5\text{Cl}$	-26.79 ± 0.26	15
C_2H_6	-20.24 ± 0.12	14	CH_3CHCl_2	-31.09 ± 0.67	16
C_3H_8	-25.02 ± 0.12	15	CH_3CCl_3	-34.01 ± 0.41	16
CH_3OOH	-31.8 ± 0.94	17	$\text{CH}_3\text{CH}_2\text{OOH}$	-39.70 ± 0.3	18
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OOH}$	-44.77 ± 0.41	18	CHCl_2OH	-65.88 ± 0.76	9

TABLE 4: Reaction Enthalpies at 298 K and Calculated Enthalpies of Formation^a

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)	
	$\Delta H^\circ_{\text{rxn}}$	ΔH_f°	$\Delta H^\circ_{\text{rxn}}$	ΔH_f°	$\Delta H^\circ_{\text{rxn}}$	ΔH_f°	$\Delta H^\circ_{\text{rxn}}$	ΔH_f°
1. $\text{CH}_2\text{ClCH}_2\text{OOH} + \text{CH}_4 \rightarrow \text{CH}_3\text{OOH} + \text{C}_2\text{H}_5\text{Cl}$	4.34	-45.09	3.35	-44.10	4.79	-45.54	5.10	-45.85
2. $\text{CH}_2\text{ClCH}_2\text{OOH} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5\text{OOH} + \text{C}_2\text{H}_5\text{Cl}$	-0.84	-45.46	-1.22	-45.08	-0.86	-45.44	-0.52	-45.78
3. $\text{CH}_2\text{ClCH}_2\text{OOH} + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_7\text{OOH} + \text{C}_2\text{H}_5\text{Cl}$	-0.32	-46.27	-1.14	-45.45	-0.20	-46.39	-0.90	-45.69
Average value and deviation ^b :								-45.77 ± 1.20
1. $\text{CHCl}_2\text{CH}_2\text{OOH} + \text{CH}_4 \rightarrow \text{CH}_3\text{OOH} + \text{CH}_2\text{Cl}_2$	1.71	-46.35	1.15	-45.79	3.44	-48.08	4.74	-49.38
2. $\text{CHCl}_2\text{CH}_2\text{OOH} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5\text{OOH} + \text{CH}_2\text{Cl}_2$	0.61	-47.97	-0.50	-46.86	1.89	-49.25	1.59	-48.95
3. $\text{CHCl}_2\text{CH}_2\text{OOH} + \text{CH}_3\text{OH} \rightarrow \text{C}_2\text{H}_5\text{OOH} + \text{CHCl}_2\text{OH}$	-11.96	-45.54	-10.75	-46.75	-9.61	-47.89	-8.17	-49.33
Average value and deviation ^b :								-49.22 ± 1.50
1. $\text{CCl}_3\text{CH}_2\text{OOH} + \text{CH}_4 \rightarrow \text{CH}_3\text{OOH} + \text{CH}_3\text{CCl}_3$	1.51	-49.43	0.19	-48.11	2.62	-50.54	2.53	-50.45
2. $\text{CCl}_3\text{CH}_2\text{OOH} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5\text{OOH} + \text{CH}_3\text{CCl}_3$	-3.67	-49.80	-4.38	-49.80	-3.03	-50.44	-3.08	-50.39
3. $\text{CCl}_3\text{CH}_2\text{OOH} + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_7\text{OOH} + \text{CH}_3\text{CCl}_3$	-3.15	-50.61	-4.30	-49.46	-2.37	-51.39	-3.47	-50.29
Average value and deviation ^b :								-50.38 ± 1.36

^a Reaction enthalpies include thermal correction and zero-point energy. Units in kcal/mol. ^b Average value and the deviation for pure enantiomer of the lowest energy at the CBSQ//B3LYP/6-31G(d,p) level.

TABLE 5: Ideal Gas-Phase Thermodynamic Properties^a

species		ΔH_f° ^b	S° ^c	C_p 300 ^c	C_p 400	C_p 500	C_p 600	C_p 800	C_p 1000	C_p 1500
CH ₂ ClCH ₂ OOH (1) ^h (2) ⁱ	TVR ^d	71.87	16.34	20.76	24.68	27.93	32.84	36.38	41.83	
	I.R. ^e	6.47	2.62	2.29	1.97	1.68	1.21	0.89	0.46	
	I.R. ^f	6.30	2.43	2.11	1.84	1.62	1.28	1.04	0.65	
	I.R. ^g	2.06	3.01	3.07	2.82	2.54	2.11	1.82	1.45	
	total	-45.47±1.20	89.24	24.41	28.23	31.32	33.77	37.44	40.13	24.41
CHCl ₂ CH ₂ OOH (1) ^h (2) ⁱ	TVR ^d	77.82	19.73	24.22	27.99	31.01	35.42	38.49	43.11	
	I.R. ^e	5.62	3.04	2.92	2.65	2.31	1.69	1.23	0.62	
	I.R. ^f	5.27	3.77	3.36	2.77	2.27	1.61	1.22	0.71	
	I.R. ^g	2.11	2.74	2.76	2.59	2.40	2.11	1.90	1.57	
	total	-48.92±1.50	92.33	29.28	33.26	35.99	38.00	40.83	42.84	46.01
CCl ₃ CH ₂ OOH (3) ^h (2) ⁱ	TVR ^d	81.69	24.02	28.38	31.82	34.47	38.22	40.74	44.46	
	I.R. ^e	6.80	1.75	1.69	1.61	1.49	1.20	0.94	0.53	
	I.R. ^f	4.96	3.87	3.58	2.97	2.43	1.71	1.30	0.79	
	I.R. ^g	2.43	2.66	2.46	2.24	2.09	1.90	1.77	1.54	
	total	-50.21±1.36	96.86	32.30	36.10	38.64	40.48	43.03	44.75	47.32

^a Thermodynamic properties are referred to a standard state of an ideal gas of at 1 atm. The enthalpy and entropy correction for mixing of rotational conformers are included. ^b Units in kcal/mol. ^c Units in cal/mol/K. ^d The sum of contributions from translations, vibrations, and external rotations. ^e Contribution from internal rotation about the C–C bond. ^f Contribution from internal rotation about the C–O bond. ^g Contribution from internal rotation about the O–O bond. ^h Symmetry number. ⁱ Optical isomer number.

TABLE 6: Ideal Gas-Phase Thermodynamic Properties

<i>T</i> (K)	CH ₂ ClCH ₂ OOH			CHCl ₂ CH ₂ OOH			CCl ₃ CH ₂ OOH		
	C_p° (cal/mol-K)	S° (cal/mol-K)	$H^\circ(T)-H^\circ(0K)$ (kcal/mol)	C_p° (cal/mol-K)	S° (cal/mol-K)	$H^\circ(T)-H^\circ(0K)$ (kcal/mol)	C_p° (cal/mol-K)	S° (cal/mol-K)	$H^\circ(T)-H^\circ(0K)$ (kcal/mol)
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	11.66	58.08	0.40	11.42	58.99	0.40	11.62	60.53	0.40
100	15.11	67.64	0.82	15.22	68.08	0.86	16.73	70.10	0.91
150	17.70	74.61	1.30	19.31	75.20	1.44	21.76	77.89	1.61
200	20.01	80.23	1.86	23.19	81.51	2.13	26.08	84.88	2.47
298.15	24.33	89.25	3.25	29.18	92.34	3.83	32.20	96.88	4.57
300	24.41	89.40	3.28	29.27	92.52	3.86	32.29	97.08	4.61
400	28.23	97.04	5.13	33.25	101.79	6.07	36.10	107.28	7.24
500	31.32	103.72	7.41	35.99	109.69	8.68	38.64	115.89	10.26
600	33.77	109.67	10.05	38.00	116.55	11.64	40.48	123.29	13.58
700	35.77	115.03	12.98	39.56	122.61	14.87	41.89	129.77	17.13
800	37.44	119.92	16.15	40.83	128.03	18.31	43.02	135.53	20.88
900	38.88	124.42	19.54	41.91	132.95	21.94	43.96	140.71	24.77
1000	40.13	128.58	23.09	42.84	137.44	25.72	44.75	145.43	28.79
1100	41.21	132.45	26.80	43.65	141.58	29.63	45.42	149.77	32.91
1200	42.17	136.08	30.65	44.36	145.42	33.65	46.00	153.77	37.12
1300	43.01	139.48	34.60	44.98	149.01	37.77	46.50	157.49	41.42
1400	43.74	142.70	38.66	45.53	152.37	41.98	46.94	160.97	45.78
1500	44.39	145.73	42.80	46.01	155.54	46.25	47.31	164.24	50.20
1600	44.96	148.62	47.02	46.44	158.53	50.60	47.64	167.31	54.67
1700	45.47	151.36	51.31	46.81	161.36	54.99	47.93	170.21	59.18
1800	45.91	153.97	55.65	47.15	164.05	59.44	48.18	172.97	63.74
1900	46.31	156.46	60.05	47.44	166.61	63.93	48.41	175.58	68.33
2000	46.66	158.84	64.50	47.70	169.05	68.47	48.60	178.08	72.95
2500	47.94	169.40	87.26	48.65	179.81	91.57	49.30	189.02	96.41
3000	48.71	178.21	110.65	49.23	188.74	115.20	49.71	198.05	120.28
3500	49.20	185.75	134.41	49.59	196.36	139.14	49.97	205.74	144.41
4000	49.53	192.34	158.44	49.84	203.00	163.30	50.13	212.43	168.71
4500	49.77	198.19	182.63	50.01	208.88	187.60	50.25	218.34	193.12
5000	49.93	203.44	206.95	50.13	214.15	212.00	50.33	223.64	217.61

$S(T)$ and $C_p(T)$ values and the entropy corrections for the rotational conformers at the different temperatures are illustrated in Tables S3–S5 for the three chlorinated ethyl hydroperoxides.

Group Additivity Correction Terms

Group additivity²⁰ is a straightforward and reasonably accurate calculation method to estimate thermodynamic properties of hydrocarbons and oxygenated hydrocarbons, but conventional group additivity does not work well for chlorocarbons or other halocarbons, as group additivity does not incorporate effects of next nearest neighbors.²¹ In this paper, we define three sets of peroxy oxygen – chlorine interaction terms that can be used with Benson type group additivity scheme for calculation of the thermodynamic properties of multichloro peroxy-hydrocarbons.

In the three chlorinated ethyl hydroperoxides, the nearest interatomic distances between the Cl atom and the O atom are 3.10 ~ 3.23 Å, so there are significant interactions between the electronegative Cl and the O atoms. The interaction values between chlorine(s) on the ethyl and the peroxy oxygen (OO/Cl, OO/Cl₂, and OO/Cl₃) are calculated from differences between the sum of defined chlorinated ethyl hydroperoxide group values and the determined thermodynamic properties of the parent compounds. The calculated interaction values are listed in Table 7. The interaction values in Table 7 indicate a several kcal/mol increase in enthalpy due to destabilizing interaction of chlorine(s) on the ethyl group with the peroxy group. The group additivity corrections for the ΔH_f° are 2.72, 3.51, and 5.02 kcal/mol for the interaction group OO/Cl, OO/Cl₂, and OO/Cl₃, respectively. Interaction terms for entropies at 298 K and heat capacities listed in Table 7 are relatively small.

TABLE 7: Thermodynamic Properties of the Peroxy-Chlorine(s) Interaction Group

interaction group	$\Delta H_f^\circ_{298}$ ^a	S°_{298} ^b	C_p300 ^b	C_p400	C_p500	C_p600	C_p800	C_p1000
INT/OO/Cl	2.72	3.20	1.15	0.88	0.46	-0.31	-0.85	-1.55
INT/OO/Cl ₂	3.51	-0.45	2.77	2.47	1.68	0.61	-0.40	-1.17
INT/OO/Cl ₃	5.02	0.48	1.95	1.43	0.61	-0.39	-1.17	-1.67

^a Units in kcal/mol. ^b Units in cal/mol/K.

Summary

Thermodynamic properties of CH₂ClCH₂OOH, CHCl₂CH₂OOH, and CCl₃CH₂OOH were calculated using density functional and ab initio methods with isodesmic reaction schemes. $\Delta H_f^\circ_{298}$ values determined by isodesmic reactions show remarkable precision at the four calculation levels. The statistical distribution of rotational conformers was taken into account for $\Delta H_f^\circ_{298}$ and S°_{298} values. S°_{298} and $C_p(T)$ ($0 \leq T/K \leq 5000$) were calculated with B3LYP/6-31G(d,p) optimized geometries and frequencies, and hindered internal rotational contributions to S°_{298} and $C_p(T)$ were calculated by intramolecular torsion

potential curves. Bond energies calculated from β -chlorinated ethyl hydroperoxides and the corresponding radicals are compared with those from previous studies. Interaction terms for peroxy group interacting with chlorine(s) on a β carbon are developed for a group additivity approach.

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Appendix**TABLE A1: Bond Energies**

reaction series	bond energy ^a (kcal/mol)	reaction series	bond energy ^b (kcal/mol)
	OO-H		OO-H
CH ₃ CH ₂ OOH → CH ₃ CH ₂ OO• + H•	85.00	CH ₃ OOH → CH ₃ OO• + H•	86.05
CH ₂ ClCH ₂ OOH → CH ₂ ClCH ₂ OO• + H•	86.38	CH ₂ ClOOH → CH ₂ ClOO• + H•	92.28
CHCl ₂ CH ₂ OOH → CHCl ₂ CH ₂ OO• + H•	87.12	CHCl ₂ OOH → CHCl ₂ OO• + H•	92.22
CCl ₃ CH ₂ OOH → CCl ₃ CH ₂ OO• + H•	87.45	CCl ₃ OOH → CCl ₃ OO• + H•	92.21
	C-H _{β}		C-H
CH ₃ CH ₂ OOH → C•H ₂ CH ₂ OOH + H•	102.76	CH ₃ CH ₂ OH → C•H ₂ CH ₂ OH + H•	102.52
CH ₂ ClCH ₂ OOH → C•HClCH ₂ OOH + H•	99.74	CH ₂ CHClOH → C•H ₂ CHClOH + H•	103.22
CHCl ₂ CH ₂ OOH → C•Cl ₂ CH ₂ OOH + H•	95.56	CHCl ₂ OH → C•Cl ₂ OH + H•	95.44
	C-Cl		C-Cl
CH ₂ ClCH ₂ OOH → C•H ₂ CH ₂ OOH + Cl•	85.42	CH ₂ ClOH → C•H ₂ OH + Cl•	83.02
CH ₂ ClCH ₂ OOH → C•HClCH ₂ OOH + Cl•	80.08	CHCl ₂ OH → C•HClOH + Cl•	80.34
CHCl ₂ CH ₂ OOH → C•Cl ₂ CH ₂ OOH + Cl•	73.74	CCl ₃ OH → C•Cl ₂ OH + Cl•	72.34
	C-O		C-O
CH ₃ CH ₂ OOH → CH ₃ CH ₂ O• + HO ₂ •	72.30	CH ₃ OOH → CH ₃ O• + HO ₂ •	70.12
CH ₂ ClCH ₂ OOH → CH ₂ ClCH ₂ O• + HO ₂ •	73.10	CH ₂ ClOOH → CH ₂ ClO• + HO ₂ •	72.94
CHCl ₂ CH ₂ OOH → CHCl ₂ CH ₂ O• + HO ₂ •	74.25	CHCl ₂ OOH → CHCl ₂ O• + HO ₂ •	71.71
CCl ₃ CH ₂ OOH → CCl ₃ CH ₂ O• + HO ₂ •	68.81	CCl ₃ OOH → CCl ₃ O• + HO ₂ •	67.61
	O-O		O-O
CH ₃ CH ₂ OOH → CH ₃ CH ₂ O• + OH•	44.69	CH ₃ OOH → CH ₃ O• + OH•	45.33
CH ₂ ClCH ₂ OOH → CH ₂ ClCH ₂ O• + OH•	43.52	CH ₂ ClOOH → CH ₂ ClO• + OH•	46.37
CHCl ₂ CH ₂ OOH → CHCl ₂ CH ₂ O• + OH•	42.91	CHCl ₂ OOH → CHCl ₂ O• + OH•	48.58

^a Bond energies are calculated in this work and based on the $\Delta H_f^\circ_{298}$ of corresponding radicals calculated in Table A2. All carbon species are determined by CBSQ calculations and working reactions except as noted. ^b Bond energies calculated in the previous studies (refs 5, 9, and 10) are used for comparison. ^c Seetula, J. A. *Phys. Chem. Chem. Phys.* **2000**, 2, 3807. ^d From THERM group additivity estimation. ^e Reference 9.

TABLE A2: Reaction Enthalpies^a at 298 K and Calculated $\Delta H_f^\circ_{298}$ of Radicals

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)	
	ΔH°_{rxn}	$\Delta H_f^\circ_{298}$	ΔH°_{rxn}	$\Delta H_f^\circ_{298}$	ΔH°_{rxn}	$\Delta H_f^\circ_{298}$	ΔH°_{rxn}	$\Delta H_f^\circ_{298}$
CH ₂ ClCH ₂ OO• + CH ₄ → CH ₃ CH ₂ OO• + CH ₃ Cl	1.22	-9.73	0.80	-9.31	2.63	-11.14	2.74	-11.25
CH ₂ ClCH ₂ OO• + C ₂ H ₆ → CH ₃ CH ₂ OO• + CH ₃ CH ₂ Cl	-2.77	-10.63	-2.77	-10.63	-1.79	-11.61	-2.27	-11.13
average value and deviation: ^b								-11.19±1.20
CHCl ₂ CH ₂ OO• + CH ₄ → CH ₃ OO• + CH ₃ CHCl ₂	0.75	-11.80	0.11	-11.16	2.19	-13.24	2.61	-13.66
CHCl ₂ CH ₂ OO• + C ₂ H ₆ → CH ₃ CH ₂ OO• + CH ₃ CHCl ₂	-4.65	-13.00	-5.29	-12.36	-3.29	-14.36	-3.50	-14.15
average value and deviation: ^b								-13.90±1.88
CCl ₃ CH ₂ OO• + CH ₄ → CH ₃ OO• + CH ₃ CCl ₃	-1.98	-11.99	-2.54	-11.43	-0.32	-13.65	0.65	-14.62
CCl ₃ CH ₂ OO• + C ₂ H ₆ → CH ₃ CH ₂ OO• + CH ₃ CCl ₃	-7.38	-13.19	-7.94	-12.63	-5.80	-14.77	-5.46	-15.11
average value and deviation: ^b								-14.86±1.62
C•HClCH ₂ OOH + CH ₄ → CH ₃ OOH + CH ₃ Cl	2.32	2.92	1.88	3.36	3.05	2.19	3.10	2.14
C•HClCH ₂ OOH + C ₂ H ₆ → CH ₃ CH ₂ OOH + CH ₃ CH ₂ Cl	-2.87	2.56	-2.69	2.38	-2.60	2.29	-2.51	2.20
average value and deviation: ^b								2.17±1.60
C•Cl ₂ CH ₂ OOH + CH ₄ → CH ₃ OOH + CH ₃ CHCl ₂	2.49	-3.97	1.77	-3.25	3.50	-4.98	4.01	-5.49
C•Cl ₂ CH ₂ OOH + C ₂ H ₆ → CH ₃ CH ₂ OOH + CH ₃ CHCl ₂	-2.70	-4.33	-2.80	-4.23	-2.15	-4.88	-1.61	-5.42
average value and deviation: ^b								-5.46±1.67

^a Reaction enthalpies include thermal correction and zero-point energy. Units in kcal/mol. ^b Average value and deviation for pure enantiomer of the lowest energy at the CBSQ/B3LYP/6-31G(d,p) level. The $\Delta H_f^\circ_{298}$ values for CH_{3-x}Cl_xC•HOOH ($x = 1\sim 3$) are not presented because the species dissociate to the corresponding aldehyde + OH exothermically with little or no barrier to dissociation (CH_{3-x}Cl_xC•HOOH → CH_{3-x}Cl_xCHO + OH). These secondary bond energies are estimated about 90 kcal/mol, but we expect abstraction bond energies to be similar to those from abstraction or from resonantly stabilized radical sites.

Supporting Information Available: Tables S1 and S2 provide total electronic energies, zero point energies, thermal correction to 298 K, and the coefficients of truncated Fourier series expansions for internal rotation potentials for three target species. Tables S3, S4, and S5 illustrate the contributions from hindered internal rotations to $S(T)$ and $C_p(T)$ values and the entropy corrections for mixing of the rotational conformers at the different temperatures for the three chlorinated ethyl hydroperoxides. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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