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Structures, Intramolecular Rotation Barriers, and Thermochemical Properties: Ethanol, α-Monoethanols, Dichloroethanols, and Corresponding Radicals Derived from H Atom Loss

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Structures and thermochemical properties on ethanol, two α-chloroethanols; ethoxy and two α-chloroethoxy radicals; α-hydroxyethyl and α-hydroxychloroethyl radical; and *β*-hydroxyethyl and two *β*-hydroxychloroethyl radicals are determined by ab initio and density functional calculations. Molecular structures and vibration 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 $C_p(T)$'s ($300 \leq T/\mathrm{K} \leq 1500$) from vibrational, translational, and external rotational contributions are calculated using the rigid-rotor-harmonic-oscillator approximation 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 hindered rotational contributions to $S°_{298}$ and $C_p(T)$'s are calculated by using direct integration over energy levels of the internal rotational potentials. The $\Delta H_f°_{298}$ is determined using several isodesmic reactions, and an evaluation of data at each calculation level results in the $\Delta H_f°_{298}$ values: -68.63 ± 1.24 and -75.72 ± 1.31 kcal/mol for $CH_3CHClOH$ and CH_3CCl_2OH, respectively. The $\Delta H_f°_{298}$ for $CH_3CHClO^•$ and $CH_3CCl_2O^•$ are -14.79 ± 2.90 and -21.85 ± 2.82 kcal/mol, respectively. The $\Delta H_f°_{298}$ for $CH_3C^•ClOH$, $C^•H_2CHClOH$, and $C^•H_2CCl_2OH$ are -25.89 ± 2.13, -17.51 ± 2.13, and -23.79 ± 2.13 kcal/mol, respectively. Bond energies for the RO−H and R−OH bonds in α-chloroethanols are 106 and 97 kcal/mol. Groups for use in Benson type additivity estimations are determined for the carbon bonded to oxygen and chlorine(s). The enthalpy values for the C/C/Cl/H/O and C/C/Cl_2/O groups are -20.53 and -27.62 kcal/mol, respectively. Hydrogen bond increment groups for the chloroethoxy, α-hydroxychloroethyl, and *β*-hydroxychloroethyl radicals are also developed.

Introduction

Accurate assessment of the environmental impact of chlorinated hydrocarbon released into the air requires a detailed understanding of their atmospheric chemistry. Chlorohydrocarbons are present in the troposphere at levels somewhat lower than those of major hydrocarbon pollutants.[1] The presence of a Cl atom on a carbon site usually reduces the C−H bond energy by about 4.0 kcal/mol,[2,3] leading to lower activation energies for abstraction of the hydrogen on the α-carbon. This may lead to a faster formation of chlorinated alkyl radicals and subsequently chlorinated alkyl hydroperoxides.[4] These species will subsequently react with NO or another organic peroxy radical to form the corresponding chlorogenated alkoxy radicals.[5] The thermochemistry of the dissociation products of chloroethanols is of interest in pollution control, atmospheric chemistry, and combustion. Reliable thermochemical properties of these oxygenated chlorocarbon species are important in analysis of their effects on environment and in evaluation of kinetics or thermodynamic equilibrium for both destruction and synthesis processes. These properties are also needed as input in chemical engineering design and in equilibrium codes.

Several experimental and theoretical studies are reported $CH_3CHClO^•$ as an important intermediate in the atmospheric oxidation of chlorine-containing organic compounds.[6−9] Wallington and Kaiser[6] reported the three-center elimination of HCl from $CH_3CHClO^•$ is a dominant decomposition pathway by experiment, and this is supported by ab initio G2(MP2, SVP) studies performed by Hou et al.[9] Hou et al. also calculated the $\Delta H_f°_{298}$ of $CH_3CHClO^•$, $CH_3C^•ClOH$, and $C^•H_2CHClOH$ at the G2(MP2, SVP) level. There are no experimental $\Delta H_f°_{298}$ values and also no published $S°_{298}$ and $C_p(T)$'s on α-chloroethanols, α-chloroethoxy, or hydroxychloroethyl radicals. This research determined the thermochemical properties on ethanol, α-mono- and dichloroethanols, and corresponding radicals derived from H atom loss using density functional and ab initio calculation methods. A set of chloro−oxy−alkyl groups and HBI groups are derived from these thermochemical property data.

Calculation Methods

All of the density functional and ab initio calculations are performed using the Gaussian-94 program suite.[10] The geometry optimization, harmonic vibration frequencies, and zero-point vibrational energies (ZPVE) are computed with the B3LYP/6-31G(d,p) level of theory. 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) (abbreviated as CBSQ//B3**) single point levels of calculation.[11−13] Total energies are corrected by ZPVE, which are scaled by 0.9806 as recommended by Scott et al.[14] Thermal correction, 0 K to 298.15 K, is taken into account using the B3LYP structure and vibration data. Restricted and open shell calculations are used for the stable and radical molecules, respectively.

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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. Potential barriers for the internal rotations are determined at the B3LYP/6-31G(d,p) calculation level and each conformer and barrier are optimized. Contributions from hindered rotors to $S°_{298}$ and $C_p(T)$ are determined using direct integration over energy levels of the intramolecular rotational potential curves. The number of optical isomers and spin degeneracy of unpaired electrons are also incorporated for calculation of $S°_{298}$.

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

$$V(\Phi) = a_0 + \sum a_i \cos(i\Phi) + \sum b_i \sin(i\Phi) \qquad i = 1-8 \tag{E1}$$

where values of the coefficients are calculated to provide the true minima and maxima of the torsional potentials with allowance of a shift of the theoretical extreme angular positions.[15−17]

The $\Delta H_f°_{298}$ for chloro-substituted species are estimated using total energies and several sets of isodesmic reactions. Reactions in Scheme 1 are used to calculate $\Delta H_f°_{298}$ of mono- and dichloroethanol.

Scheme 1

$$CH_3CH_{2-x}Cl_xOH + CH_4 \rightarrow CH_3OH + CH_3CH_{3-x}Cl_x \tag{1.1}$$

$$CH_3CH_{2-x}Cl_xOH + CH_4 \rightarrow C_2H_5OH + CH_{4-x}Cl_x \tag{1.2}$$

$$CH_3CH_{2-x}Cl_xOH + C_2H_6 \rightarrow C_2H_5OH + CH_3CH_{3-x}Cl_x \tag{1.3}$$

$$CH_3CH_{2-x}Cl_xOH + C_2H_6 \rightarrow n\text{-}C_3H_7OH + CH_{4-x}Cl_x \tag{1.4}$$

$$CH_3CH_{2-x}Cl_xOH + C_2H_6 \rightarrow CH_3OH + CH_3CH_{2-x}Cl_xCH_3 \tag{1.5}$$

$$CH_3CH_{2-x}Cl_xOH + n\text{-}C_3H_8 \rightarrow n\text{-}C_3H_7OH + CH_3CH_{3-x}Cl_x \tag{1.6}$$

$$CH_3CH_{2-x}Cl_xOH + CH_3OH \rightarrow C_2H_5OH + CH_{3-x}Cl_xOH \tag{1.7}$$

Reactions in Scheme 2 are used to calculate $\Delta H_f°_{298}$ of the mono- and dichloroethoxy radicals.

Scheme 2

$$CH_3CH_{2-x}Cl_xO^\bullet + CH_4 \rightarrow CH_3CH_{2-x}Cl_xOH + CH_3^\bullet \tag{2.1}$$

$$CH_3CH_{2-x}Cl_xO^\bullet + C_2H_6 \rightarrow CH_3CH_{2-x}Cl_xOH + C_2H_5^\bullet \tag{2.2}$$

$$CH_3CH_{2-x}Cl_xO^\bullet + CH_3Cl \rightarrow CH_3CH_{2-x}Cl_xOH + CH_2Cl^\bullet \tag{2.3}$$

$$CH_3CH_{2-x}Cl_xO^\bullet + CH_3OH \rightarrow CH_3CH_{2-x}Cl_xOH + CH_3O^\bullet \tag{2.4}$$

$$CH_3CH_{2-x}Cl_xO^\bullet + C_2H_5OH \rightarrow CH_3CH_{2-x}Cl_xOH + C_2H_5O^\bullet \tag{2.5}$$

$$CH_3CH_{2-x}Cl_xO^\bullet + CH_4 \rightarrow CH_3CH_{3-x}Cl_x + CH_3O^\bullet \tag{2.6}$$

$$CH_3CH_{2-x}Cl_xO^\bullet + C_2H_6 \rightarrow CH_3CH_{3-x}Cl_x + C_2H_5O^\bullet \tag{2.7}$$

Reactions in Scheme 3 are used for $\Delta H_f°_{298}$ of the β-hydroxyl-mono- and dichloroethyl radicals.

Scheme 3

$$CH_2^\bullet CH_{2-x}Cl_xOH + CH_4 \rightarrow CH_3CH_{2-x}Cl_xOH + CH_3^\bullet \tag{3.1}$$

$$CH_2^\bullet CH_{2-x}Cl_xOH + C_2H_6 \rightarrow CH_3CH_{2-x}Cl_xOH + C_2H_5^\bullet \tag{3.2}$$

$$CH_2^\bullet CH_{2-x}Cl_xOH + CH_3Cl \rightarrow CH_3CH_{2-x}Cl_xOH + CH_2Cl^\bullet \tag{3.3}$$

$$CH_2^\bullet CH_{2-x}Cl_xOH + CH_3OH \rightarrow CH_3CH_{2-x}Cl_xOH + C^\bullet H_2OH \tag{3.4}$$

$$CH_2^\bullet CH_{2-x}Cl_xOH + C_2H_5OH \rightarrow CH_3CH_{2-x}Cl_xOH + CH_3C^\bullet HOH \tag{3.5}$$

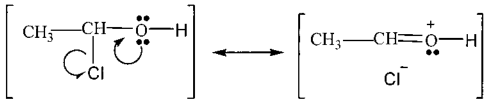
$CH_3C^\bullet ClOH$ is estimated using isodesmic reactions similar to those in Scheme 3. The basic requirement of an isodesmic reaction is bond conservation, where the number of each of bond type is conserved in the reaction. An isodesmic reaction will lead to more accurate results if groups are also conserved in the reaction, because the next nearest neighbor interaction is then conserved. The accuracy to near 1 kcal/mol by this enthalpy estimation method is illustrated in several previous studies.[15−19] All the reactions in the reaction schemes are isodesmic except for reactions 2.1−2.3, which are useful for comparison, and demonstration of the importance of isodesmic reactions. Reactions 2.4 and 2.5 conserve groups in addition to conservation of bond types (group isodesmic), and we consider these the best reactions for evaluation of the $\Delta H_f°_{298}$, as error cancellation should be optimal.

Calculations at each level of theory are performed on the stable conformer(s) of each compound, and the $\Delta H_f°_{298}$ of each conformer is calculated using isodesmic reactions. Final $\Delta H_f°_{298}$ values are from a statistical distribution of rotational conformers.

Results and Discussion

Geometries. The lowest energy conformation for the two chloroethanols and three hydroxyl chloroethyl radicals consistently has the hydroxyl H atom gauche to the maximum number of chlorine atoms, as illustrated in the Supporting Information (Table S1), despite an apparent steric penalty. These lowest energy conformations exhibit the anomeric effect like those of chloromethanols reported by Schneider,[20] Omoto,[21] and Sun et al.[19] This preference is ascribed to the delocalization of the lone pair e$^-$ on the oxygen with the antibonding σ* orbital of the C−Cl bond; it is also supported by the electrostatic repulsion between the nonbonding e$^-$ pair of oxygen and electronegative Cl atom(s) and intramolecular interaction between the hydroxyl H atom and the Cl atom.[22]

It can be seen from Table S1 that the C−O bond length decreases significantly with chlorine substitution. This is due to the anomeric effect where the nonbonding e$^-$ pair on oxygen is mixing with the antibonding orbital of the C−Cl bond.[20,21,23] In valence bond terminology, this would be described as



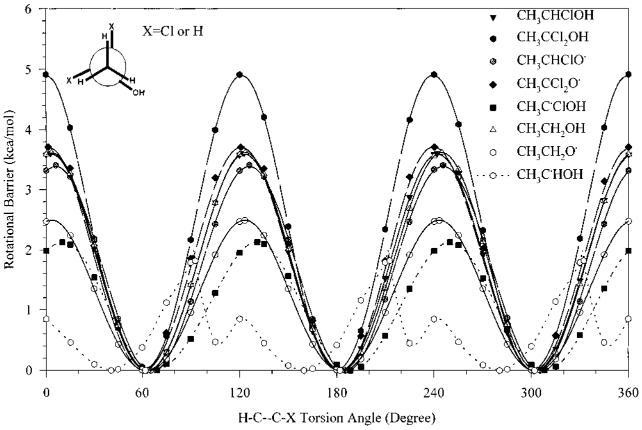


Figure 1. Potential barriers for internal rotation about the C−C bond of C_2H_5OH, $CH_3CHClOH$, CH_3CCl_2OH, $C_2H_5O^•$, $CH_3CHClO^•$, $CH_3CCl_2O^•$, $CH_3C^•HOH$, and $CH_3C^•ClOH$. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. The geometries at the points of minima and maxima are fully optimized.

The anomeric effect can also be seen in the C−Cl bond length, which is longer than the normal C−Cl bond. The O−H bond increases with increased chlorine substitution, and bond strength gets stronger (see the bond energy discussion below).

The density functional structure predicts planar (sp^2) vs tetrahedral (sp^3) on the hydroxyethyl and hydroxychloroethyl radicals. The $\angle H_c-C-C-H_c$ dihedral angles in $C^•H_2CH_2OH$ and $C^•H_2CHClOH$ are 170.1° and 168.0°, which suggests a nonplanar structure. However, the $\angle H_c-C-C-H_c$ and the $\angle C-C-O-H$ dihedral angles in $C^•H_2CCl_2OH$ both are 180.0°, indicating there is a mirror plane between the two chlorine atoms, i.e., C_s symmetry in $C^•H_2CCl_2OH$. The inversion frequencies for $C^•H_2CH_2OH$, $C^•H_2CHClOH$, and $C^•H_2CCl_2OH$ are calculated in this work to be 458.2, 666.5, and 539.2 cm^{-1}, respectively. The symmetry number is assigned as 1 for $C^•H_2CH_2OH$ and $C^•H_2CHClOH$ and 2 for $C^•H_2CCl_2OH$ on the basis of these data.

Rotational Barriers. Potential barriers for internal rotations of all the species are calculated at the B3LYP/6-31G(d,p) level. Potential energy as a 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. Each minimum and maximum on the torsional potential are fully optimized. The barriers for internal rotations are calculated from the differences between the total energy of each conformation and that of the most stable conformer. Data on total energies at 0 K and calculated rotation barriers vs the dihedral angle for each rotational structure of the three stable (chloro)ethanols and the eight related radicals are presented in the Supporting Information (Table S2). The coefficients of the Fourier expansion components, a_i and b_i in eq E1 are listed in the Supporting Information (Table S3).

The calculated rotational barriers about the C−C bond of CH_3CH_2OH, $CH_3CHClOH$, CH_3CCl_2OH, $CH_3CH_2O^•$, $CH_3CHClO^•$, $CH_3CCl_2O^•$, $CH_3C^•HOH$, and $CH_3C^•ClOH$ are shown in Figure 1. All the curves for C−C torsion potential are symmetric and show a 3-fold barrier except $CH_3C^•HOH$, which shows a 6-fold barrier. The barrier heights for C−C torsion are 3.62, 3.61, and 4.91 kcal/mol for CH_3CH_2OH, $CH_3CHClOH$, and CH_3CCl_2OH; 2.49, 3.41, and 3.71 kcal/mol for $CH_3CH_2O^•$, $CH_3CHClO^•$, and $CH_3CCl_2O^•$; and 1.82 and 2.13 kcal/mol for $CH_3C^•HOH$ and $CH_3C^•ClOH$. The above data show the barrier for the C−C torsion increases with increasing α-chlorine substitution on ethanol, ethoxy, and α-hydroxyethyl radical. The barriers for CH_3CH_2OH vs $CH_3CHClOH$, are, however, quite similar, 3.62 and 3.61 at the B3LYP level. We further evaluate these two barriers using the MP2(FULL)/6-31G(d) level calculation; the values are slightly higher but also similar: 4.04 and 4.28, respectively. The reason for the similarity in barriers for CH_3CH_2OH and $CH_3CHClOH$ is likely due to the anomeric effect[21] in $CH_3CHClOH$. The data also show that C−C torsion barriers for (chloro)ethanols are higher than those of the corresponding (chloro)ethoxy radicals, which may in part be due to steric hindrance of the hydroxyl hydrogen.

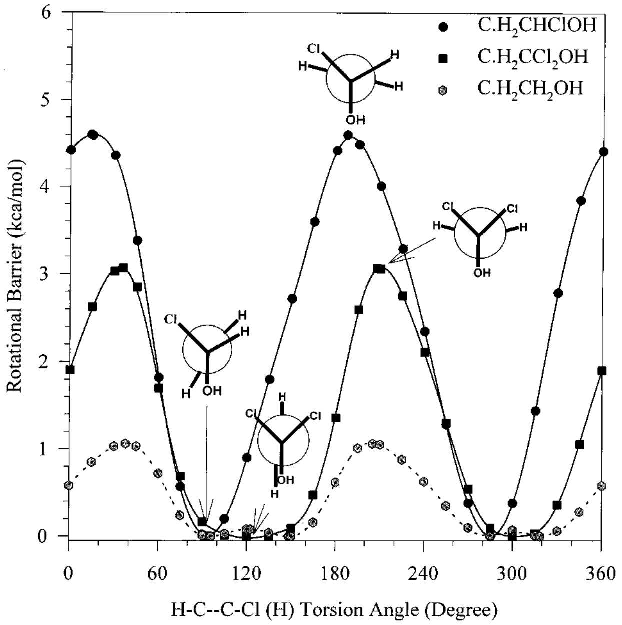


Figure 2. Potential barriers for internal rotation about the C−C bond of $C^•H_2CH_2OH$, $C^•H_2CHClOH$, and $C^•H_2CCl_2OH$. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. The geometries at the points of minima and maxima are fully optimized.

Figure 2 shows the calculated rotational barriers about the C−C bond for $C^•H_2CH_2OH$, $C^•H_2CHClOH$, and $C^•H_2CCl_2OH$. These C−C torsion potentials show a 2-fold barrier for both the chlorinated hydroxyethyl radicals but a 4-fold barrier in $C^•H_2CH_2OH$. The H- -OH eclipsed conformer is the most stable for the C−C torsion of $C^•H_2CCl_2OH$ due to the interaction of H atom on the $-C^•H_2$ group and the O atom (the interatomic distance 2.483 Å). In contrast, the H- -OH gauche structure (the $\angle H_c-C-C-Cl$ dihedral 207.56°) lacks the above interaction due to a longer interatomic distance, 2.930 Å. This gauche structure is 3.07 kcal/mol higher energy and corresponds to the maximum point on the potential curve. Similar maxima and minima structures exist in $C^•H_2CHClOH$ and $C^•H_2CH_2OH$. The C−C rotation barrier in $C^•H_2CHClOH$ calculated at the B3LYP level is 4.60 kcal/mol, which is 1.53 kcal/mol higher than the barrier in $C^•H_2CCl_2OH$. MP2/6-31G(d) calculations in this work also show a decrease in barrier in $C^•H_2CCl_2OH$ relative to $C^•H_2CHClOH$ and they also predict partial sp^2 geometry for the $-CH_2^•$ groups.

The higher barrier for $C^•H_2CHClOH$ suggests that the H- -OH eclipsed conformer of $C^•H_2CHClOH$ has extra stability. This $C^•H_2CHClOH$ radical exhibits hyperconjugation between the $-CH_2^•$ center and the σ^* (C−Cl) molecular orbital in its lowest energy conformer.[21] This effective orbital overlap is possible because the dihedral $\angle H_c-C-C-H_c$ and $\angle H_c-C-C-O$ in the minimum energy conformer are 32.2° and −25.1°, respectively, so the p orbital in the $-CH_2^•$ center and the σ^* (C−Cl) orbital are nearly parallel. This reduces the minima

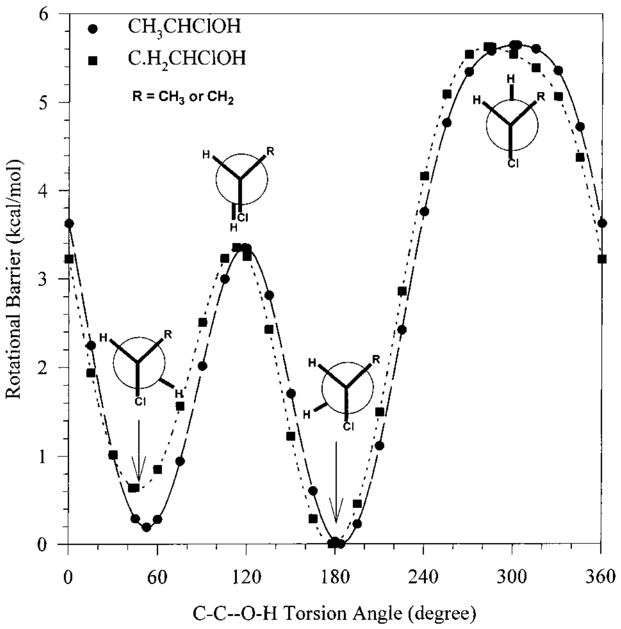


Figure 3. Potential barriers for internal rotation about the C−O bond of $CH_3CHClOH$ and $C^{\bullet}H_2CHClOH$. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. The geometries at the points of minima and maxima are fully optimized.

energy for $C^{\bullet}H_2CHClOH$ and gives it a higher barrier than either the parent or $C^{\bullet}H_2CCl_2OH$.

The calculated rotational barriers about the C−O bond of $CH_3CHClOH$ and $C^{\bullet}H_2CHClOH$ are shown in Figure 3. The torsion potential curves for rotation about the C−O bonds in $CH_3CHClOH$ and $C^{\bullet}H_2CHClOH$ are similar. The most stable conformer is R- -H (R = CH_3 or CH_2) anti conformer, and its energy is lower than that of the R- -H gauche conformer. This is because an oxygen nonbonding e^- pair eclipsed to the H atom on the α-carbon in the R- -H anti conformer, but eclipsed to the R group on the α-carbon in the R- -H gauche conformer. The maxima points on the potential curves correspond to the structures that the hydroxyl H atom is anti to the Cl atom on α-carbon because the two nonbonding e^- pairs from oxygen are gauche to the Cl atom. This preference can also be ascribed to the anomeric effect, the delocalization of the lone pair e^- on the oxygen with the antibonding σ^* orbital of the C−Cl bond. This phenomenon is similar to that in the chloromethanol, which is observed by our previous study.[19]

Figure 4 shows the calculated rotational barriers about the C−O bond of CH_3CH_2OH, $C^{\bullet}H_2CH_2OH$, CH_3CCl_2OH, and $C^{\bullet}H_2CCl_2OH$. The C−O torsion potential curves for CH_3CCl_2OH and $C^{\bullet}H_2CCl_2OH$ are similar and have the same maximum barrier of 5.68 kcal/mol. The R- -H anti structure is the stable conformation with the two nonbonding e^- pairs from oxygen gauche to the two Cl atoms. The R- -H gauche conformers have higher energies than those of the R- -H anti conformers because of the three gauche interactions between two nonbonding e^- pairs and the Cl atom (only two of these interactions in the R- -H anti conformers). The energy difference between the two conformers calculated at the CBSQ//B3** level is 3.27 kcal/mol for CH_3CCl_2OH and 2.68 kcal/mol for $C^{\bullet}H_2CCl_2OH$. This is in agreement with the energy difference for similar conformers in $CHCl_2OH$, 2.94 kcal/mol at the same level of calculation. These values support that a gauche interaction between a Cl atom and an O atom nonbonding e^- pair increases energy in the molecule by ca. 3 kcal/mol.[19] The C−O torsion potential for CH_3CH_2OH and $C^{\bullet}H_2CH_2OH$ are also similar and they have lower barriers relative to CH_3CCl_2OH and $C^{\bullet}H_2CCl_2OH$.

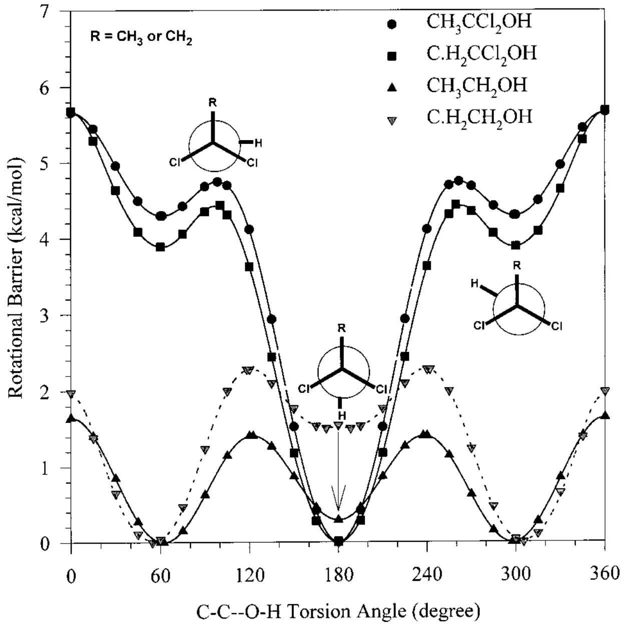


Figure 4. Potential barriers for internal rotation about the C−O bond of CH_3CH_2OH, $C^{\bullet}H_2CH_2OH$, CH_3CCl_2OH, and $C^{\bullet}H_2CCl_2OH$. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. The geometries at the points of minima and maxima are fully optimized.

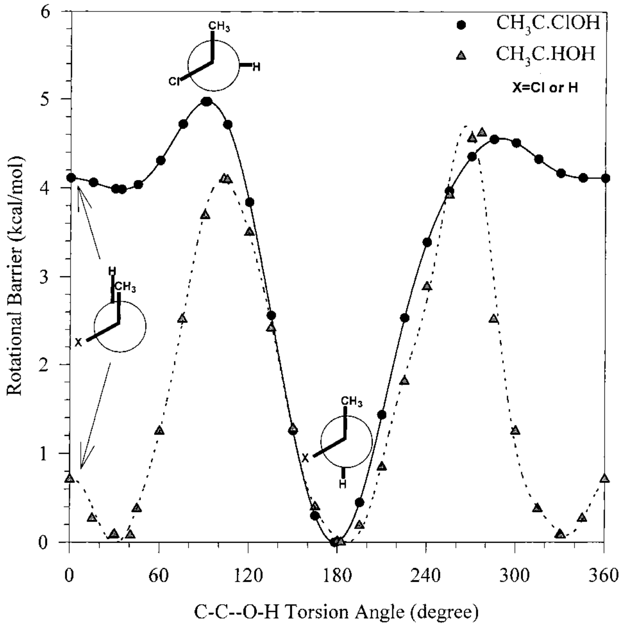


Figure 5. Potential barriers for internal rotation about the C−O bond of $CH_3C^{\bullet}HOH$ and $CH_3C^{\bullet}ClOH$. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. The geometries at the points of minima and maxima are fully optimized.

The calculated rotational barriers about the C−O bond of $CH_3C^{\bullet}HOH$ and $CH_3C^{\bullet}ClOH$ are shown in Figure 5. The C−O torsion potential for $CH_3C^{\bullet}ClOH$ has a maximum corresponding to the structure with a C−C−O−H dihedral of 91.30°. In this structure, the two nonbonding e^- pairs from the O atom are eclipsed with the Cl atom and the $-CH_3$ group, with energy increased by 4.97 kcal/mol relative to that of the stable conformer, which has the two nonbonding e^- pairs gauche to the Cl atom and methyl group. The C−O torsion potential for $CH_3C^{\bullet}HOH$ also has a similar curve; however, the CH_3- -H eclipsed structure for $CH_3C^{\bullet}ClOH$ has energy 3.43 kcal/mol higher than that of the CH_3- -H eclipsed structure for $CH_3C^{\bullet}HOH$. This is because the nonbonding e^- pair from the O atom

TABLE 1: $\Delta H_{f}^{\circ}{}_{298}$ for Standard Species in the Reaction Schemes[a]

species	$\Delta H_{f}^{\circ}{}_{298}$ (kcal/mol)	species	$\Delta H_{f}^{\circ}{}_{298}$ (kcal/mol)
CH_4	$-17.89^b \pm 0.07$	$C^\bullet Cl_2OH$	-20.54 ± 1.83^j
CH_3Cl	$-19.60^c \pm 0.12$	$CH_3^\bullet$	34.82 ± 0.2^g
CH_2Cl_2	$-22.83^b \pm 0.29$	$C_2H_5^\bullet$	28.80 ± 0.50^n
CH_3OH	$-48.08^d \pm 0.05$	$CH_2Cl^\bullet$	27.7 ± 2.0^h
C_2H_6	$-20.24^d \pm 0.12$	$C^\bullet H_2OH$	-3.97 ± 0.22^i
CH_3CH_2Cl	$-26.84^c \pm 0.26$	$CH_3C^\bullet HOH$	-13.34 ± 0.84^j
CH_3CHCl_2	$-31.09^c \pm 0.29$	$CH_3O^\bullet$	4.10 ± 1.0^k
C_3H_8	-25.02 ± 0.12^e	$C_2H_5O^\bullet$	-3.90 ± 1.27^j
$CH_3CHClCH_3$	$-35.00^d \pm 0.56$	$CH_3CHCl^\bullet$	19.15 ± 2.0^l
$CH_3CCl_2CH_3$	$-42.23^f \pm 1.0$	$CH_3CCl_2^\bullet$	12.43^l
C_2H_5OH	$-56.12^g \pm 0.2$	$C^\bullet H_2CH_2OH$	-5.70 ± 0.85^m
n-C_3H_7OH	-60.97 ± 0.12^d	$Cl^\bullet$	28.92 ± 0.3^g
CH_2ClOH	-58.07 ± 0.69^j	$H^\bullet$	52.10 ± 0.001^g
$CHCl_2OH$	-65.88 ± 0.76^j	$OH^\bullet$	9.43 ± 0.3^g
$C^\bullet HClOH$	-14.46 ± 1.75^j		

[a] The uncertainties are evaluated from refs 24 and 25. [b] Reference 26. [c] Reference 27. [d] Reference 28. [e] Reference 24. [f] Reference 31. [g] Reference 29. [h] Reference 32. [i] Reference 33. [j] Reference 19. [k] Reference 34. [l] Reference 35. [m] By this work, see Table 2. [n] Reference 30.

is eclipsed to the H atom in $CH_3C^\bullet HOH$ but eclipsed to the Cl atom in $CH_3C^\bullet ClOH$.

Enthalpy of Formation ($\Delta H_{f}^{\circ}{}_{298}$). The total electronic energies at 0 K determined 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) levels, scaled ZPVE's, thermal correction to 298.15 K are listed in the Supporting Information (Table S4). The spin expectation values, $\langle S^2 \rangle$, range from 0.760 to 0.781 for the eight target radicals in this work. The values are close to the correct value of 0.75 and suggest no significant error (due to spin contamination) for these radicals.

The $\Delta H_{f}^{\circ}{}_{298}$'s for chloro-substituted species are estimated using total energies and isodesmic reactions. 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 $\Delta H^{\circ}_{rxn,298}$ is calculated. Since $\Delta H_{f}^{\circ}{}_{298}$ of three compounds, have been experimentally determined or theoretical calculated, the unknown enthalpy of formation of target compound is obtained.

As an example, the following formula illustrates the calculation of $\Delta H_{f}^{\circ}{}_{298}(CH_3CHClO^\bullet)$:

$$\Delta H^{\circ}_{rxn,298} = E_{298}(C_2H_5O^\bullet) + E_{298}(CH_3CH_2Cl) - E_{298}(CH_3CHClO^\bullet) - E_{298}(C_2H_6)$$

$$\Delta H_{f}^{\circ}{}_{298}(CH_3CHClO^\bullet) = \Delta H_{f}^{\circ}{}_{298}(C_2H_5O^\bullet) + \Delta H_{f}^{\circ}{}_{298}(CH_3CH_2Cl) - \Delta H_{f}^{\circ}{}_{298}(C_2H_6) - \Delta H^{\circ}_{rxn,298}$$

The $\Delta H_{f}^{\circ}{}_{298}$ and their respective uncertainties for standard species used in the working reactions are listed in Table 1. The selection of these values is fully discussed by the previous study.[19] The $\Delta H_{f}^{\circ}{}_{298}$ of $C^\bullet H_2CH_2OH$ is calculated by this work to be −5.70 ± 0.85 kcal/mol at the CBSQ//B3** level (Table 2). It is in good agreement with Curtiss[36] et al.'s value, −5.9 kcal/mol, at the G2 level.

TABLE 2: Reaction Enthalpies and Enthalpies of Formation of the $C^\bullet H_2CH_2OH$ Radical[a]

reaction series	ΔH°_{rxn} (kcal/mol)	$\Delta H_{f}^{\circ}{}_{298}$ (kcal/mol)
$C^\bullet H_2CH_2OH + CH_3OH \rightarrow C^\bullet H_2OH + C_2H_5OH$	−6.29	−5.72
$C^\bullet H_2CH_2OH + C_2H_6 \rightarrow C_2H_5^\bullet + C_2H_5OH$	−1.38	−5.70
$C^\bullet H_2CH_2OH + CH_4 \rightarrow CH_3^\bullet + C_2H_5OH$	2.28	−5.69
average value and deviation		**−5.70 ± 0.85**

[a] The reaction enthalpies and $\Delta H_{f}^{\circ}{}_{298}$ are calculated at the CBSQ//B3** level.

1. Mono- and Dichloroethanols. The reaction enthalpies and $\Delta H_{f}^{\circ}{}_{298}$'s for the monochloroethanols and dichloroethanols obtained from the reaction schemes are tabulated in Table 3. The results for $\Delta H_{f}^{\circ}{}_{298}$'s in Table 3 show very good consistency for $CH_3CHClOH$ over the seven reactions and all the calculation methods. The $\Delta H_{f}^{\circ}{}_{298}$ for CH_3CCl_2OH derived from the seven reaction series show consistency over all reactions for the higher level density functional calculation; but the $\Delta H_{f}^{\circ}{}_{298}$'s for dichloroethanol derived from reaction series 1, 2, and 3 in the CBSQ calculations result in values that are ca. 3 kcal/mol lower than values of reaction series 4−7. The density function results agree with CBSQ results in reactions 4−7. We suggest the difference in CBSQ values is due to the changes to the environment of the dichlorinated carbon in the different reactions schemes. Specifically, the methyl group is retained on the $-CCl_2-$ carbon in reaction series 4−7. The methyl group is substituted with a H atom on this $-CCl_2-$ carbon, in reactions 1−3. The higher level density functional calculations do not show this problem. These data suggest (i) substitution of a methyl group with a hydrogen atom does not lead to good cancellation of errors, and (ii) reactions 4−7 are preferred.

G3MP2 calculations with seven working reactions and MP2-(FULL)/6-31G(d) geometries are used to further validate the enthalpy data. The results from G3MP2 calculation show good agreement in $\Delta H^{\circ}_{rxn,298}$ and $\Delta H_{f}^{\circ}{}_{298}$ vs reaction set, with the CBSQ//B3** data (see Table 3). We therefore select CBSQ values from the reaction series 4−7 for our recommended values on both $CH_3CHClOH$ and CH_3CCl_2OH. The enthalpy on the pure enantiomer of lowest energy for $CH_3CHClOH$ is −68.72 ± 1.24 kcal/mol and for CH_3CCl_2OH is −75.75 ± 1.31 kcal/mol.

2. Chloroethoxy and Hydroxy-Chloroethyl Radicals. The $\Delta H_{f}^{\circ}{}_{298}$ of chloroethoxy and hydroxychloroethyl radicals are calculated based on the $\Delta H_{f}^{\circ}{}_{298}$'s for the chloroethanols and several isodesmic reaction series (Table 4). Reaction series 4−7 for the chloroethoxy radicals are isodesmic, while reactions 1−3 are not. The $\Delta H_{f}^{\circ}{}_{298}$ for the two chloroethoxy radicals show remarkable consistency at the CBSQ//B3** level for isodesmic reactions, where the standard deviation is within 0.2 kcal/mol. The DFT and QCISD(T) calculations for the isodesmic reactions show deviation of ca. ±1 kcal/mol with the CBSQ values. The DFT and QCISD(T) calculations result in still larger variations for **non**isodesmic reaction series 1−3. CBSQ//B3** calculation results for nonisodesmic reactions are in satisfactory agreement with the isodesmic reactions but consistently result in 0.5 kcal/mol higher values for the two chloromethoxy radicals.

The recommended $\Delta H_{f}^{\circ}{}_{298}$ for the two chloroethoxy radicals are an average of four isodesmic reactions at the CBSQ//B3** calculation level. The $\Delta H_{f}^{\circ}{}_{298}$ are −14.79 ± 2.90 and −21.85 ± 2.82 kcal/mol for $CH_3CHClO^\bullet$ and $CH_3CCl_2O^\bullet$ respectively.

The $\Delta H_{f}^{\circ}{}_{298}$ on the pure enantiomer of lowest energy for the three hydroxychloroethyl radicals are an average over the five isodesmic reactions at the CBSQ//B3** level: −25.92 ± 2.13, −17.62 ± 2.13, and 23.85 ± 2.13 kcal/mol for $CH_3C^\bullet ClOH$, $C^\bullet H_2CHClOH$, and $C^\bullet H_2CCl_2OH$, respectively. The CBSQ values show excellent agreement across the five isodesmic reaction series with a standard deviation on the order of 0.01 kcal/mol. The QCISD(T) also show very good agreement with CBSQ results.

The error limits of $\Delta H_{f}^{\circ}{}_{298}$ for above species are calculated by adding the deviations between the isodesmic reactions and the maximum uncertainties in the $\Delta H_{f}^{\circ}{}_{298}$ of reference species.

TABLE 3: 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)		G3MP2//MP2(full)/ 6-31G(d)	
	$\Delta H^\circ_{\mathrm{rxn}}$	$\Delta H_f^\circ{}_{298}$	$\Delta H^\circ_{\mathrm{rxn}}$	$\Delta H_f^\circ{}_{298}$	$\Delta H^\circ_{\mathrm{rxn}}$	$\Delta H_f^\circ{}_{298}$	$\Delta H^\circ_{\mathrm{rxn}}$	$\Delta H_f^\circ{}_{298}$	$\Delta H^\circ_{\mathrm{rxn}}$	$\Delta H_f^\circ{}_{298}$
1. $CH_3CHClOH + CH_4 \rightarrow C_2H_5OH + CH_3Cl$	10.85	−68.68	10.22	−66.34	10.96	−68.79	11.22	−69.05	11.40	−69.23
2. $CH_3CHClOH + C_2H_6 \rightarrow n\text{-}C_3H_7OH + CH_3Cl$	9.28	−69.61	8.72	−69.05	8.83	−69.16	8.44	−68.77	8.66	−68.99
3. $CH_3CHClOH + CH_3OH \rightarrow C_2H_5OH + CH_2ClOH$	1.65	−67.76	1.93	−68.04	2.62	−68.73	2.96	−69.07	2.98	−69.09
4. $CH_3CHClOH + CH_4 \rightarrow CH_3OH + C_2H_5Cl$	12.33	−69.36	11.08	−68.11	12.10	−69.13	11.94	−68.97	12.16	−69.19
5. $CH_3CHClOH + C_2H_6 \rightarrow C_2H_5OH + C_2H_5Cl$	6.86	−69.58	6.09	−68.81	6.54	−69.26	6.21	−68.93	6.42	−69.14
6. $CH_3CHClOH + C_3H_8 \rightarrow n\text{-}C_3H_7OH + C_2H_5Cl$	6.90	−69.69	6.32	−69.11	6.62	−69.41	6.21	−69.00	6.49	−69.28
7. $CH_3CHClOH + C_2H_6 \rightarrow CH_3OH + CH_3CHClCH_3$	8.20	−71.04	6.77	−69.61	6.58	−69.42	5.13	−67.97	5.73	−68.57
average value and deviation[b]								**−68.72 ± 0.50**		**−69.05 ± 0.32**
1. $CH_3CCl_2OH + CH_4 \rightarrow CH_3CH_2OH + CH_2Cl_2$	15.53	−76.59	13.88	−74.94	16.96	−78.02	17.28	−78.34	16.63	−77.69
2. $CH_3CCl_2OH + C_2H_6 \rightarrow n\text{-}C_3H_7OH + CH_2Cl_2$	13.96	−77.52	12.38	−75.94	14.83	−78.39	14.51	−78.07	13.88	−77.44
3. $CH_3CCl_2OH + CH_3OH \rightarrow C_2H_5OH + CHCl_2OH$	1.86	−75.78	1.98	−75.90	3.90	−77.82	4.38	−78.30	3.99	−77.91
4. $CH_3CCl_2OH + CH_4 \rightarrow CH_3OH + CH_3CHCl_2$	15.14	−76.42	12.91	−74.19	15.38	−76.66	14.53	−75.81	14.51	−75.79
5. $CH_3CCl_2OH + C_2H_6 \rightarrow C_2H_5OH + CH_3CHCl_2$	9.67	−76.64	7.93	−74.90	9.81	−76.78	8.81	−75.78	8.77	−75.74
6. $CH_3CCl_2OH + C_3H_8 \rightarrow n\text{-}C_3H_7OH + CH_3CHCl_2$	9.71	−76.75	8.16	−75.20	9.89	−76.93	8.80	−75.84	8.84	−75.88
7. $CH_3CCl_2OH + C_2H_6 \rightarrow CH_3OH + CH_3CCl_2CH_3$	10.40	−80.47	8.18	−78.25	8.23	−78.30	5.49	−75.56	5.63	−75.70
average value and deviation[b]								**−75.75 ± 0.13**		**−75.78 ± 0.08**

[a] Reaction enthalpies include thermal correction and zero-point energy. Units in kcal/mol. [b] The deviation are between the isodesmic reactions (see text).

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)	
	$\Delta H^\circ_{\mathrm{rxn}}$	$\Delta H_f^\circ{}_{298}$	$\Delta H^\circ_{\mathrm{rxn}}$	$\Delta H_f^\circ{}_{298}$	$\Delta H^\circ_{\mathrm{rxn}}$	$\Delta H_f^\circ{}_{298}$	$\Delta H^\circ_{\mathrm{rxn}}$	$\Delta H_f^\circ{}_{298}$
1. $CH_3CHClO^\bullet + CH_4 \rightarrow CH_3^\bullet + CH_3CHClOH$	6.28	−22.20	2.65	−18.57	2.23	−18.15	−1.78	−14.14
2. $CH_3CHClO^\bullet + C_2H_6 \rightarrow C_2H_5^\bullet + CH_3CHClOH$	1.52	−21.11	−2.05	−17.54	−0.75	−18.84	−5.44	−14.15
3. $CH_3CHClO^\bullet + CH_3Cl \rightarrow CH_2Cl^\bullet + CH_3CHClOH$	0.24	−21.57	−3.44	−17.89	−2.82	−18.51	−7.16	−14.17
4. $CH_3CHClO^\bullet + CH_3OH \rightarrow CH_3O^\bullet + CH_3CHClOH$	−1.19	−15.26	−0.74	−15.71	−2.33	−14.12	−1.83	−14.62
5. $CH_3CHClO^\bullet + C_2H_5OH \rightarrow C_2H_5O^\bullet + CH_3CHClOH$	−1.38	−15.03	−1.15	−15.26	−2.24	−14.17	−1.78	−14.63
6. $CH_3CHClO^\bullet + CH_4 \rightarrow CH_3O^\bullet + CH_3CH_2Cl$	11.14	−15.99	10.34	−15.19	9.77	−14.62	10.10	−14.95
7. $CH_3CHClO^\bullet + C_2H_6 \rightarrow C_2H_5O^\bullet + CH_3CH_2Cl$	5.48	−15.98	4.94	−15.44	4.30	−14.80	4.44	−14.94
average value and deviation[b]								**−14.79 ± 0.19**
1. $CH_3CCl_2O^\bullet + CH_4 \rightarrow CH_3^\bullet + CH_3CCl_2OH$	1.40	−24.41	−1.56	−21.45	−2.66	−20.35	−1.68	−21.33
2. $CH_3CCl_2O^\bullet + C_2H_6 \rightarrow C_2H_5^\bullet + CH_3CCl_2OH$	−3.36	−23.32	−6.26	−20.42	−5.64	−21.04	−5.34	−21.34
3. $CH_3CCl_2O^\bullet + CH_3Cl \rightarrow CH_2Cl^\bullet + CH_3CCl_2OH$	−4.64	−23.78	−7.65	−20.77	−7.71	−20.71	−7.06	−21.36
4. $CH_3CCl_2O^\bullet + CH_3OH \rightarrow CH_3O^\bullet + CH_3CCl_2OH$	−6.07	−17.47	−4.95	−18.59	−7.22	−16.32	−1.74	−21.80
5. $CH_3CCl_2O^\bullet + C_2H_5OH \rightarrow C_2H_5O^\bullet + CH_3CCl_2OH$	−6.26	−17.24	−5.36	−18.14	−7.13	−16.37	−1.68	−21.82
6. $CH_3CCl_2O^\bullet + CH_4 \rightarrow CH_3O^\bullet + CH_3CHCl_2$	9.07	−18.17	7.96	−17.06	8.16	−17.26	12.79	−21.89
7. $CH_3CCl_2O^\bullet + C_2H_6 \rightarrow C_2H_5O^\bullet + CH_3CHCl_2$	3.41	−18.16	2.57	−17.32	2.68	−17.43	7.13	−21.88
average value and deviation[b]								**−21.85 ± 0.04**
1. $CH_3C^\bullet ClOH + CH_4 \rightarrow CH_3^\bullet + CH_3CHClOH$	12.83	−28.75	11.79	−27.71	10.02	−25.94	9.99	−25.91
2. $CH_3C^\bullet ClOH + C_2H_6 \rightarrow C_2H_5^\bullet + CH_3CHClOH$	8.07	−27.66	7.14	−26.73	7.04	−26.63	6.33	−25.92
3. $CH_3C^\bullet ClOH + CH_3Cl \rightarrow CH_2Cl^\bullet + CH_3CHClOH$	6.79	−28.12	5.72	−27.05	4.97	−26.30	4.60	−25.93
4. $CH_3C^\bullet ClOH + CH_3OH \rightarrow C^\bullet H_2OH + CH_3CHClOH$	2.25	−26.77	2.23	−26.75	1.74	−26.26	1.42	−25.94
5. $CH_3C^\bullet ClOH + C_2H_5OH \rightarrow CH_3C^\bullet HOH + CH_3CHClOH$	0.23	−26.05	0.21	−26.03	0.75	−26.57	0.10	−25.92
average value and deviation[b]								**−25.92 ± 0.01**
1. $C^\bullet H_2CHClOH + CH_4 \rightarrow CH_3^\bullet + CH_3CHClOH$	5.17	−21.09	4.42	−20.34	0.81	−16.73	1.69	−17.61
2. $C^\bullet H_2CHClOH + C_2H_6 \rightarrow C_2H_5^\bullet + CH_3CHClOH$	0.41	−20.00	−0.23	−19.36	−2.17	−17.42	−1.97	−17.62
3. $C^\bullet H_2CHClOH + CH_3Cl \rightarrow CH_2Cl^\bullet + CH_3CHClOH$	−0.87	−20.46	−1.66	−19.67	−4.24	−17.09	−3.70	−17.63
4. $C^\bullet H_2CHClOH + CH_3OH \rightarrow C^\bullet H_2OH + CH_3CHClOH$	−5.41	−19.11	−5.15	−19.37	−7.47	−17.05	−6.88	−17.64
5. $C^\bullet H_2CHClOH + C_2H_5OH \rightarrow CH_3C^\bullet HOH + CH_3CHClOH$	−7.42	−18.40	−7.16	−18.66	−8.46	−17.36	−8.20	−17.62
average value and deviation[b]								**−17.62 ± 0.01**
1. $C^\bullet H_2CCl_2OH + CH_4 \rightarrow CH_3^\bullet + CH_3CCl_2OH$	3.89	−26.90	3.31	−26.32	−0.11	−22.90	0.82	−23.83
2. $C^\bullet H_2CCl_2OH + C_2H_6 \rightarrow C_2H_5^\bullet + CH_3CCl_2OH$	−0.87	−25.81	−1.34	−25.34	−3.09	−23.59	−2.84	−23.84
3. $C^\bullet H_2CCl_2OH + CH_3Cl \rightarrow CH_2Cl^\bullet + CH_3CCl_2OH$	−2.14	−26.28	−2.77	−25.65	−5.17	−23.25	−4.56	−23.86
4. $C^\bullet H_2CCl_2OH + CH_3OH \rightarrow C^\bullet H_2OH + CH_3CCl_2OH$	−6.69	−24.92	−6.26	−25.35	−8.39	−23.22	−7.75	−23.86
5. $C^\bullet H_2CCl_2OH + C_2H_5OH \rightarrow CH_3C^\bullet HOH + CH_3CCl_2OH$	−8.70	−24.21	−8.27	−24.64	−9.39	−23.52	−9.06	−23.85
								−23.85 ± 0.01

[a] Reaction enthalpies include thermal correction and zero-point energy. Units in kcal/mol. [b] Average value calculated at the CBSQ//B3** level, and the deviation are between the isodesmic reactions (see text).

Comparison with Literature Enthalpies. The $\Delta H_f^\circ{}_{298}$ for monochloroethanol and the corresponding radicals are found in the literature for comparisons. Sekušak et al.[37] estimated $\Delta H_f^\circ{}_{298}$ of $CH_3CHClOH$ to be −69.7 kcal/mol by Benson's group additivity method, and this is in agreement with our recommend value, −68.63 ± 1.24 kcal/mol. Sekušak et al. also calculated the $\Delta H_f^\circ{}_{298}$ of $C^\bullet H_2CHClOH$ at the MP2/aug-cc-pVTZ level to be −23.0 kcal/mol by reaction $CH_2CHCl + OH^\bullet \rightarrow C^\bullet H_2CHClOH$, which is a nonisodesmic reaction. Wallington et al.[6] estimated the $\Delta H_f^\circ{}_{298}$ of $CH_3CHClO^\bullet$ to be −18.9 kcal/mol by assuming that the difference in the $\Delta H_f^\circ{}_{298}$ between chloromethoxy and methoxy radicals is the same as that between α-chloroethoxy and ethoxy radicals. Hou et al.[9] calculated the $\Delta H_f^\circ{}_{298}$ for $CH_3CHClO^\bullet$, $CH_3C^\bullet ClOH$, and $C^\bullet H_2CHClOH$ at the G2(MP2, SVP) level to be −17.8, −29.7, and −21.3 kcal/mol, respectively; however, they did not provide

TABLE 5: Enthalpy and Energy Difference of the Conformers, Relative Fraction, and Overall $\Delta H_f°_{298}$

	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)	$\Delta H_f°_{298}$[c] (kcal/mol)	relative fraction (%)	final $\Delta H_f°_{298}$ (kcal/mol)
$CH_3CHClOH$ (1)[a]					−68.72	59.18	
$CH_3CHClOH$ (1)[b]	0.17	0.44	0.24	0.22	−68.50	40.82	−68.63
CH_3CCl_2OH (1)[a]					−75.75	99.20	
CH_3CCl_2OH (2)[b]	4.07	3.66	3.49	3.27	−72.48	0.40	−75.72
$CH_3C^{\bullet}ClOH$ (1)[a]					−25.92	98.79	
$CH_3C^{\bullet}ClOH$ (1)[b]	3.79	3.16	3.26	2.61	−23.32	1.21	−25.89
$C^{\bullet}H_2CHClOH$ (1)[a]					−17.62	62.79	
$C^{\bullet}H_2CHClOH$ (1)[b]	0.59	0.75	0.36	0.31	−17.32	37.21	−17.51
$C^{\bullet}H_2CCl_2OH$ (1)[a]					−23.85	97.88	
$C^{\bullet}H_2CCl_2OH$ (2)[b]	3.76	3.45	2.05	2.68	−21.17	1.06	−23.79

[a] The rotational conformer with the lowest energy. [b] The rotational conformer with higher energy. [c] Enthalpy of formation at 298 K calculated at the CBSQ//B3LYP/6-31G(d,p) level.

TABLE 6: Bond Energy Calculations

reaction series	bond energy (kcal/mol)
RO−H	
$CH_3CH_2OH \rightarrow CH_3CH_2O^{\bullet} + H^{\bullet}$	104.32
$CH_3CHClOH \rightarrow CH_3CHClO^{\bullet} + H^{\bullet}$	105.94
$CH_3CCl_2OH \rightarrow CH_3CCl_2O^{\bullet} + H^{\bullet}$	105.97
R−α-H	
$CH_3CH_2OH \rightarrow CH_3C^{\bullet}HOH + H^{\bullet}$	94.88
$CH_3CHClOH \rightarrow CH_3C^{\bullet}ClOH + H^{\bullet}$	94.84
R−β-H	
$CH_3CH_2OH \rightarrow C^{\bullet}H_2CH_2OH + H^{\bullet}$	102.52
$CH_3CHClOH \rightarrow C^{\bullet}H_2CHClOH + H^{\bullet}$	103.22
$CH_3CCl_2OH \rightarrow C^{\bullet}H_2CCl_2OH + H^{\bullet}$	104.03
R−Cl	
$CH_3CHClOH \rightarrow CH_3C^{\bullet}HOH + Cl^{\bullet}$	84.21
$CH_3CCl_2OH \rightarrow CH_3C^{\bullet}ClOH + Cl^{\bullet}$	78.75
R−ROH	
$CH_3CH_2OH \rightarrow CH_3^{\bullet} + C^{\bullet}H_2OH$	86.97
$CH_3CHClOH \rightarrow CH_3^{\bullet} + C^{\bullet}HClOH$	88.99
$CH_3CCl_2OH \rightarrow CH_3^{\bullet} + C^{\bullet}Cl_2OH$	90.00
R−OH	
$CH_3CH_2OH \rightarrow CH_3CH_2^{\bullet} + OH^{\bullet}$	94.35
$CH_3CHClOH \rightarrow CH_3CHCl^{\bullet} + OH^{\bullet}$	97.21
$CH_3CCl_2OH \rightarrow CH_3CCl_2^{\bullet} + OH^{\bullet}$	97.58

calculation details or indicate the method of analysis. Our recommended $\Delta H_f°_{298}$ values for $CH_3CHClO^{\bullet}$, $CH_3C^{\bullet}ClOH$, and $C^{\bullet}H_2CHClOH$ are consistently 3−4 kcal/mol higher than data estimated by Hou et al.[9] The consistent difference between our values and those of Hou et al. could result from the differences in $\Delta H_f°_{298}$ of the parent $CH_3CHClOH$, which is used in each working reaction.

We therefore performed the G3MP2 calculations, noted above, for the two saturated chloroethanols. The G3MP2 calculations show excellent agreement with the other calculations in this study. The precision of our calculated enthalpies on $CH_3CHClOH$ over a range of calculation methods and working reactions (Table 3) does not provide any support for a different value. The good agreement we observe over the several calculation levels for α-chloroethanol and the corresponding radicals provide support that our calculations are consistent across different calculation methods. The QCISD(T) results also indicate that our values are consistent with HF and MP2 calculations. The high level QCISD(T)/6-31G(d,p), CBSQ//B3**, and G3MP2 calculations all predict very similar enthalpies. Our recommended data are based on analysis of conformer energies from internal rotations and use of the lowest energy conformers.

Enthalpy of Rotational Conformers. Two conformers are present in chloroethanols and hydroxyl chloroethyl radicals (see Figures 3−5); one is R- -H (R = CH_3 or CH_2) anti conformer and the other is R- -H gauche conformer. The total electronic energies of these 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. The energy differences between the conformers are listed in Table 5. The $\Delta H_f°_{298}$ of the rotational conformers are determined from values calculated at the CBSQ//B3** level using isodesmic reaction schemes. The statistical distribution and overall $\Delta H_f°_{298}$ of the chloroethanols and hydroxychloroethyl radicals are also listed in Table 5. It can be seen from Table 5 that the energy difference between the conformers decreases for the higher level calculations. The energy differences at the CBSQ//B3** calculation level are used to calculate the statistical distribution of rotational conformers.

Bond Energies. RO−H, R−OH, R−H, and R−Cl bond dissociation energies are presented in Table 6. They are estimated using the $\Delta H_f°_{298}$ of chloroethanols and the radicals from this work, plus reference radicals (see Table 1).

The R−OH bond energies increase from 94.35 kcal/mol in CH_3CH_2-OH to 97 kcal/mol in $CH_3CHCl-OH$ and CH_3CCl_2-OH. The second chlorine does not appear to affect an increase on the R−OH bond energies. This can be explained by a negative hyperconjugation effect. The hydroxyl group includes two nonbonding e^- pairs centered on oxygen, one pair can interact strongly with the $\sigma^*(C-Cl_1)$ orbital; however, the other pair cannot effectively overlap with the $\sigma^*(C-Cl_2)$ orbital. The RO−H bond energy for mono- and dichloroethanol increases 1.6 kcal/mol relative to that of ethanol; this is because the O−H bond is heterolytic rather than homolytic, and it is slightly stabilized by negative hyperconjugation even though the O−H bond is not directly perturbed by the chlorine(s).[20]

The C−Cl bond energies decrease from 84.21 to 78.75 kcal/mol with successive addition of chlorine. However, the C−COH bond energy increases from 86.97 in CH_3-CH_2OH to 88.99 kcal/mol in $CH_3-CHClOH$ and to 90.00 kcal/mol in CH_3-CCl_2OH. The C−α-H bond energies in ethanol and chloroethanol are quite similar; they show a very slight decrease from 94.88 to 94.84 with the monochlorine substitution. Normally, we would have expected a decrease in bond energy on the C−α-H bond in chloroethanol relative to ethanol using the trends of C−H bond energies in the series CH_4, CH_3Cl, CH_2Cl_2, and $CHCl_3$ and CH_3OH, CH_2ClOH, and $CHCl_2OH$ we have studied.[19] We have not been able to find any indication of this trend in the C−α-H bond of CH_3CH_2OH and $CH_3CHClOH$ in our calculations. In contrast, the C−β-H bond energies in CH_3CH_2OH, $CH_3CHClOH$, and CH_3CCl_2OH show a consistent increase: 102.52, 103.22, and 104.03 kcal/mol, respectively.

TABLE 7: Ideal Gas-Phase Thermodynamic Properties[a]

species		$\Delta H_f°_{298}$[b]	$S°_{298}$[c]	C_p(300 K)[c]	C_p(400 K)	C_p(500 K)	C_p(600 K)	C_p (800 K)	C_p (1000 K)	C_p (1500 K)
CH_3CH_2OH	TVR[d]		59.12	12.11	15.57	19.00	22.05	27.00	30.76	36.79
(3)[h]	IR[e]		3.66	2.17	2.26	2.21	2.08	1.81	1.60	1.31
	IR[f]		4.00	1.61	1.45	1.33	1.25	1.15	1.10	1.05
	total[g]	−56.12± 0.2	66.78	15.89	19.29	22.54	25.38	29.97	33.47	39.15
$CH_3CHClOH$	TVR[d]		67.13	15.25	18.94	22.29	25.13	29.56	32.83	38.02
(3)[h]	IR[e]		4.22	2.07	2.17	2.12	2.01	1.76	1.57	1.30
(2)[i]	IR[f]		2.52	1.80	2.05	2.15	2.17	2.07	1.90	1.56
	total[g]	−68.63 ± 1.24	75.22	19.12	23.15	26.56	29.31	33.39	36.31	40.88
CH_3CCl_2OH	TVR[d]		71.64	19.14	22.91	26.03	28.56	32.36	35.09	39.36
(3)[h]	IR[e]		3.93	1.91	2.09	2.16	2.15	2.01	1.83	1.49
	IR[f]		1.10	1.95	2.76	3.32	3.52	3.23	2.71	1.84
	total[g]	−75.72 ± 1.31	76.77	23.00	27.75	31.51	34.23	37.60	39.63	42.68
$CH_3CH_2O^\bullet$	TVR[d]		61.74	13.44	16.54	19.52	22.16	26.41	29.63	34.67
(3)[h]	IR[e]		4.59	2.08	1.98	1.82	1.67	1.45	1.31	1.15
	total[g]	−3.90 ± 1.27	66.33	15.52	18.52	21.34	23.83	27.86	30.94	35.82
$CH_3CHClO^\bullet$	TVR[d]		69.42	16.06	19.51	22.52	25.01	28.80	31.56	35.80
(3)[h]	IR[e]		4.21	2.07	1.96	1.90	1.84	1.73	1.63	1.42
(2)[i]	total[g]	−14.79 ± 2.90	73.63	18.13	21.47	24.42	26.85	30.53	33.19	37.22
$CH_3CCl_2O^\bullet$	TVR[d]		74.74	20.14	23.37	26.02	28.14	31.32	33.58	37.00
(3)[h]	IR[e]		4.19	2.07	2.18	2.14	2.04	1.80	1.60	1.31
	total[g]	−21.85 ± 2.82	78.93	22.21	25.55	28.16	30.18	33.12	35.18	38.31
$CH_3C^\bullet HOH$	TVR[d]		60.39	12.30	15.28	18.11	20.58	24.54	27.55	32.42
(3)[h]	IR[e]		5.22	1.57	1.42	1.32	1.25	1.16	1.11	1.05
	IR[f]		3.31	1.52	1.66	1.70	1.69	1.60	1.49	1.30
	total[g]	−13.34 ± 0.84	68.92	15.39	18.36	21.13	23.52	27.30	30.15	34.77
$CH_3C^\bullet ClOH$	TVR[d]		67.03	15.00	18.14	20.91	23.23	26.80	29.43	33.57
(3)[h]	IR[e]		4.84	2.06	1.88	1.69	1.54	1.35	1.24	1.11
	IR[f]		1.25	2.18	2.99	3.41	3.45	2.98	2.45	1.68
	total[g]	−25.89 ± 2.13	73.26	19.24	23.01	26.02	28.22	31.13	33.12	36.36
$C^\bullet H_2CH_2OH$	TVR[d]		60.84	12.94	15.97	18.77	21.17	24.99	27.88	32.58
(1)[j]	IR[e]		4.86	1.42	1.29	1.21	1.15	1.09	1.06	1.02
	IR[f]		3.36	2.28	2.09	1.84	1.65	1.40	1.27	1.12
	total[g]	−13.50 ± 3.0	69.06	16.64	19.35	21.82	23.97	27.48	30.21	34.72
$C^\bullet H_2CHClOH$	TVR[d]		71.40	16.06	19.26	21.94	24.10	27.37	29.78	33.67
(1)[j]	IR[e]		3.21	2.05	2.27	2.34	2.30	2.09	1.86	1.48
(2)[i]	IR[f]		2.40	2.18	2.27	2.28	2.24	2.07	1.88	1.53
	total[g]	−17.51 ± 2.13	78.33	20.29	23.80	26.56	28.64	31.53	33.52	36.68
$C^\bullet H_2CCl_2OH$	TVR[d]		74.63	20.01	23.29	25.72	27.57	30.20	32.06	35.04
(2)[h]	IR[e]		4.13	1.79	1.82	1.76	1.68	1.52	1.39	1.21
	IR[f]		1.31	2.07	2.80	3.24	3.34	2.99	2.51	1.74
	total[g]	−23.79 ± 2.13	80.30	23.87	27.90	30.72	32.59	34.71	35.96	37.99

[a] Thermodynamic properties are referred to a standard state of an ideal gas of at 1 atm. Torsional frequencies are excluded in the calculations of entropies and heat capacities. Instead, a more exact contribution from hindered rotations about the C−C and C−O bond is included. $\Delta H_f°_{298}$ for CH_3CH_2OH, $CH_3CH_2O^\bullet$, $C^\bullet H_2CH_2OH$, and $CH_3C^\bullet HOH$ are from Table 1. [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−C bond. [f] Contribution from internal rotation about the C−O bond. [g] Symmetry number is taken into account ($-R$ ln(symmetry number)). [h] Symmetry number. [i] Optical isomer number. [j] CH_2 group is not planar (see text), and symmetry number is 1.

Entropy ($S°_{298}$) and Heat Capacity ($C_p(T)$'s ($300 \leq T/\mathrm{K} \leq 1500$)). $S°_{298}$ and $C_p(T)$'s calculation results using the B3LYP/6-31G(d,p) determined geometries and harmonic frequencies are summarized in Table 7. Harmonic vibrational frequencies and moments of inertia are listed in Supporting Information Table S5. The two lowest frequencies (one in $CH_3CH_2O^\bullet$, $CH_3CHClO^\bullet$, and $CH_3CCl_2O^\bullet$) are omitted in calculation of $S°_{298}$ and $C_p(T)$'s; but we replace their contributions with values from analysis of the internal rotations. TVR represents the sum of the contributions from translation, vibration, and external rotation for $S°_{298}$ and $C_p(T)$'s. IR represents the contributions from hindered internal rotations about C−C and C−O bonds for $S°_{298}$ and $C_p(T)$'s. The calculations are based on optimized geometries and rotational potential curves from the B3LYP/6-31G(d,p) data. There are differences in barrier height calculated at the B3LYP/6-31G(d,p) and the MP2(FULL)/6-31G(d) levels of theory, as discussed in the rotation barrier section. The resulting differences in $S°_{298}$ and $C_p(T)$'s are however small. In the most extreme case, the barrier height varies by 2 kcal/mol for $C^\bullet H_2CCl_2OH$ in the two calculations. The resulting difference in the contribution to $S°_{298}$ is ca. 0.7 cal/(mol K), and the maximum difference for the contribution to $C_p(T)$'s is ca. 0.5 cal/(mol K). This indicates that the maximum error for the contribution to $S°_{298}$ and $C_p(T)$'s from one internal rotor is less than 0.7 cal/(mol K).

The standard entropies also include correction from rotational conformers. This correction is calculated by the following formula for 1 mol of mixture:[38]

$$\Delta S_{\mathrm{mixing}} = -R\sum n_i \ln(n_i) \qquad \text{(E2)}$$

where n_i is the equilibrium mole fraction of the ith form. $\Delta S_{\mathrm{mixing}}$ represents the entropy of mixing of rotational conformations or optical conformations.

Group Additivity Values. The C/C/Cl/H/O and $C/C/Cl_2/O$ group values are derived from the thermodynamic property data of $CH_3CHClOH$ and CH_3CCl_2OH, respectively. The group values for $\Delta H_f°_{298}$ and C_p's of C/C/Cl/H/O are calculated on the basis of

$$(CH_3CHClOH) = (C/C/Cl/H/O) + (C/C/H_3) + (O/C/H)$$

TABLE 8: Group Values

groups	$\Delta H_f°_{298}$[b]	$S°_{298}$[c]	C_p(300 K)[c]	C_p(400 K)	C_p(500 K)	C_p(600 K)	C_p (800 K)	C_p (1000 K)	C_p (1500 K)
$C/C/H_3$[c]	−10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
O/C/H[c]	−37.90	29.07	4.30	4.50	4.82	5.23	6.02	6.61	7.44
C/C/Cl/H/O	−20.53	16.54	8.63	10.81	12.34	13.29	14.35	14.93	15.86
$C/C/Cl_2/O$	−27.62	19.47	12.51	15.41	17.29	18.21	18.56	18.25	17.66

[a] Units in kcal/mol. [b] Units in cal/(mol K). [c] Reference 39.

TABLE 9: Hydrogen Bond Increment (HBI) Group Values

groups[a]	bond energy[b]	$S°_{298}$[c]	C_p(300 K)[c]	C_p(400 K)	C_p(500 K)	C_p(600 K)	C_p (800 K)	C_p (1000 K)	C_p (1500 K)
$CH_3CH_2O^•$	104.32	0.93	−0.37	−0.77	−1.20	−1.56	−2.11	−2.52	−3.33
$CH_3CHClO^•$	105.94	−1.59	−0.99	−1.68	−2.14	−2.46	−2.86	−3.12	−3.66
$CH_3CCl_2O^•$	105.97	2.16	−0.79	−2.20	−3.35	−4.05	−4.48	−4.45	−4.37
$CH_3C^•HOH$	94.88	2.14	−0.50	−0.93	−1.41	−1.87	−2.67	−3.31	−4.38
$CH_3C^•ClOH$	94.84	−1.96	0.12	−0.14	−0.54	−1.09	−2.26	−3.19	−4.52
$C^•H_2CH_2OH$	102.52	0.09	0.75	0.06	−0.72	−1.41	−2.48	−3.26	−4.42
$C^•H_2CHClOH$	103.22	0.93	1.17	0.65	0.00	−0.67	−1.86	−2.79	−4.20
$C^•H_2CCl_2OH$	104.03	2.73	0.88	0.16	−0.78	−1.64	−2.89	−3.68	−4.69

[a] For efficiency in name length, these HBI groups are abbreviated in the BD files of Therm program[40] as follows: $CCO^•$, $CCClO^•$, $CCCl_2O^•$, $CC^•OH$, $CC^•ClOH$, $C^•COH$, $C^•CClOH$, and $C^•CCl_2OH$. Therm is available (free by writing e-mail to the authors). [b] Units in kcal/mol. [c] Units in cal/(mol K).

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

$$(CH_3CHClOH) = (C/C/Cl/H/O) + (C/C/H_3) + (O/C/H) + R\ln(OI) - R\ln(\sigma)$$

where $R = 1.987$ cal/(mol K), OI stands for optical isomer number and σ is the symmetry number. The group values of $C/C/Cl_2/O$ are estimated in the same manner. The thermochemical properties on the $C/C/H_3$ and O/C/H group are taken from the existing literature value.[39] The two carbon−chlorine−oxygen group values derived in this work are listed in Table 8, which shows that the group values for $\Delta H_f°_{298}$ decrease with the increased number of chlorine atoms.

Hydrogen Bond Increment Group Values. HBI[40] (hydrogen bond increment) group values are derived for the chloro−oxy−ethyl radicals in this study, using the thermodynamic property data of chloroethoxy and hydroxychloroethyl radicals and parent chloroethanols.

As an example, the bond energy of $CH_3CHClO{-}H$ is based on the $\Delta H°_{rxn,298}$ of the homolytic reaction: $(CH_3CHClOH) = (CH_3CHClO^•) + H$.

$\Delta S°_{298}$ and ΔC_p are determined more directly, as the differences in respective properties of the molecule vs the radical in such a way that the HBI values for $S°_{298}$ and $C_p(T)$ are added to the parent values to form the radical.

$$\text{HBI } C_p(T_i)(CH_3CHClO^•) = C_p(T_i)(CH_3CHClO^•) - C_p(T_i)(CH_3CHClOH)$$

$$\text{HBI } S°_{298}(CH_3CHClO^•) = S°_{298}(CH_3CHClO^•) - S°_{298}(CH_3CHClOH) + R\ln(\sigma_{CH_3CHClO}/\sigma_{CH_3CHClOH})$$

Effects for changes in symmetry between the radical and parent are not included in the HBI group but are included in evaluation of the entropy of each species separately. The following species have optical isomer number of 2 due to the different constituents on the carbon bonded with chlorine: $CH_3CHClOH$, $CH_3CHClO^•$, and $C^•H_2CHClOH$. The HBI values for other radical species are estimated in the same manner as $CH_3CHClO^•$ above, and they are listed in Table 9.

The HBI group values for the bond energy of $CH_3CH_2O^•$ and $CH_3CHClO^•$ are similar to the values of $CH_3O^•$ and $CH_2ClO^•$ derived from previous work,[19] ca. 105 kcal/mol. The HBI group values for the bond energy of $CH_3C^•HOH$ and $CH_3C^•ClOH$ are similar to those of $C^•H_2OH$ and $C^•HClOH$,[19] ca. 95 kcal/mol. The HBI group values of entropy for $CH_3O^•$ and $CCl_3O^•$ are −4.18 and −0.58 cal/(mol K) from the previous work,[19] these two values did not include the electronic orbital degeneracy of 2 by C_{3v} symmetry because the optimized geometries at the B3LYP/6-31G(d,p) level resulted in C_s symmetry for the two molecules. The C_s symmetry is due to the Jahn−Taller distortion and a vibronic coupling where the asymmetric vibrational e modes couple to the degenerate E electronic states.[41] Barckholtz et al.[41] report that an effective electronic degeneracy of $CH_3O^•$ is 2 because of the dynamic nature of the Jahn−Taller effect and the relatively larger zero-point vibration energy in $CH_3O^•$ (degeneracy is in addition to the spin states). When the electronic orbital degeneracy for $CH_3O^•$ and $CCl_3O^•$ is 2, the $S°_{298}$ for $CCl_3O^•$ is 80.41 cal/(mol K) rather than 79.03 cal/(mol K), and the HBI group values for entropy of $CH_3O^•$ and $CCl_3O^•$ are −2.80 and +0.80 cal/(mol K). For $CH_3CH_2O^•$, the substitution of a hydrogen in $CH_3O^•$ with a methyl group perturbs the C_{3v} geometry and thus slightly lifts the electronic degeneracy present in $CH_3O^•$. At room temperature, the HBI group value of entropy for $CH_3CH_2O^•$ is −0.45 cal/(mol K) without the electronic orbital degeneracy. However, Ramond et al.[42] report that the splitting between the ground $\tilde{A}^2A''$ and the first $\tilde{X}^2A'$ excited states of $CH_3CH_2O^•$ is very small, 355 ± 10 cm^{-1}. The effective electronic degeneracy of $CH_3CH_2O^•$ at room temperature can then be considered as 2, and this gives the HBI group values of entropy for $CH_3CH_2O^•$ is 0.93 cal/(mol K). The electronic degeneracy present in $CH_3O^•$ for $CH_3CHClO^•$ and $CH_3CCl_2O^•$ radicals will be removed by the orbital splitting.

Summary

Thermodynamic properties of ethanol, α-chloroethanol, α-dichloroethanol, and corresponding radicals derived from H atom loss in chloroethanols and parent ethanol are calculated using density functional and ab initio methods with several isodesmic reaction schemes. $\Delta H_f°_{298}$'s determined by the DFT, QCISD(T), and CBSQ//B3** calculations over widely varied isodesmic reaction schemes show remarkably good precision for chloroethanols, chloroethoxy radicals, and hydroxychloroethyl radicals. $S°_{298}$ and $C_p(T)$'s ($300 \leq T/K \leq 1500$)) are determined with B3LYP/6-31G(d,p) optimized geometries and frequencies, hindered internal rotational contributions to $S°_{298}$ and $C_p(T)$'s are calculated by intramolecular torsion potential curves, and the entropy corrections for the mixing of rotational conformers are included. Thermodynamic properties on C/C/Cl/H/O and C/C/Cl_2/O groups are determined for use in group additivity. The group increment values for (chloro)ethoxy and hydroxy(chloro)ethyl radicals are also determined.

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Supporting Information Available: Geometrical parameters of ethanol, α-chloroethanol, α-dichloroethanol, and corresponding radicals (Table S1). Total energies by torsion angle and internal rotational barriers above species (Table S2) and coefficients of truncated Fourier series representation expansions for internal rotation potentials (Table S3). The total electronic energies at 0 K determined 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) levels, scaled ZPVE's, and thermal correction to 298.15 K (Table S4). Harmonic vibrational frequencies and moments of inertia determined at the B3LYP/6-31G(d,p) level (Table S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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