Structures, Rotational Barriers, Thermochemical Properties, and Additivity Groups for 2-Propanol, 2-Chloro-2-propanol and the Corresponding Alkoxy and Hydroxyalkyl Radicals

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Structures, internal rotational barriers, and thermochemical properties of 2-propanol, 2-chloro-2-propanol, isopropoxy radical, 1-chloro-1-methylethoxy, 2-hydroxypropyl, and 2-chloro-2-hydroxypropyl were computed by ab initio and density functional calculations. Molecular structures and vibration frequencies were 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) and CBSQ//B3LYP/6-31G(d,p) levels. The S°_{298} and $C_p(T)$'s ($0 \le T \le 5000$ K) from vibrational, translational, and external rotational contributions were calculated using statistical mechanics based on the vibrational frequencies and structures obtained from the density functional study. Potential barriers for the internal rotations were calculated at the B3LYP/6-31G(d,p) level, and hindered rotational contributions to S°_{298} and $C_p(T)$'s were calculated by using direct integration over energy levels of the internal rotational potentials. The $\Delta H^\circ_{f,298}$ values for the above species were calculated using several isodesmic reactions for each species, and bond energies were also determined. The C/C$_2$/Cl/O group value was derived for use in Benson-type group additivity. Hydrogen bond increment groups for $C_2CO^\bullet$, $C_2CClO^\bullet$, $C^\bullet C(C)OH$, and $C^\bullet C(C)ClOH$ were also developed. The recommended $\Delta H^\circ_{f,298}$ values for $(CH_3)_2CHOH$, $(CH_3)_2CHO^\bullet$, $C^\bullet H_2(CH_3)CHOH$, $(CH_3)_2CClOH$, $(CH_3)_2CClO^\bullet$, and $C^\bullet H_2CCl(OH)CH_3$ are -69.19 ± 2.2, -11.85 ± 1.9, -14.95 ± 2.8, -79.83 ± 2.1, -25.88 ± 2.0, and -29.00 ± 2.8 kcal/mol, respectively. The radical $(CH_3)_2CClO^\bullet$ has low stability with a short atmospheric lifetime. Bond energies for the methyl hydrogens and the hydroxyl hydrogen are 102 and 105 kcal/mol in 2-propanol and 103 and 106 kcal/mol in 2-chloro-2-propanol. The recommended HBI values for oxy(chloro)alkanes are presented for use in group additivity.

Introduction

The thermochemistry of chloromethanols, chloroethanols, and the corresponding (chloro)alkoxy and hydroxy(chloro)alkyl radicals derived from H atom loss has been reported in our previous studies,[1,2] in which group additively values were derived for primary carbons with oxygen, carbon, chlorine, and hydrogen substituents. This study completes the thermochemistry for this series of oxygen and chlorine substituents on alkyl carbons, specifically secondary carbon groups with oxygen and chlorine bonds. These thermochemical parameters are important in evaluating thermochemical stability of reaction paths in the atmosphere and in combustion environments. These values also provide a base for estimation of equilibria and energies for simple dissociation reactions.

There are, to our knowledge, no estimates of thermochemical properties of secondary chlorohydroxy or chloroether alkanes. Wallington et al.[3,4] studied the stability and infrared spectra of mono-, di-, and trichloromethanol, and reported that the chlorinated methanols decayed with first-order kinetics to HCl and the corresponding carbonyl compound via a heterogeneous mechanism. They also found the rate constants for the decompositions of mono-, di-, and trichloromethanol to be $(3.4 \pm 0.2) \times 10^{-3}$, $(5.5 \pm 0.3) \times 10^{-3}$, and $(9.9 \pm 0.2) \times 10^{-3}$ s^{-1}, respectively. The lower limit for the homogeneous gas-phase lifetime of mono- and dichloromethanol was found to be 660 and 110 s, and the rate of homogeneous decomposition of trichloromethanol was slower having at least 31 kcal/mol of activation energy with an estimated lifetime on the order of days.

There is some data in the literature on chloroalkoxy radicals. Wu and Carr[5,6] reported that the rate constant of the unimolecular three-center elimination of HCl from $CH_2ClO^\bullet$ at 10 Torr can be expressed by an Arrhenius form: $k(T) = (7.7 \pm 2.3)\,e^{-(4803 \pm 772)/T} \times 10^9$ s^{-1}, with the activation energy ca. 9.5 kcal/mol, and a lifetime for $CH_2ClO^\bullet$ of less than 1 μs. Wallington[7] and Kaiser[8] reported the evidence for the three-center elimination of HCl from $CH_3CHClO^\bullet$ by experiment. Hou et al.[9] studied the decomposition and isomerization of $CH_3CHClO^\bullet$ radical by ab initio G2(MP2, SVP) calculation and provided theoretical support for the above experimental result. They reported that the three-center elimination of HCl is the most favorable path for the decomposition of chloroethoxy, and that the critical transition state for this channel lies 7.4 kcal/mol above $CH_3CHClO^\bullet$. The Cl elimination path is slightly higher, 8.2 kcal/mol. Their estimated total rate of decomposition of chloroethoxy under typical tropospheric conditions is 3×10^5 s^{-1}, and the lifetime of $CH_3CHClO^\bullet$ is 3.3 μs.

Schneider et al.[10] investigated the bond strength trends in the series of halogenated methanols using ab initio molecular orbital theory and found that the O−H bond strength is increased with the degree of halogenation in a manner that coincides with the effectiveness of negative hyperconjugation between the methyl and hydroxyl groups. These phenomena were also observed by Sun and Bozzelli.[1,2] Khatoon et al.[11] studied the reactions of 2-C_3H_7OD with Cl atoms in a discharge flow reactor and a Laval

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nozzle reactor at room temperature and at pressures of a few millibar and reported that abstraction from the alkyl structure was the thermodynamically favored route, forming mainly secondary radicals. In our previous study on ethanol and chloroethanols, we determined that the carbon−hydrogen bond energy on the β-carbon of ethanol and chloroethanols is increased relative to normal primary bonds. This suggests that the bond energies on the methyl carbons of 2-propanol are higher than normal primary C−H (101.6 kcal/mol) bonds and thus may be comparable in strength to the hydroxyl O−H bonds (104 kcal/mol), this is in agreement with Khatoon et al.'s results.

This study determines the thermochemical properties and internal rotation barriers in 2-propanol, 2-chloro-2-propanol, and the corresponding (chloro)alkoxy and hydroxy(chloro)alkyl radicals derived from H atom loss using density functional and ab initio calculation methods. The stabilities of the (chloro)-alkyl and (chloro)alkoxy radicals are also discussed. The group value for the secondary carbon, a chloro-oxy-dialkyl central group, was derived. This is the final central atom group in our calculations for the series of oxy-chlorocarbon groups, and there is no tertiary carbon in this series. Several hydrogen bond increment (HBI)[12] group values for the corresponding radicals are also derived, and evaluation of mono-, di-, tricarbon (chloro)-alcohol HBI values results in the recommended oxy(chloro)-alkanes HBI values for use in group additivity.[13]

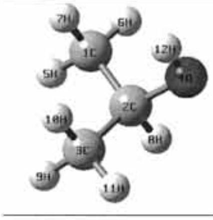
Calculation Methods

All of the density functional and ab initio calculations were performed using the Gaussian 94[14] and Gaussian 98[15] program suites. The geometry optimization, harmonic vibration frequencies, and zero-point vibrational energies (ZPVE) were computed at the B3LYP/6-31G(d,p) level. The optimized geometry parameters were used to obtain total electronic energies at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), and CBSQ//B3LYP/6-31G(d,p) (abbreviated as CBSQ//B3**) single-point levels of calculation.[16−18] Total energies were corrected by ZPVEs, which were scaled by 0.9806 as recommended by Scott et al.[19] Thermal correction was taken into account using the B3LYP structure and vibrations. Restricted and open-shell calculations were used for the stable molecules and radicals, respectively.

The selection of a calculation method was fully discussed in the previous studies.[1,20] Here, we only give a brief summary: B3LYP/6-31G(d,p) includes polarized functions on both the hydrogen and heavy atoms and was reported to yield accurate geometries and reasonable energies when used with isodesmic or homodesmic working reactions.[21,22] Byrd et al.[22] and Curtiss et al.[23] reported that B3LYP/6-31G(d,p) provides accurate structures for compounds with elements up to atomic number 10. B3LYP/6-311+G(3df,2p) has a larger basis set with diffuse functions allowing more overlap of the Cl electrons. CBSQ//B3LYP/6-31G(d,p) employs an improved geometry and ZPE at the B3LYP/6-31G(d,p) level with a correction for spin contamination for the open-shell systems.

Contributions of vibration, translation, and external rotation to entropies and heat capacities were calculated from scaled vibrational frequencies and moments of inertia of the optimized structures. Contributions from hindered rotors to S°_{298} and $C_p(T)$'s were determined using direct integration over energy levels of the intramolecular rotational potential curves, which can be represented by a truncated Fourier series expansion.[24] The number of optical isomers and spin degeneracy of unpaired electrons were also incorporated for calculation of S°_{298}.

TABLE 1: Geometrical 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]		
	$(CH_3)_2CHOH$								
	r21	1.5300	a321	112.63	d4213	234.60	236	1090	1512
	r32	1.5300	a421	111.11	d5123	299.70	274	1151	1522
	r42	1.4296	a512	111.42	d6123	179.02	309	1194	3029
	r51	1.0952	a612	110.34	d7123	59.34	357	1319	3033
	r61	1.0935	a712	110.66	d8213	120.63	427	1368	3053
	r71	1.0978	a821	108.76	d9321	60.29	472	1412	3096
	r82	1.0969	a932	111.42	d10321	300.65	819	1422	3107
	r93	1.0952	a1032	110.66	d11321	180.97	924	1430	3128
	r103	1.0978	a1132	110.34	d12421	63.13	941	1498	3130
	r113	1.0935	a1242	107.19			975	1499	3790
	r124	0.9675							
							12.91	226.57	381.05
	$(CH_3)_2CHO^\bullet$								
	r21	1.5381	a321	113.77	d4213	230.45	203	1051	1509
	r32	1.5381	a421	112.55	d5123	302.02	244	1089	1518
	r42	1.3749	a512	111.15	d6123	181.06	355	1169	2851
	r51	1.0944	a612	110.23	d7123	61.70	392	1204	3046
	r61	1.0927	a712	109.94	d8213	119.13	450	1263	3052
	r71	1.0948	a821	107.62	d9321	57.98	809	1394	3120
	r82	1.1151	a932	111.15	d10321	298.30	895	1419	3126
	r93	1.0944	a1032	109.94	d11321	178.94	916	1494	3139
	r103	1.0948	a1132	110.23			988	1499	3141
	r113	1.0928							
							196.32	225.23	373.91
	$C^\bullet H_2CH(OH)CH_3$								
	r21	1.4923	a321	112.96	d4213	234.09	136	962	1507
	r32	1.5329	a421	111.08	d5123	339.65	251	1031	1509
	r42	1.4355	a512	121.71	d6123	167.34	339	1145	2978
	r51	1.0850	a612	119.25	d7213	120.60	363	1168	3039
	r61	1.0851	a721	109.51	d8321	60.20	423	1258	3108
	r72	1.1026	a832	111.07	d9321	300.40	443	1346	3136
	r83	1.0953	a932	110.69	d10321	180.59	566	1408	3158
	r93	1.0963	a1032	110.08	d11421	54.72	838	1415	3267
	r103	1.0928	a1142	106.55			910	1465	3786
	r114	0.9678							
							200.67	216.75	369.84
	$(CH_3)_2CClOH$								
	r21	1.5188	a321	114.24	d4213	242.73	244	946	1493
	r32	1.5243	a421	107.22	d5213	125.94	278	1014	1509
	r42	1.8995	a521	107.59	d6521	182.02	293	1025	1514
	r52	1.3843	a652	108.68	d7123	297.86	305	1131	3052
	r65	0.9678	a712	108.68	d8123	178.93	362	1161	3064
	r71	1.0950	a812	109.98	d9123	57.89	400	1276	3125
	r81	1.0911	a912	110.86	d10321	62.23	448	1384	3143
	r91	1.0909	a1032	108.64	d11321	302.12	475	1424	3154
	r103	1.0953	a1132	111.27	d12321	181.69	553	1436	3171
	r113	1.0915	a1232	110.83			829	1491	3798
	r123	1.0940							
							376.92	593.87	617.63
	$(CH_3)_2CClO^\bullet$								
	r21	1.5489	a321	112.66	d5213	122.56	226	911	1489
	r32	1.5481	a421	106.32	d6321	180.64	262	959	1490
	r42	1.9094	a521	109.59	d7123	299.37	270	1001	1512
	r52	1.3178	a632	109.89	d8123	179.36	298	1069	3069
	r63	1.0904	a712	108.73	d9123	59.54	335	1129	3072
	r71	1.0930	a812	109.92	d10321	60.64	366	1201	3159
	r81	1.0904	a912	108.83	d11321	300.47	387	1381	3162
	r91	1.0909	a1032	108.73			549	1417	3176
	r103	1.0930	a1132	108.89			815	1477	3178
	r113	1.0909		243.91					
							358.27	582.35	624.68
	$C^\bullet H_2CCl(OH)CH_3$								
	r21	0.9680	a312	108.83	d4312	65.07	168	673	1474
	r31	1.3674	a431	106.26	d5312	175.58	257	823	1500
	r43	2.0598	a531	111.24	d6531	168.51	266	962	1513
	r53	1.4455	a653	119.88	d7531	336.79	277	1025	3053
	r65	1.0819	a753	119.10	d8312	312.39	350	1062	3129
	r75	1.0826	a831	114.88	d9831	55.75	398	1177	3165
	r83	1.5182	a983	110.78	d10831	176.09	425	1316	3191
	r98	1.0930	a1083	111.07	d11831	296.16	474	1406	3308
	r108	1.0905	a1183	108.46			478	1430	3801
	r118	1.0958							
							366.93	606.51	628.91

[a] Bond length in Å. [b] Bond angle in deg. [c] Dihedral angle in deg. [d] Frequencies in cm^{-1}. [e] Moments of inertia in amu $bohr^2$.

The $\Delta H^\circ_{f,298}$ were calculated using total energies and isodesmic reactions with group balance if possible. Isodesmic reactions are hypothetical reactions in which the number of electron pairs and the bonds of the same type are conserved on both sides of the equation so that only the relationship among the bonds is altered. The calculated energy of the reactions will reflect the deviation from additivity of bond energy that describes the altered relationship among the bonds. Isodesmic working reactions provide higher accuracy even at lower calculation levels because the nature of bonds is conserved and the inherent errors associated with the computation tend to appear in both reactants and products and are partially cancelled.

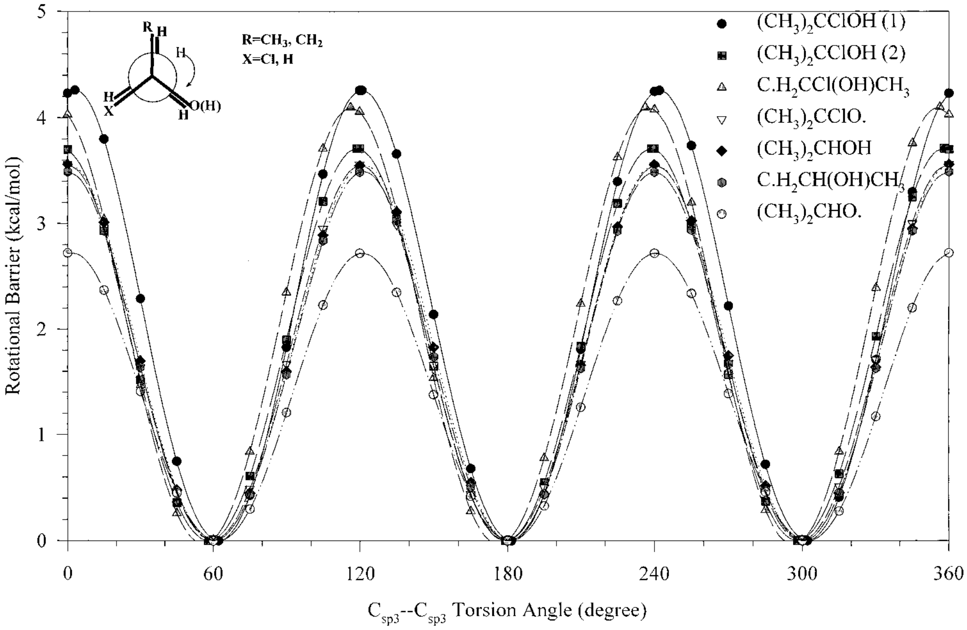


Figure 1. Potential barriers for internal rotation about the C—C bond of $(CH_3)_2CHOH$, $(CH_3)_2CClOH$, $(CH_3)_2CHO^{\bullet}$, $(CH_3)_2CClO^{\bullet}$, $C^{\bullet}H_2CH(OH)CH_3$, and $C^{\bullet}H_2CCl(OH)CH_3$. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Lines are Fourier expansion with the coefficients listed in the Supporting Information (Table S2).

Accuracy near 0.5 kcal/mol by this enthalpy estimation method was illustrated in several previous studies.[1,2]

Results and Discussion

Geometries. The optimized geometric parameters along with vibrational frequencies and moments of inertia for six target species are presented in Table 1. The lowest energy conformations of $(CH_3)_2CClOH$, $(CH_3)_2CClO^{\bullet}$, and $C^{\bullet}H_2CCl(OH)CH_3$ exhibit the anomeric effect, that is, a delocalization of the lone pair electron on the oxygen with the antibonding σ^* orbital of the C—Cl bond. Due to the anomeric effect, the C—O bond length decreases significantly with chlorine substitution (1.4296 Å in $(CH_3)_2CHOH$, 1.3843 Å in $(CH_3)_2CClOH$; 1.3749 Å in $(CH_3)_2CHO^{\bullet}$, 1.3178 Å in $(CH_3)_2CClO^{\bullet}$; 1.4354 Å in $C^{\bullet}H_2CH(OH)CH_3$, 1.3674 Å in $C^{\bullet}H_2CCl(OH)CH_3$). The anomeric effect can also be seen in the C—Cl bond length, which is longer than a normal C—Cl bond (1.8995 Å in $(CH_3)_2CClOH$, 1.9094 Å in $(CH_3)_2CClO^{\bullet}$, 2.0598 Å in $C^{\bullet}H_2CCl(OH)CH_3$) as predicted by the DFT calculations. The C—Cl bond in $C^{\bullet}H_2CCl(OH)CH_3$ is 0.1 Å longer than in the other two chloro species due to hyperconjugation between the $-CH_2^{\bullet}$ center and the σ^*(C—Cl) molecular orbital in its lowest energy conformer. Because p$-\pi$ orbital overlap implies transfer of electron density, the C—Cl bond becomes weaker and longer, while the C—C bond gets stronger and shorter. The C—C bond length in $C^{\bullet}H_2CCl(OH)CH_3$ is 1.44 Å, which is shorter than the normal 1.53 Å. The MP2(full)/6-31G(d,p) geometry optimization predicts tight structures for these species and gives the C—Cl bond length 1.8299, 1.8294, and 1.8640 Å, respectively; these data also suggest that an anomeric effect and hyperconjugation exist in these species.

The DFT calculations predict a nonplanar structure for the $-C^{\bullet}H_2$ group in 2-hydroxypropyl and 2-chloro-2-hydroxypropyl radicals, in which the inversion frequencies for the methylene group are 566.0 and 672.8 cm^{-1}, respectively. The density functional optimized geometry for $(CH_3)_2CHOH$ gives the $\angle H_c-C-O-H_o$ dihedral angle 180.0°, indicating that there is a mirror plane between the two methyl groups, that is, C_s symmetry in $(CH_3)_2CHOH$. The density functional structure also predicts C_s symmetry in $(CH_3)_2CHO^{\bullet}$. The symmetry number is assigned as 18 for $(CH_3)_2CHOH$ and $(CH_3)_2CHO^{\bullet}$ on the basis of these data.

Rotational Barriers. Potential energy as a function of torsion angle was 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. $C^{\bullet}H_2CCl(OH)CH_3$ is an exception; here, the C—Cl bond length was constrained when scanning the $H_c-C-C-O$ and $C-C-O-H$ dihedral angles in $C^{\bullet}H_2CCl(OH)CH_3$. This is a result of the weak C—Cl bond in this radical; it requires only 18 kcal/mol for β-scission to form 2-hydroxypropene + Cl atom. The barrier of a given rotation was then calculated as the difference between the highest points on the potential energy surface and the corresponding most stable conformer. The geometries at the points of minima and maxima were fully optimized when possible.

The calculated rotational barriers about the $CH_3-C_{sp^3}$ bond of the six target species are shown in Figure 1. All of the curves for $C_{sp^3}-C_{sp^3}$ torsion potential are symmetric and show a threefold symmetry with barriers between 2.72 and 4.26 kcal/mol. The barriers for the $CH_3-C_{sp^3}$ torsion of chloro-substituted species are higher than those of nonchlorinated species, and the barriers for stable parent are higher than those of the corresponding radicals probably due to reduced steric effect by the radical carbon groups. Two $C_{sp^3}-C_{sp^3}$ rotational curves for $(CH_3)_2CClOH$ are shown in Figure 1, and one is 0.55 kcal/mol higher than the other because the hydroxyl H atom orients toward one methyl group resulting in a steric interaction.

Figure 2 shows the twofold rotational barriers about the $CH_2-C_{sp^3}$ bond for $C^{\bullet}H_2CCl(OH)CH_3$ and $C^{\bullet}H_2CH(OH)CH_3$. The H—OH eclipsed conformer of $C^{\bullet}H_2CCl(OH)CH_3$ has the lowest energy because of the interaction between the H atom in the $-CH_2$ group and the O atom (interatomic distance is 2.528 Å). The barrier height for $C^{\bullet}H_2CCl(OH)CH_3$ is 3.6 kcal/mol higher than that of $C^{\bullet}H_2CH(OH)CH_3$, probably still because of the electrostatic interaction between the Cl atom and the H atom on the $-C^{\bullet}H_2$ group (the interatomic distance is 2.83 Å) on the barrier top.

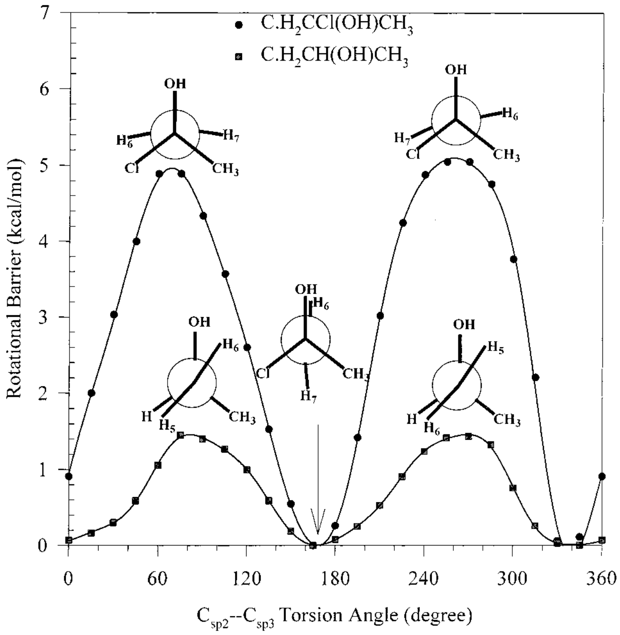


Figure 2. Potential barriers for internal rotation about the C—C bond of $C^\bullet H_2CH(OH)CH_3$ and $C^\bullet H_2CCl(OH)CH_3$. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Lines are Fourier expansion with the coefficients listed in the Supporting Information (Table S2).

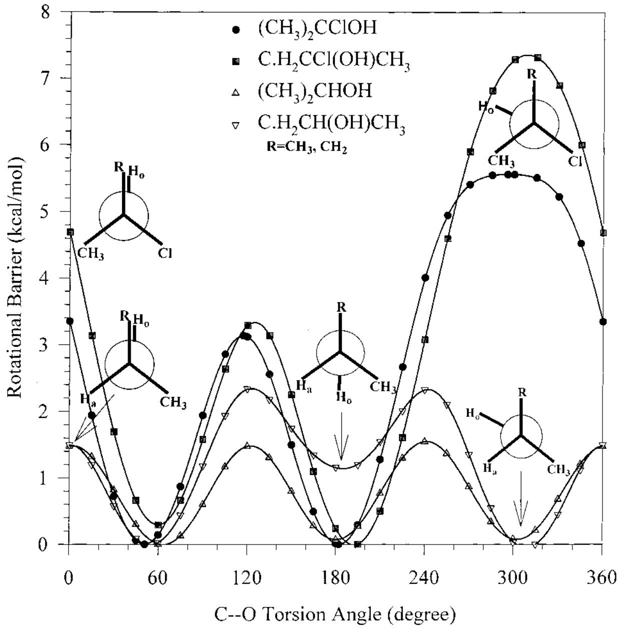


Figure 3. Potential barriers for internal rotation about the C—O bond of $(CH_3)_2CClOH$, $(CH_3)_2CClOH$, $C^\bullet H_2CH(OH)CH_3$, and $C^\bullet H_2CCl(OH)CH_3$. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Lines are Fourier expansion with the coefficients listed in the Supporting Information (Table S2).

TABLE 2: $\Delta H^\circ_{f,298}$ for Standard Species Used in the Reactions

species	$\Delta H^\circ_{f,298}$ (kcal/mol)	species	$\Delta H^\circ_{f,298}$ (kcal/mol)
CH_4	−17.89 ± 0.07 (Cox)[25]	$CH_3O^\bullet$	4.10 ± 1.0 (Tsang)[26]
C_2H_6	−20.24 ± 0.12 (Cox)[25]	$C_2H_5O^\bullet$	−3.90 ± 1.27 (Sun)[1]
C_3H_8	−25.02 ± 0.12 (Pedley)[27]	$C^\bullet H_2OH$	−3.97 ± 0.22 (Sun)[1]
CH_3Cl	−19.57 ± 0.12 (Pedley)[27]	$CH_3C^\bullet HOH$	−13.34 ± 0.84 (Sun)[1]
C_2H_5Cl	−26.79 ± 0.26 (Pedley)[27]	$C^\bullet H_2CH_2OH$	−5.70 ± 0.85 (Sun)[2]
$(CH_3)_2CHCl$	−35.00 ± 0.56 (Stull)[28]	$(CH_3)_2C^\bullet OH$	−25.6 ± 3 (Holmes)[29]
CH_3OH	−48.07 ± 0.05 (Cox)[25]	$Cl^\bullet$	28.92 ± 2 (Stull)[30]
C_2H_5OH	−56.21 ± 0.10 (Pedley)[27]	$H^\bullet$	52.10 ± 0.001 (Stull)[30]
CH_2ClOH	−58.07 ± 0.69 (Sun)[1]	$OH^\bullet$	8.89 ± 0.09 (Ruscic)[31]
$CH_3^\bullet$	34.82 ± 0.2 (Stull)[30]	$CH_2{=}CHCH_3$	4.78 ± 0.19 (Pedley)[27]
$C_2H_5^\bullet$	28.80 ± 0.50 (Marshall)[32]	syn-$CH_2{=}CHOH$	−30.59 ± 0.55 (Pedley)[27]
$CH_2Cl^\bullet$	27.7 ± 2.0 (Holmes)[33]	$CH_2{=}C(OH)CH_3$	−39.91 (Turecek)[34]
$CH_3CHCl^\bullet$	19.3 ± 2.0 (Holmes)[33]	CH_3CHO	−39.70 ± 0.12 (Pedley)[27]
$(CH_3)_2C^\bullet H$	22.0 ± 0.5 (Tsang)[26]	CH_3COCH_3	−52.23 ± 0.14 (Wiberg)[35]
$(CH_3)_2C^\bullet Cl$	7.15 ± 0.72 (Seetula)[36]	$CH_3C(O)Cl$	−58.03 ± 0.19 (Pedley)[27]

The calculated rotational barriers about the C—O bond of $(CH_3)_2CClOH$, $C^\bullet H_2CCl(OH)CH_3$, $(CH_3)_2CHOH$, and $C^\bullet H_2CH(OH)CH_3$ are shown in Figure 3. There are three conformers in $(CH_3)_2CHOH$; two are the $H_o{-}H_\alpha$ gauche conformers (subscript "o" stands for oxygen atom), and one is the $H_o{-}H_\alpha$ anti conformer. The energy for the H_o-H_α anti conformer is only 0.08 kcal/mol lower than that of the H_o-H_α gauche conformer, so the three conformers should be equally populated at room temperature. For $C^\bullet H_2CH(OH)CH_3$, there are two $H_o{-}CH_2$ gauche conformers and one $H_o{-}CH_2$ anti conformer. The energy for the $H_o{-}CH_2$ anti conformer is 1.16 kcal/mol higher than that of $H_o{-}CH_2$ gauche conformer. For $C^\bullet H_2CCl(OH)CH_3$, the $H_o{-}CH_2$ gauche conformer is 0.29 kcal/mol higher than that of the $H_o{-}CH_2$ anti conformer. The maxima on the potential curves of $(CH_3)_2CClOH$ and $C^\bullet H_2CCl(OH)CH_3$ correspond to the structures in which the hydroxyl H atom is anti to the Cl atom on the α-carbon due to anomeric effects. This phenomenon is similar to those in the chloromethanol and chloroethanol observed in our previous study.[1,2]

Enthalpy of Formation. The total electronic energies at 0 K determined at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), and CBSQ//B3LYP/6-31G(d,p) levels, scaled ZPVEs, and thermal corrections to 298.15 K for six target species are listed in the Supporting Information (Table S1). The spin expectation values, $\langle S^2 \rangle$, range from 0.760 to 0.786 for the target radicals and suggest no significant error for pure doublet radicals due to spin contamination.

The $\Delta H^\circ_{f,298}$ values are estimated using total energies and 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 $\Delta H^\circ_{f,298}$ of the reference compounds, the uncertainty of the ZPVEs and the thermal corrections, and the choice of the isodesmic reactions. The $\Delta H^\circ_{f,298}$ and their uncertainties for standard species used in the reactions are listed in Table 2. The uncertainty of ZPVEs and thermal correction is small relative to other errors. Scott and Radom[19] report rms errors of ±0.1 kcal/mol for ZPVE after scaling by 0.9806 for B3LYP/6-31G(d) and rms errors of ±0.01 kcal/mol for thermal correction from 0 to 298 K in DFT. We assume that the uncertainty from ZPVEs and the thermal correction in our calculation has the same error ranges and assign the cumulative ZPVEs and the thermal energy uncertainties to be 0.44 kcal/mol in an isodesmic reaction. The reaction enthalpies and $\Delta H^\circ_{f,298}$ values for six target species obtained from eight isodesmic reactions are tabulated in Table 3. The results for

TABLE 3: Reaction Enthalpies at 298 K and Calculated Enthalpies of Formation[a]

	B3LYP /6-31G(d,p)		B3LYP /6-311+G(3df,2p)		CBSQ//B3LYP /6-31G(d,p)	
reaction series	ΔH°_{rxn}	$\Delta H^\circ_{f,298}$	ΔH°_{rxn}	$\Delta H^\circ_{f,298}$	ΔH°_{rxn}	$\Delta H^\circ_{f,298}$
1.1 $(CH_3)_2CHOH + CH_4 \rightarrow CH_3OH + C_3H_8$	9.26	−64.47	8.33	−63.54	10.12	−65.33
1.2 $(CH_3)_2CHOH + CH_4 \rightarrow C_2H_5OH + C_2H_6$	5.40	−63.87	5.07	−63.54	7.16	−65.63
1.3 $(CH_3)_2CHOH + C_2H_6 \rightarrow C_2H_5OH + C_3H_8$	3.79	−64.69	3.35	−64.25	4.40	−65.30
1.4 $(CH_3)_2CHOH + C_2H_6 \rightarrow CH_3OH + i\text{-}C_4H_{10}$	6.86	−66.77	5.63	−65.54	5.06	−64.97
1.5 $(CH_3)_2CHOH + CH_3Cl \rightarrow CH_3OH + CH_3CHClCH_3$	2.76	−66.27	1.62	−65.13	1.08	−64.59
1.6 $(CH_3)_2CHOH + CH_3Cl \rightarrow CH_2ClOH + C_3H_8$	0.06	−63.58	0.04	−63.56	1.86	−65.38
1.7 $(CH_3)_2CHOH + CH_3Cl \rightarrow CH_3CHClOH + C_2H_6$	−5.44	−63.86	−5.15	−64.15	−4.05	−65.25
1.8 $(CH_3)_2CHOH + C_2H_5Cl \rightarrow CH_3CHClOH + C_3H_8$	−3.07	−63.79	−2.75	−64.11	−1.82	−65.04
average value and deviation[b]					−65.19 ± 0.31	
2.1 $(CH_3)_2CHO^\bullet + CH_4 \rightarrow C_3H_8 + CH_3O^\bullet$	8.28	−11.31	7.65	−10.68	8.86	−11.89
2.2 $(CH_3)_2CHO^\bullet + C_2H_6 \rightarrow C_3H_8 + C_2H_5O^\bullet$	2.61	−11.29	2.26	−10.94	3.20	−11.88
2.3 $(CH_3)_2CHO^\bullet + CH_3OH \rightarrow (CH_3)_2CHOH + CH_3O^\bullet$	−0.99	−12.02	−0.68	−12.33	−1.26	−11.75
2.4 $(CH_3)_2CHO^\bullet + C_2H_5OH \rightarrow (CH_3)_2CHOH + C_2H_5O^\bullet$	−1.18	−11.79	−1.09	−11.88	−1.20	−11.77
2.5 $(CH_3)_2CHO^\bullet + CH_3OH \rightarrow CH_3CH_2CH_2OH + CH_3O^\bullet$	2.85	−11.64	2.90	−11.69	3.13	−11.92
2.6 $(CH_3)_2CHO^\bullet + C_2H_5OH \rightarrow CH_3CH_2CH_2OH + C_2H_5O^\bullet$	2.66	−11.41	2.49	−11.24	3.19	−11.94
2.7 $(CH_3)_2CHO^\bullet + CH_2ClOH \rightarrow (CH_3)_2CHOH + CH_2ClO^\bullet$	−0.69	−11.56	−1.07	−11.18	−0.50	−11.75
2.8 $(CH_3)_2CHO^\bullet + CH_3CHClOH \rightarrow (CH_3)_2CHOH + CH_3CHClO^\bullet$	0.20	−11.55	0.06	−11.41	0.58	−11.93
average value and deviation[b]					−11.85 ± 0.08	
3.1 $C^\bullet H_2CH(OH)CH_3 + CH_4 \rightarrow (CH_3)_2CHOH + CH_3^\bullet$	4.04	−16.52	3.83	−16.31	2.55	−15.03
3.2 $C^\bullet H_2CH(OH)CH_3 + C_2H_6 \rightarrow (CH_3)_2CHOH + C_2H_5^\bullet$	−0.72	−15.43	−0.87	−15.28	−1.11	−15.04
3.3 $C^\bullet H_2CH(OH)CH_3 + CH_3OH \rightarrow (CH_3)_2CHOH + C^\bullet H_2OH$	−6.54	−14.54	−5.83	−15.25	−6.01	−15.07
3.4 $C^\bullet H_2CH(OH)CH_3 + C_2H_5OH \rightarrow (CH_3)_2CHOH + CH_3C^\bullet HOH$	−8.55	−13.86	−7.86	−14.55	−7.33	−15.08
3.5 $C^\bullet H_2CH(OH)CH_3 + C_2H_5OH \rightarrow (CH_3)_2CHOH + C^\bullet H_2CH_2OH$	0.95	−15.72	0.37	−15.14	0.27	−15.04
3.6 $C^\bullet H_2CH(OH)CH_3 + CH_2ClOH \rightarrow (CH_3)_2CHOH + C^\bullet HClOH$	−7.32	−14.26	−6.41	−15.17	−6.59	−14.99
3.7 $C^\bullet H_2CH(OH)CH_3 + CH_3CHClOH \rightarrow (CH_3)_2CHOH + C^\bullet H_2CHClOH$	−1.13	−14.07	−0.63	−13.44	0.87	−14.94
3.8 $C^\bullet H_2CH(OH)CH_3 + CH_3CHClOH \rightarrow (CH_3)_2CHOH + CH_3C^\bullet ClOH$	−8.78	−13.67	−8.08	−14.37	−7.43	−15.02
average value and deviation[b]					−15.03 ± 0.05	
4.1 $(CH_3)_2CClOH + CH_4 \rightarrow (CH_3)_2CHOH + CH_3Cl$	11.21	−78.08	10.36	−77.23	13.03	−79.90
4.2 $(CH_3)_2CClOH + CH_4 \rightarrow CH_2ClOH + C_3H_8$	11.27	−76.47	10.40	−75.60	14.88	−80.08
4.3 $(CH_3)_2CClOH + CH_4 \rightarrow CH_3CHClOH + C_2H_6$	5.76	−76.74	5.21	−76.19	8.97	−79.95
4.4 $(CH_3)_2CClOH + C_2H_6 \rightarrow (CH_3)_2CHOH + CH_3CH_2Cl$	7.22	−78.96	6.24	−77.98	8.02	−79.76
4.5 $(CH_3)_2CClOH + C_2H_6 \rightarrow CH_3CHClOH + C_3H_8$	4.15	−77.56	3.49	−76.90	6.20	−79.61
4.6 $(CH_3)_2CClOH + CH_3OH \rightarrow (CH_3)_2CHOH + CH_2ClOH$	2.00	−77.18	2.07	−77.25	4.76	−79.94
4.7 $(CH_3)_2CClOH + CH_3OH \rightarrow CH_3CHClOH + C_2H_5OH$	0.29	−76.96	0.23	−76.90	3.25	−79.92
4.8 $(CH_3)_2CClOH + CH_2ClOH \rightarrow 2CH_3CHClOH$	−1.35	−77.84	−1.70	−77.49	0.29	−79.48
average value and deviation[b]					−79.83 ± 0.20	
5.1 $(CH_3)_2CClO^\bullet + CH_4 \rightarrow CH_3CHClO^\bullet + C_2H_6$	5.54	−22.68	5.11	−22.25	8.96	−26.10
5.2 $(CH_3)_2CClO^\bullet + CH_4 \rightarrow CH_2ClO^\bullet + C_3H_8$	10.16	−22.42	9.16	−21.42	13.78	−26.04
5.3 $(CH_3)_2CClO^\bullet + C_2H_6 \rightarrow CH_3CHClO^\bullet + C_3H_8$	3.92	−23.49	3.39	−22.96	6.19	−25.76
5.4 $(CH_3)_2CClO^\bullet + C_3H_8 \rightarrow CH_3CHClO^\bullet + \text{iso-}C_4H_{10}$	3.14	−24.98	2.42	−24.26	3.90	−25.74
5.5 $(CH_3)_2CClO^\bullet + CH_3OH \rightarrow CH_3O^\bullet + (CH_3)_2CClOH$	−1.41	−26.24	−0.84	−26.81	−1.85	−25.80
5.6 $(CH_3)_2CClO^\bullet + C_2H_5OH \rightarrow C_2H_5O^\bullet + (CH_3)_2CClOH$	−1.61	−26.00	−1.25	−26.36	−1.79	−25.81
5.7 $(CH_3)_2CClO^\bullet + CH_2ClOH \rightarrow CH_2ClO^\bullet + (CH_3)_2CClOH$	−1.11	−25.78	−1.23	−25.65	−1.10	−25.79
5.8 $(CH_3)_2CClO^\bullet + CH_3CHClOH \rightarrow CH_3CHClO^\bullet + (CH_3)_2CClOH$	−0.23	−25.76	−0.10	−25.89	−0.02	−25.97
average value and deviation[b]					−25.88 ± 0.14	
6.1 $C^\bullet H_2CCl(OH)CH_3 + CH_4 \rightarrow (CH_3)_2CClOH + CH_3^\bullet$	5.47	−32.59	4.74	−31.86	1.99	−29.10
6.2 $C^\bullet H_2CCl(OH)CH_3 + C_2H_6 \rightarrow (CH_3)_2CClOH + C_2H_5^\bullet$	0.71	−31.50	0.04	−30.83	−1.67	−29.11
6.3 $C^\bullet H_2CCl(OH)CH_3 + CH_3Cl \rightarrow (CH_3)_2CClOH + CH_2Cl^\bullet$	−0.57	−31.96	−1.39	−31.13	−3.40	−29.13
6.4 $C^\bullet H_2CCl(OH)CH_3 + CH_3OH \rightarrow (CH_3)_2CClOH + C^\bullet H_2OH$	−5.11	−30.61	−4.92	−30.80	−6.58	−29.14
6.5 $C^\bullet H_2CCl(OH)CH_3 + C_2H_5OH \rightarrow (CH_3)_2CClOH + CH_3C^\bullet HOH$	−7.12	−29.93	−6.95	−30.10	−7.90	−29.15
6.6 $C^\bullet H_2CCl(OH)CH_3 + C_2H_5OH \rightarrow (CH_3)_2CClOH + C^\bullet H_2CH_2OH$	2.38	−31.79	1.28	−30.68	−0.30	−29.11
6.7 $C^\bullet H_2CCl(OH)CH_3 + CH_2ClOH \rightarrow (CH_3)_2CClOH + C^\bullet HClOH$	−5.89	−30.32	−5.50	−30.72	−7.16	−29.06
6.8 $C^\bullet H_2CCl(OH)CH_3 + CH_3CHClOH \rightarrow (CH_3)_2CClOH + CH_3C^\bullet ClOH$	−7.35	−29.73	−7.17	−29.92	−8.00	−29.09
average value and deviation[b]					−29.11 ± 0.03	

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

$\Delta H^\circ_{f,298}$ values in Table 3 show good consistency for six target species over eight working reactions and the three 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 cancelled to a significant extent and lead to reliable results. Ab initio calculations show remarkable consistency at the CBSQ//B3** level at which the standard deviation is within 0.3 kcal/mol. The $\Delta H^\circ_{f,298}$ values for target radicals are based on the $\Delta H^\circ_{f,298}$ values of the parent molecules in this work. The calculated $\Delta H^\circ_{f,298}$ for $(CH_3)_2CHOH$ in this work is −69.19 kcal/mol, which is similar to the results of Atkinson et al.,[37] −69.15; Frenkel et al.,[38] −69.18; Snelson et al.,[39] −69.19; and Cohen,[40] −69.20 kal/mol. The $\Delta H^\circ_{f,298}$ for $(CH_3)_2CHO^\bullet$ is calculated to be −11.87 kal/mol at the CBSQ//B3** level, which shows agreement with Ramond et al.'s value, −11.0 ± 1.2 kcal/mol,[41] which derived from the $\Delta H^\circ_{f,298}$ of $(CH_3)_2CHOH$ and electron affinities.

The recommended $\Delta H^\circ_{f,298}$ values for $(CH_3)_2CHOH$, $(CH_3)_2CHO^\bullet$, $C^\bullet H_2(CH_3)CHOH$, $(CH_3)_2CClOH$, $(CH_3)_2CClO^\bullet$, and $C^\bullet H_2CCl(OH)CH_3$ are −69.19 ± 2.2, −11.85 ± 1.9, −14.95 ± 2.8, −79.83 ± 2.1, −25.88 ± 2.0, and −29.00 ± 2.8 kcal/mol, respectively, which are the average values from eight reactions for each species at the CBSQ//B3** calculation level,

TABLE 4: Bond Energy Calculations

reaction series	bond energy (kcal/mol)
RO—H	
$(CH_3)_2CHOH \rightarrow (CH_3)_2CHO^\bullet + H^\bullet$	105.44
$(CH_3)_2CClOH \rightarrow (CH_3)_2CClO^\bullet + H^\bullet$	106.05
R_β—H	
$(CH_3)_2CHOH \rightarrow C^\bullet H_2CH(OH)CH_3 + H^\bullet$	102.34
$(CH_3)_2CClOH \rightarrow C^\bullet H_2CCl(OH)CH_3 + H^\bullet$	102.93
R—Cl	
$(CH_3)_2CClOH \rightarrow (CH_3)_2C^\bullet OH + Cl^\bullet$	83.15
R—ROH	
$(CH_3)_2CHOH \rightarrow CH_3C^\bullet HOH + CH_3^\bullet$	86.67
$(CH_3)_2CClOH \rightarrow CH_3C^\bullet ClOH + CH_3^\bullet$	88.76
R—OH	
$(CH_3)_2CHOH \rightarrow (CH_3)_2C^\bullet H + OH^\bullet$	96.15
$(CH_3)_2CClOH \rightarrow (CH_3)_2C^\bullet Cl + OH^\bullet$	95.94

TABLE 5: Comparison for the Bond Energy Derived from Monochloroalcohols

	bond energy (kcal/mol)					
species	RO—H	R—OH	R—Cl	R—ROH	R_α—H	R_β—H
CH_3OH	104.28	92.33	*a*	*a*	96.21	*a*
CH_2ClOH	105.04	95.20	83.02	*a*	95.71	*a*
CH_3CH_2OH	104.32	94.35	*a*	86.97	94.88	102.52
$CH_3CHClOH$	105.94	97.21	84.21	88.99	94.84	103.22
$(CH_3)_2CHOH$	105.44	96.15	*a*	86.67	91.69	102.34
$(CH_3)_2CClOH$	106.05	95.94	83.15	88.76	*a*	102.93

[a] Bond does not exist.

at which the statistical distribution of rotational conformers is included. The error limits of $\Delta H^\circ_{f,298}$ were calculated by adding the deviations between the working reactions, the errors from ZPVEs and thermal corrections, and the maximum uncertainties in the $\Delta H^\circ_{f,298}$ of reference species.

RO—H, R—OH, R—H, and R—Cl bond dissociation energies in Table 4 were calculated using the $\Delta H^\circ_{f,298}$ values above and the $\Delta H^\circ_{f,298}$ of reference radicals in Table 2. These bond energies are very similar to those derived from chloromethanol and α-chloroethanol in previous work,[1,2] and a comparison for these bond energies derived from monochloroalcohols is listed in Table 5. Bond energies on 2-propanol for the methyl hydrogens are 102 kcal/mol, and the hydroxyl hydrogen bond energy is 105 kcal/mol. Bond energies in 2-chloro-2-propanol are 103 kcal/mol for the methyl hydrogens and 106 kcal/mol for the hydroxyl hydrogen.

Entropy and Heat Capacity. S°_{298} and $C_p(T)$'s ($300 \leq T \leq 1500$ K) calculation results using the B3LYP/6-31G(d,p) geometries and harmonic frequencies are summarized in Table 6. The torsion frequencies are omitted in the calculation of S°_{298} and $C_p(T)$; 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 and was calculated using the program "SMCPS".[42] I.R. represents the contributions from hindered internal rotations about C—C and C—O bonds for S°_{298} and $C_p(T)$ and was calculated by the program "ROTATOR".[43] 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 the Supporting Information (Table S2). An example of input and output data

TABLE 6: Ideal Gas-Phase Thermodynamic Properties[a]

species		$\Delta H^\circ_{f,298}$[b]	S°_{298}[c]	C_p300[c]	C_p400[c]	C_p500[c]	C_p600[c]	C_p800[c]	C_p1000[c]	C_p1500[c]
$(CH_3)_2CHOH$ (18)[h]	TVR[d]		60.44	15.86	20.86	25.64	29.83	36.56	41.65	49.75
	I.R.[e]		4.21	2.23	2.25	2.16	2.02	1.69	1.40	0.89
	I.R.[e]		4.22	2.04	2.14	2.09	1.98	1.74	1.56	1.29
	I.R.[f]		4.02	1.58	1.45	1.34	1.26	1.16	1.11	1.05
	total[g]	−65.19 ± 2.2	72.89	21.71	26.70	31.23	35.09	41.15	45.71	52.98
$(CH_3)_2CClOH$ (9)[h]	TVR[d]		67.81	19.56	24.65	29.23	33.12	39.23	43.77	50.99
	I.R.[e]		4.16	2.04	2.14	2.11	2.01	1.78	1.59	1.31
	I.R.[e]		3.99	1.97	2.13	2.16	2.10	1.90	1.71	1.39
	I.R.[f]		2.46	1.71	1.98	2.10	2.13	2.04	1.89	1.56
	total[g]	−79.83 ± 2.1	78.43	25.27	30.91	35.60	39.37	44.95	48.96	55.26
$(CH_3)_2CHO^\bullet$ (18)[h]	TVR[d]		61.94	16.19	21.08	25.61	29.51	35.69	40.30	47.50
	I.R.[e]		4.52	2.23	2.13	1.96	1.79	1.53	1.36	1.08
	I.R.[f]		4.52	2.23	2.13	1.96	1.79	1.53	1.36	1.08
	total[g]	−11.85 ± 1.9	70.98	20.66	25.34	29.52	33.09	38.75	43.02	49.66
$(CH_3)_2CClO^\bullet$ (9)[h]	TVR[d]		70.57	20.45	25.19	29.37	32.88	38.33	42.36	48.66
	I.R.[e]		5.31	2.19	2.23	2.15	2.02	1.75	1.53	1.14
	I.R.[f]		5.31	2.19	2.23	2.15	2.02	1.75	1.53	1.14
	total[g]	−25.88 ± 2.0	81.18	24.84	29.65	33.67	36.92	41.84	45.42	50.93
$C^\bullet H_2CH(OH)CH_3$ (3)[h] (2)[i]	TVR[d]		67.05	16.54	21.14	25.3	28.84	34.43	38.65	45.45
	I.R.[e]		4.64	1.74	1.54	1.39	1.29	1.18	1.12	1.05
	I.R.[e]		4.24	2.07	2.15	2.09	1.97	1.73	1.54	1.28
	I.R.[f]		3.49	2.19	1.97	1.75	1.58	1.36	1.24	1.11
	total[g]	−14.95 ± 2.8	81.19	22.54	26.79	30.53	33.69	38.70	42.55	48.90
$C^\bullet H_2CCl(OH)CH_3$ (3)[h] (2)[i]	TVR[d]		73.44	20.21	24.81	28.72	31.95	36.94	40.65	46.61
	I.R.[e]		4.07	2.01	2.16	2.17	2.10	1.89	1.69	1.38
	I.R.[e]		2.89	2.00	2.33	2.49	2.51	2.33	2.08	1.61
	I.R.[f]		3.44	2.16	2.20	2.19	2.16	2.06	1.93	1.65
	total[g]	−29.00 ± 2.8	85.15	26.38	31.49	35.57	38.72	43.22	46.35	51.25

[a] Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm. Torsional frequencies are excluded from 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. [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] Symmetry number is taken into account ($-R$ ln(symmetry number)). [h] Symmetry number. [i] Optical isomer number. The $-CH_2$ group is not planar, and the standard entropies include the entropy of mixing of rotational conformations or optical conformations.

TABLE 7: Ideal Gas-Phase Thermodynamic Properties

T (K)	$C_p°$ (cal/(mol K))	$S°$ (cal/(mol K))	$H°(T) -$ $H°(0\ K)$ (kcal/mol)	$C_p°$ (cal/(mol K))	$S°$ (cal/(mol K))	$H°(T) -$ $H°(0\ K)$ (kcal/mol)	$C_p°$ (cal/(mol K))	$S°$ (cal/(mol K))	$H°(T) -$ $H°(0\ K)$ (kcal/mol)
		$(CH_3)_2CHOH$			$(CH_3)_2CHO^{\bullet}$			$C^{\bullet}H_2CH(OH)CH_3$	
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	9.39	49.17	0.40	9.53	48.36	0.40	9.23	55.44	0.40
100	11.94	55.80	0.81	11.86	54.86	0.81	11.95	62.59	0.81
150	14.62	60.93	1.26	13.96	59.72	1.27	15.19	68.14	1.27
200	16.95	65.36	1.80	16.07	63.88	1.82	17.91	73.00	1.83
298.15	21.62	72.89	3.13	20.57	70.98	3.19	22.46	81.19	3.23
300	21.71	73.02	3.16	20.66	71.11	3.22	22.54	81.33	3.26
400	26.70	79.91	5.00	25.34	77.64	5.08	26.79	88.52	5.15
500	31.23	86.34	7.33	29.52	83.72	7.42	30.53	94.98	7.48
600	35.09	92.37	10.11	33.09	89.40	10.18	33.69	100.87	10.19
700	38.35	98.02	13.27	36.13	94.72	13.30	36.38	106.30	13.23
800	41.15	103.33	16.78	38.75	99.71	16.73	38.70	111.33	16.54
900	43.58	108.32	20.57	41.03	104.40	20.43	40.75	116.02	20.10
1000	45.71	113.03	24.62	43.02	108.83	24.35	42.55	120.42	23.87
1100	47.57	117.49	28.89	44.75	113.01	28.48	44.15	124.56	27.82
1200	49.20	121.72	33.36	46.25	116.97	32.78	45.56	128.46	31.94
1300	50.63	125.73	37.99	47.55	120.73	37.23	46.81	132.16	36.20
1400	51.88	129.55	42.78	48.68	124.30	41.81	47.92	135.68	40.58
1500	52.98	133.19	47.69	49.66	127.70	46.51	48.90	139.02	45.08
1600	53.95	136.67	52.72	50.52	130.95	51.31	49.76	142.20	49.67
1700	54.81	139.99	57.85	51.26	134.05	56.19	50.53	145.24	54.35
1800	55.56	143.17	63.07	51.90	137.01	61.16	51.21	148.15	59.10
1900	56.23	146.22	68.37	52.47	139.85	66.19	51.81	150.94	63.92
2000	56.83	149.15	73.74	52.96	142.58	71.28	52.35	153.61	68.80
2500	58.98	162.21	101.41	54.68	154.72	97.45	54.31	165.52	93.91
3000	60.27	173.21	130.02	55.64	164.93	124.42	55.49	175.54	119.83
3500	61.08	182.68	159.20	56.22	173.70	151.88	56.23	184.15	146.24
4000	61.61	190.97	188.76	56.58	181.37	179.66	56.71	191.69	172.99
4500	61.97	198.33	218.59	56.83	188.18	207.66	57.03	198.39	199.96
5000	62.22	204.94	248.61	57.00	194.30	235.82	57.24	204.41	227.10
		$(CH_3)_2CClOH$			$(CH_3)_2CClO^{\bullet}$			$C^{\bullet}H_2CCl(OH)CH_3$	
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	8.19	53.18	0.40	9.48	53.55	0.40	9.11	56.70	0.40
100	11.08	59.57	0.82	13.16	61.21	0.84	12.43	64.48	0.83
150	15.18	64.83	1.34	16.64	67.22	1.42	16.55	70.50	1.37
200	18.87	69.71	2.00	19.55	72.41	2.13	20.22	75.86	2.05
298.15	25.16	78.43	3.66	24.74	81.18	3.89	26.27	85.15	3.79
300	25.27	78.59	3.69	24.84	81.33	3.93	26.38	85.31	3.82
400	30.91	86.64	5.91	29.65	89.14	6.22	31.49	93.64	6.08
500	35.60	94.04	8.61	33.67	96.19	8.95	35.57	101.13	8.76
600	39.37	100.87	11.73	36.92	102.62	12.07	38.72	107.90	11.80
700	42.42	107.17	15.21	39.59	108.51	15.51	41.20	114.06	15.13
800	44.95	112.99	19.00	41.84	113.94	19.22	43.22	119.69	18.72
900	47.11	118.41	23.04	43.76	118.98	23.16	44.90	124.88	22.51
1000	48.96	123.47	27.32	45.42	123.67	27.31	46.35	129.68	26.49
1100	50.58	128.21	31.79	46.86	128.07	31.63	47.60	134.16	30.63
1200	51.98	132.66	36.43	48.11	132.20	36.10	48.70	138.34	34.92
1300	53.22	136.87	41.23	49.19	136.09	40.70	49.66	142.28	39.33
1400	54.30	140.85	46.16	50.12	139.76	45.42	50.50	145.99	43.85
1500	55.26	144.63	51.21	50.93	143.25	50.24	51.25	149.50	48.46
1600	56.10	148.22	56.35	51.64	146.56	55.15	51.91	152.82	53.16
1700	56.84	151.64	61.59	52.25	149.70	60.13	52.49	155.99	57.94
1800	57.49	154.91	66.91	52.78	152.70	65.19	53.00	159.00	62.79
1900	58.08	158.03	72.30	53.25	155.57	70.30	53.46	161.88	67.69
2000	58.59	161.02	77.75	53.66	158.31	75.47	53.87	164.63	72.65
2500	60.47	174.31	105.74	55.08	170.45	101.93	55.35	176.82	98.06
3000	61.58	185.44	134.56	55.89	180.56	129.10	56.23	186.99	124.18
3500	62.27	194.99	163.91	56.38	189.22	156.70	56.77	195.70	150.75
4000	62.69	203.33	193.60	56.69	196.77	184.59	57.10	203.31	177.61
4500	62.96	210.73	223.52	56.90	203.45	212.68	57.29	210.04	204.67
5000	63.13	217.37	253.62	57.05	209.46	240.91	57.40	216.08	231.88

for the “SMCPS” and “ROTATOR” programs is also provided in the Supporting Information (Appendix).

The entropy correction, $\Delta S_{\text{mixing}} = -R\sum n_i \ln(n_i)$, for rotational conformers was included in the entropy calculation,[13] where ΔS_{mixing} represents the entropy of mixing of rotational conformers or optical conformers and n_i is the Boltzmann equilibrium mole fraction of the ith form. Here, Boltzmann mole fractions at different temperatures were calculated on the basis of the energy difference for rotational conformers at 0 K. $C^{\bullet}H_2CH(OH)CH_3$ and $C^{\bullet}H_2CCl(OH)CH_3$ have an optical isomer number of two because of the different constituents on the central carbon. The thermochemical parameters for heat capacity, entropy, and

TABLE 8: Reduced Vibrational Frequencies (cm^{-1})

species	vib 1	deg 1[a]	vib 2	deg 2[a]	vib 3	deg 3[a]	mean vib.	total deg[a]
$(CH_3)_2CHOH$	478.0	9.687	1455.2	12.346	3561.9	6.467	1221.3	28.5
$(CH_3)_2CClOH$	403.5	10.160	1220.0	12.217	3256.9	6.123	1015.5	28.5
$(CH_3)_2CHO^{\bullet}$	498.6	9.322	1465.8	10.910	3369.7	5.767	1197.7	26.0
$(CH_3)_2CClO^{\bullet}$	453.8	11.775	1442.4	9.599	3620.2	4.626	1006.4	26.0
$C^{\bullet}H_2C_{H}(OH)CH_3$	374.6	8.498	1287.5	10.108	3219.2	6.894	1093.1	25.5
$C^{\bullet}H_2CCl(OH)CH_3$	355.4	10.037	1143.2	10.722	3344.3	4.741	881.2	25.5

[a] Deg stands for degeneracy number of the frequency.

SCHEME 1

	ΔH^{o}_{rxn} (kcal/mol)	E_a (kcal/mol)
$C^{\bullet}H_2CH(OH)CH_3 \rightarrow CH_2{=}CHCH_3 + OH^{\bullet}$	28.62	28.62
$C^{\bullet}H_2CH(OH)CH_3 \rightarrow$ syn-$CH_2{=}CHOH + CH_3^{\bullet}$	19.18	29.02 (CBSQ)
$(CH_3)_2CHO^{\bullet} \rightarrow CH_3CHO + CH_3^{\bullet}$	6.97	13.22 (CBSQ)

SCHEME 2

	ΔH^{o}_{rxn} (kcal/mol)	E_a (kcal/mol)
$C^{\bullet}H_2CCl(OH)CH_3 \rightarrow CH_2{=}C(OH)CH_3 + Cl^{\bullet}$	18.01	18.01
$(CH_3)_2CClO^{\bullet} \rightarrow CH_3COCH_3 + Cl^{\bullet}$	2.57	2.57
$(CH_3)_2CClO^{\bullet} \rightarrow CH_3C(O)Cl + CH_3^{\bullet}$	2.67	10.75 (CBSQ)

enthalpy corrections ($0 \leq T \leq 5000$ K) for the six target species in this work are listed in Table 7. The thermochemical properties of 2-propanol in Table 7 show agreement with the values calculated by Chao[38] at TRC using the methods of statistical thermodynamics based on spectral data.

A reduced set of vibrational frequencies for each of the six target species was derived from the heat capacity data, which include contribution from internal rotations,[44] and these data are listed in Table 8. The reduced vibrational frequency sets can be used to derive the molar partition function, Q_{vib}, for vibration.[13] This Q_{vib} will contribute to the total partition function for the calculation of thermodynamic properties such as Gibbs free energy, Helmhotz free energy, internal energy, enthalpy, entropy, and heat capacities. The reduced set of vibrational frequencies can also be used to estimate molecular density of states, $\rho(E)$, for Rice–Ramsperger–Kassel–Marcus (RRKM) analysis.[44]

The results for heat capacity, entropy, and enthalpy corrections in Table 7 were also fitted by analytical equations: $C_p = C_{p,0} + a(1 - e^{-bT})$, $S = S_0 + aT^b$, and $H = H_0 + aT$, respectively; the coefficients and variances for the fitting equations are listed in Supporting Information (Table S3).

Relative Stability of the Alkyl and Alkoxy Radicals. The C–Cl bond is usually ca. 10 kcal/mol weaker than the C–C or C–H bonds and this should lead to interesting stabilities for the intermediate chloro-radicals in the atmosphere. Scheme 1 shows the ΔH°_{rxn} and E_a for the two nonchlorinated alkyl radicals undergoing β-scission to eliminate a methyl or a OH radical; the isopropoxy radical dissociation to CH_3CHO and methyl has a lower ΔH°_{rxn} value with the transition state lying 13.22 kcal/mol above $(CH_3)_2CHO^{\bullet}$ calculated at the CBSQ//B3** level.

Scheme 2 shows the ΔH°_{rxn} and E_a for Cl elimination from one secondary chlorocarbon radical where ΔH°_{rxn} is 18 kcal/mol, but the chloroisopropoxy radical has a similar bond strength for C–Cl and C–CH_3. The $\Delta H^{\circ}_{f,298}$ values used in Schemes 1 and 2 are listed in Table 2. The alkylalkoxy and chloroalkoxy radical systems are both unstable with short atmospheric lifetimes. We note that there is no barrier (above the ΔH°_{rxn}) for the Cl elimination reaction of $C^{\bullet}H_2CCl(OH)CH_3$ and its half-life at 298 K can be qualitatively estimated to be ~1.1 s, which is sufficient time for the radical to undergo association with O_2 under atmospheric and low-temperature combustion conditions. Wu and Carr[5,6] reported that the lifetime for $CH_2ClO^{\bullet}$ is less than 1 μs. Hou et al.[9] reported that the three-center elimination of HCl is the most favorable channel for $CH_3CHClO^{\bullet}$ decomposition and estimated the lifetime of $CH_3CHClO^{\bullet}$ under the typical tropospheric conditions to be 3.3 μs. The stability of these chloroalkoxy radicals is low, but these intermediate radicals are formed by $OH^{\bullet}$ radical addition to chloroolefins in the atmosphere and by $OH^{\bullet}$, $O^{\bullet}$, and $HO_2^{\bullet}$ addition to unsaturated chlorocarbons in combustion environments. The thermochemical properties of these radicals are important in describing the reaction paths and the products of the first- and second-dissociation reactions.

Group Additivity Values and HBI Group Values. The method for derivation of central group and hydrogen bond increment (HBI) groups has been illustrated in previous studies.[1,2] The C/C2/Cl/O group value in Table 9 was derived from the thermodynamic property data of $(CH_3)_2CClOH$. The group values for $\Delta H^{\circ}_{f,298}$ and $C_p(T)$ of C/C2/Cl/O were calculated on the basis of the reaction

$$(CH_3CCl(OH)CH_3) = (C/C_2/Cl/O) + 2(C/C/H_3) + (O/C/H)$$

and S°_{298} of C/C2/Cl/O was calculated by considering symmetry correction:

$$(CH_3CCl(OH)CH_3) = (C/C_2/Cl/O) + 2(C/C/H_3) + (O/C/H) - R\ln(s)$$

where $R = 1.987$ cal/(mol K) and s stands for symmetry number. The thermochemical properties for the C/C/H3 and O/C/H groups were taken from the literature.[45] $\Delta H^{\circ}_{f,298}$ in the HBI implementation group is the bond enthalpy of the R–H cleavage reaction at the indicated site. ΔS°_{298} and $\Delta C_p(T)$ in HBI groups are the differences in respective properties of the molecule and the radical such that, when HBI increment groups for ΔS°_{298} and $\Delta C_p(T)$ are added to the parent, the result is the corresponding value for the radical. Entropy values are intrinsic, that is, the correction for spin degeneracy of the electronic state and gain and loss of an optical isomer are included when appropriate, but symmetry for either parent or radical is not included in HBI groups.

Table 9 lists chloro-oxy-alkyl central group data from mono-, di-, and tricarbon chloroalcohols by this work and previous

TABLE 9: Central Group and Hydrogen Bond Increment (HBI) Group Values

central group	$\Delta H^\circ_{f,298}$ [b]	S°_{298} [c]	C_p300 [c]	C_p400 [c]	C_p500 [c]	C_p600 [c]	C_p800 [c]	C_p1000 [c]	C_p1500 [c]
			Monocarbon Chloro-oxy-hydrocarbon Central Group						
$C/Cl/H_2/O$	−20.17	36.55	8.88	11.18	13.02	14.35	16.09	17.27	19.19
$C/Cl_2/H/O$	−27.98	41.93	12.61	15.71	17.73	18.80	19.62	19.94	20.60
$C/Cl_3/O$	−28.06	50.54	16.34	18.45	19.65	20.28	20.82	21.06	21.46
			Dicarbon Chloro-oxy-hydrocarbon Central Group						
$C/C/Cl/H/O$	−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
			Tricarbon Chloro-oxy-hydrocarbon Central Group						
$C/C_2/Cl/O$	−21.53	−15.82	8.59	10.73	11.98	12.56	12.89	12.81	12.66

HBI group[a]	bond energy[b]	S°_{298} [c]	C_p300 [c]	C_p400 [c]	C_p500 [c]	C_p600 [c]	C_p800 [c]	C_p1000 [c]	C_p1500 [c]
				Alkoxy Group					
$CH_3O^\bullet$	104.28	−2.80	−0.88	−0.83	−1.02	−1.28	−1.79	−2.26	−3.16
$CCO^\bullet$	103.65	−0.90	−0.52	−0.85	−1.24	−1.59	−2.11	−2.52	−3.32
$C_2CO^\bullet$	105.44	−1.90	−1.05	−1.36	−1.71	−2.00	−2.40	−2.69	−3.32
				Chloroalkoxy HBI Group					
$CClO^\bullet$	105.04	−0.94	−1.00	−1.41	−1.85	−2.20	−2.69	−3.02	−3.63
$CCClO^\bullet$	105.94	−1.59	−0.99	−1.68	−2.14	−2.46	−2.86	−3.12	−3.66
$CCCl_2O^\bullet$	105.97	2.16	−0.79	−2.20	−3.35	−4.05	−4.48	−4.45	−4.37
$C_2CClO^\bullet$	106.11	2.75	−0.44	−1.26	−1.93	−2.45	−3.11	−3.54	−4.32
				Di-, Trichloromethoxy HBI Group					
$CCl_2O^\bullet$	110.33	1.17	−1.33	−2.50	−3.28	−3.63	−3.71	−3.65	−3.81
$CCl_3O^\bullet$	109.01	0.80	−0.84	−1.30	−1.67	−1.95	−2.40	−2.77	−3.50
				Hydroxyalkyl HBI Group					
$C^\bullet H_2OH$	96.21	−2.15	0.44	0.34	−0.10	−0.67	−1.77	−2.68	−4.10
$CC^\bullet OH$	94.88	2.14	−0.50	−0.93	−1.41	−1.87	−2.67	−3.31	−4.38
				Hydroxy-α-chloroalkyl HBI Group					
$C^\bullet ClOH$	95.71	0.10	0.70	0.72	0.19	−0.58	−2.04	−3.08	−4.47
$C^\bullet Cl_2OH$	97.44	2.26	−0.25	−1.97	−3.22	−3.90	−4.44	−4.64	−5.03
$CC^\bullet ClOH$	94.84	−1.96	0.12	−0.14	−0.54	−1.09	−2.26	−3.19	−4.52
				Hydroxy-β-(chloro)ethyl HBI Group					
$C^\bullet COH$	102.52	0.09	0.75	0.06	−0.72	−1.41	−2.48	−3.26	−4.42
$C^\bullet CClOH$	103.22	0.93	1.17	0.65	0.00	−0.67	−1.86	−2.79	−4.20
$C^\bullet CCl_2OH$	104.03	2.73	0.88	0.16	−0.78	−1.64	−2.89	−3.68	−4.69
				Hydroxy-β-(chloro)propyl HBI Group					
$C^\bullet C(OH)C$	102.26	4.74	0.83	0.10	−0.70	−1.40	−2.45	−3.16	−4.09
$C^\bullet CCl(OH)C$	102.81	4.54	1.11	0.59	−0.03	−0.65	−1.74	−2.62	−4.01

[a] H atoms are assumed to fill valence. [b] Units in kcal/mol. [c] Units in cal/(mol K).

TABLE 10: Recommended Hydrogen Bond Increment Group Values

HBI group[a]	bond energy[b]	S^o_{298} [c]	C_p300 [c]	C_p400 [c]	C_p500 [c]	C_p600 [c]	C_p800 [c]	C_p1000 [c]	C_p1500 [c]
$CCO^\bullet$	104.55	−1.40	−0.79	−1.11	−1.48	−1.80	−2.26	−2.61	−3.32
$CCClO^\bullet$	106.03	0.58	−0.72	−1.47	−2.04	−2.46	−2.99	−3.33	−3.99
$CCCl_2O^\bullet$	106.00	1.37	−0.75	−1.84	−2.69	−3.25	−3.73	−3.89	−4.18
$CC^\bullet OH$	100.44	1.76	−0.63	−1.38	−2.05	−2.56	−3.20	−3.60	−4.28
$CC^\bullet ClOH$	97.64	−0.10	−0.25	−0.76	−1.30	−1.83	−2.73	−3.40	−4.40
$C^\bullet COH$	102.39	2.42	0.79	0.08	−0.71	−1.41	−2.47	−3.21	−4.26
$C^\bullet CClOH$	103.02	2.74	1.14	0.62	−0.02	−0.66	−1.80	−2.71	−4.11
$C^\bullet CCl_2OH$	103.52	2.73	1.01	0.39	−0.40	−1.15	−2.35	−3.19	−4.40

[a] H atoms are assumed to fill valence. [b] Units in kcal/mol. [c] Units in cal/(mol K).

work.[1,2] The HBI group values for $C_2CO^\bullet$, $C_2CClO^\bullet$, $C^\bullet C(OH)C$, and $C^\bullet CCl(OH)C$ derived from this work are also listed in Table 9 for comparison with other HBI groups from C_1-C_2 chloroalcohols.[1,2] It can be seen from Table 9 that the enthalpy and heat capacity for HBI groups with similar chemical environments are similar; this suggests that these HBI groups can be used to predict accurate thermochemical properties of other radicals with similar chemical environments. The entropies are however slightly different even in the same series. For example, in the alkoxy series, the HBI values for the entropy of $CH_3O^\bullet$, $CCO^\bullet$, and $C_2CO^\bullet$ are −2.80, −0.90, and −1.90 cal/(mol K), respectively, while bond energies and heat capacities remain similar. This is a result of the nature of intrinsic entropy in the different molecules. A complete set of recommended HBI values with average entropy for use in general group additivity applications is listed in Table 10.

Summary

Thermodynamic properties of 2-propanol, 2-chloro-2-propanol and the corresponding (chloro)alkoxy and hydroxy-(chloro)alkyl radicals were calculated using density functional and ab initio methods with eight isodesmic reaction schemes. $\Delta H^\circ_{f,298}$'s determined by widely varied isodesmic reactions show remarkable precision at the CBSQ//B3** level. The statistical distribution of rotational conformers were taken into account for $\Delta H^\circ_{f,298}$, S°_{298} and $C_p(T)$'s ($0 \leq T \leq 5000$ K) were determined 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. Thermodynamic properties of the C/C_2/Cl/O group were determined for group additivity application. The HBI group values for $C_2CO^\bullet$, $C_2CClO^\bullet$, $C^\bullet C(C)OH$, and $C^\bullet C(C)ClOH$ were also derived, and a complete set of oxy(chloro)-alkanes HBI values for use in general group additivity applications are recommended. The radical $(CH_3)_2CClO^\bullet$ has low stability because of the low ΔH°_{rxn} value to bond scission, and its lifetime is short. This completes a series of publications on the thermochemical properties of oxychloro hydrocarbon groups for saturated alkanes with previous data in refs 1 and 2.

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Supporting Information Available: Tables S1 and S2 providing the total electronic energies and the coefficients of truncated Fourier series representation expansions for internal rotation potentials for six target species, Table S3 providing the coefficients and variances of equations for fitting heat capacities, entropies, and enthalpy of corrections, an appendix containing examples illustrating the use of "SMCPS" and "ROTATOR" programs. This material is available free of charge via the Internet at http://pubs.acs.org.

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