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Structures, Rotational Barriers, and Thermodynamic Properties of C_2 Vinyl and Chlorovinyl Alcohols and Additivity Groups

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Vinyl and chlorovinyl alcohol species result from the addition of OH radicals to chlorinated olefins under both atmospheric and combustion conditions. Stable vinyl and chlorovinyl alcohols are formed by breaking the C−Cl bonds (β-scission reactions), weaker relative to the newly formed C−OH bonds. Thermochemical properties, $\Delta H^\circ_{f\,298}$, S°_{298}, and $C^\circ_p(T)$ (300 K ≤ T ≤ 1500 K), are computed by density functional B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p), ab initio QCISD(T)/6-31G(d′), and composite CBS-Q calculation methods for seven chlorovinyl alcohols: $CH_2{=}COHCl$ (**1**), (*E*)-$CHCl{=}CHOH$ (**2**), (*Z*)-$CHCl{=}CHOH$ (**3**), $CCl_2{=}CHOH$ (**4**), (*E*)-$CHCl{=}COHCl$ (**5**), (*Z*)-$CHCl{=}COHCl$ (**6**), and $CCl_2{=}CClOH$ (**7**). Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) level of theory. Vibration frequencies are scaled for zero-point energies and thermal corrections. Two isodesmic reactions are utilized at each calculation level to determine the $\Delta H^\circ_{f\,298}$ value of each species. Contributions to S°_{298} and $C^\circ_p(T)$ from translation, vibration, and external rotation are calculated using the rigid-rotor-harmonic-oscillator approximation based on the B3LYP/6-31G(d,p) structures. Hindered internal rotational contributions to entropies and heat capacities are calculated by summation over the energy levels obtained from direct diagonalizations of the Hamiltonian matrix of the internal rotation. The calculated $\Delta H^\circ_{f\,298}$ values show that the *syn* (**s**) conformations of **2**, **3**, **4**, **5**, and **7** are more stable than their *anti* (**a**) forms, which are the same as vinyl alcohol ($CH_2{=}CHOH$). For **1** and **6**, the **a** forms have lower energies than the **s** forms due to intramolecular hydrogen bonding between Cl and hydroxyl H. The ideal gas phase $\Delta H^\circ_{f\,298}$ (in kcal/mol) calculated in this study are −38.30 ± 2.50 for $CH_2{=}CClOH$ (**1a**), −34.29 ± 2.75 for (*E*)-$CHCl{=}CHOH$ (**2s**), −38.33 ± 2.57 for (*Z*)-$CHCl{=}CHOH$ (**3s**), −40.51 ± 3.02 for $CCl_2{=}CHOH$ (**4s**), −43.40 ± 3.02 for (*E*)-$CHCl{=}CClOH$ (**5s**), −41.15 ± 3.40 for (*Z*)-$CHCl{=}CClOH$ (**6a**), and −44.03 ± 3.23 for $CCl_2{=}CClOH$ (**7s**,). The $O/C_D/H$ group (for group additivity) is evaluated from seven *syn* nonchlorinated simple enols, including vinyl alcohol, 1- and 2-methyl vinyl alcohols, 2,2-dimethyl vinyl alcohol, 1,2,2-trimethyl vinyl alcohol, 2-ethyl vinyl alcohol, and 2-propyl vinyl alcohol and compared with literature data. Standard enthalpies of formation of three new groups—one central-atom $C_D/Cl/O$ group and two interaction groups, HB (for intramolecular hydrogen bonding) and *anti* (for *anti* conformers)—are derived as 2.34, −2.28, and 0.98 kcal/mol, respectively. Standard enthalpies of formation of C_2HCl_3 and C_2Cl_4 are re-evaluated as −2.86 and −4.53 kcal/mol for use in isodesmic reaction schemes.

Introduction

Chlorocarbons are chemicals widely used as solvents in syntheses and in cleaning agents, as synthesis starting materials, and as materials in polymers, pesticides, and other product manufacturing. Chlorocarbons and other halocarbon compounds are deposited in the atmosphere from the evaporation of these solvents and other anthropogenic activities. They often exhibit relatively long tropospheric lifetimes due to their slow reaction rates with the OH radical.

The kinetic pathways of OH radical addition to vinyl chloride reaction systems, such as $C_2H_3Cl + OH$,[1,2] $C_2HCl_3 + OH$,[3] and $C_2Cl_4 + OH$,[4] have been evaluated. Stable chlorovinyl alcohols are the important products from OH addition to the α and/or β carbon site(s) of vinyl chlorides because the C−Cl bonds are weaker than the newly formed C−OH bonds. The Cl elimination occurs rapidly even at room temperature: the lifetime of the $C_2H_3Cl + OH$ addition adduct $C^{\bullet}H_2CHClOH$ is ca. 10^{-7} s at 298 K.[1]

Previous studies on enols, including theoretical calculations, have shown that simple enols (monofunctional enols that are not stabilized by extra resonance or internal hydrogen bonding and have no significant steric effects) prefer planar *syn* (dihedral angle ϕHO−CC = 0°) conformations in the gas phase.[5−7] The form of antiperiplanar orientation (ϕHO−CC = 180°) is 0.3−3.0 kcal/mol higher in energy than the form of synperiplanar orientation.[8,9]

Turecek and Cramer[9] calculated the standard enthalpies of formation from isodesmic and isogyric reactions at the G2(MP2) level for six enols, $CH_2{=}CHOH$, $CH_2{=}C(OH)CH_3$, (*E*)- and (*Z*)-$CHCH_3{=}CHOH$, and (*E*)- and (*Z*)-$CHCH_3{=}C(CH_3)OH$. The *syn* forms are found to be thermodynamically more stable for five out of the six enols, and $\Delta G^\circ_{298}(anti - syn)$ is calculated to be in the range of 1.4−5.6 kJ/mol. The only exception is (*Z*)-propen-1-ol, which has $\Delta G^\circ_{298}(anti - syn) = -0.5$ kJ/mol although its $\Delta H^\circ_{f\,298}(anti - syn)$ is positive (+1.2 kJ/mol). Turecek et al. also studied the substitution effects of methyl groups on the heat of formation using a complete series of methyl-substituted enols.[10]

Keeffe and Kresge report that the hydroxyl group can stabilize the C═C bond more effectively in the gas phase than in aqueous solution.[11] D_{OH}, a “wholly enthalpic” double-bond stabilization

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term, is calculated from available experimental data to be 8.1 ± 0.6 and 5.4 ± 0.5 kcal/mol for gas and aqueous phases, respectively. They indicate that their results apply only to simple enols. If the enol is chlorinated, the effect of Cl substituents on the energy difference between *syn* and *anti* conformers is unknown.

Two slightly more bulky vinyl ethers, (Z)-$\mathrm{CH(OCH_3){=}CHCH_3}$ and $\mathrm{CH(O(CH_3)_3){=}CH_2}$, are computed at ab initio HF/3-21G and MP2/6-31G* levels by Liebold et al.[8] Both compounds show a single conformer with a slightly nonplanar *anti* structure of the C═C−O−C skeleton. The *syn* forms are unfavorable due to the steric interactions. The experimental structures of these two species as determined through gas electron diffraction are reproduced well by MP2/6-31G* calculations. A double-minimum potential curve for internal rotor around the O−C bond is obtained for each compound.

There is little literature available for the thermodynamic properties of enol chlorides. Melius calculated the structures, moments of inertia, and frequencies of some chlorovinyl alcohols, such as *anti*- and *syn*-$\mathrm{CH_2{=}CClOH}$, *anti*- and *syn*-(E)-CHCl═CHOH, *anti*- and *syn*-(Z)-CHCl═CHOH, *anti*- and *syn*-(E)-CHCl═CClOH, *anti*- and *syn*-(Z)-CHCl═CClOH, and *anti*- and *syn*-$\mathrm{CCl_2{=}CClOH}$, at the HF/6-31G(d) level of theory, and Melius calculated the enthalpy and the free energy using the BAC-MP4 method.[12]

Thermodynamic property data on the chlorovinyl alcohol species are needed for the evaluation of atmospheric and combustion reaction paths and kinetic processes of chlorocarbons, which include the stability of intermediate of adducts and the prediction of final products. Thermodynamic properties are also needed for kinetic modeling and in equilibrium codes. This study estimates fundamental thermodynamic properties, $\Delta H^\circ_{\mathrm{f}\ 298}$, S°_{298}, and $C^\circ_p(T)$ for the *anti* (**a**) and *syn* (**s**) forms of seven chlorinated vinyl alcohols, $\mathrm{CH_2{=}COHCl}$ (**1**), (E)-CHCl═CHOH (**2**), (Z)-CHCl═CHOH (**3**), $\mathrm{CCl_2{=}CHOH}$ (**4**), (E)-CHCl═COHCl (**5**), (Z)-CHCl═COHCl (**6**), and $\mathrm{CCl_2{=}COHCl}$ (**7**), using density functional and ab initio calculation methods. The enthalpy of formation of each chlorovinyl alcohol is determined at each calculation level using two isodesmic reactions.

Methodology

All calculations are performed using the Gaussian94 program suite.[13] The structures of the *anti* (**a)** and *syn* (**s)** forms of seven enol chlorides are fully optimized at the B3LYP/6-31G(d,p) level of theory. Harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. Then B3LYP/6-31G(d,p)-optimized geometrical parameters are used to obtain the total electronic energies in B3LYP/6-31G-(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d′), and CBS-Q single-point calculations.[14−16] The prime in 6-31G(d′) indicates the basis set orbitals of Petersson et al.[17,18]

Curtiss et al.[19] report that B3LYP/6-31G(d,p) provides highly accurate structures for compounds with elements up to atomic number 10. Durant[20,21] has compared density functional calculations BH, H, and B3LYP with MP2 and Hartree−Fock methods for geometry and vibration frequencies. He reports that these density functional methods provide improved geometries and vibration frequencies relative to those of MP2 at reduced computation expense. Petersson currently recommends B3LYP or BLYP for CBS calculations of geometries and frequencies.[22,23] Wong and Radom show that the less expensive B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) procedure calculates quite well the barriers (transition states) of methyl radical addition to alkenes, with a mean absolute deviation of about 1.3 kcal/mol from experimental values.[24]

1. $\boldsymbol{\Delta H^\circ_{\mathrm{f}\ 298}}$**.** Standard enthalpies of formation are determined using the total energies obtained by the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d′), and CBS-Q calculation methods and two generic isodesmic reactions. Total energies are corrected by ZPVE's, which are scaled by 0.9806, as recommended by Scott and Radom.[25] Thermal corrections (0−298 K) are calculated to estimate H_{298} from H_0.[26]

The following two isodesmic reactions are selected to determine the $\Delta H^\circ_{\mathrm{f}\ 298}$ of *anti*-1-chlorovinyl alcohol (**1a**):

$$\textit{anti-}\mathit{CH_2{=}COHCl}\ (\mathbf{1a}) + \mathrm{C_2H_4} \rightarrow \textit{anti-}\mathrm{CH_2{=}CHOH} + \mathrm{C_2H_3Cl} \quad (\mathrm{R1_{\mathbf{1a}}})$$

$$\textit{anti-}\mathit{CH_2{=}COHCl}\ (\mathbf{1a}) + \mathrm{C_2H_3Cl} \rightarrow \textit{anti-}\mathrm{CH_2{=}CHOH} + \mathrm{CH_2{=}CCl_2} \quad (\mathrm{R2_{\mathbf{1a}}})$$

The basic requirement of an isodesmic reaction is that the number of each bond type is conserved in products and reactants, which leads to the cancellation of systematic errors in the molecular orbital calculations.[26] Density functional and ab initio calculations with ZPVE and thermal corrections are performed for all species in reaction set $\mathrm{R1_{\mathbf{1a}}}$ and $\mathrm{R2_{\mathbf{1a}}}$, and the enthalpy change of each reaction is calculated. Since the $\Delta H^\circ_{\mathrm{f}\ 298}$ values of all species but **1a** in the above isodesmic reactions are known, the $\Delta H^\circ_{\mathrm{f}\ 298}$ of the target species (in italics), i.e., *anti*-$\mathrm{CH_2{=}COHCl}$ (**1a**), is obtained from these data and the calculated $\Delta H_{\mathrm{rxn},298}$. Eight $\Delta H^\circ_{\mathrm{f}\ 298}$'s (from four different calculation levels on each of two isodesmic reactions, $\mathrm{R1_{\mathbf{1a}}}$ and $\mathrm{R2_{\mathbf{1a}}}$) are determined for **1a**. The **a** form of vinyl alcohol is used in the isodesmic reactions for the **a** form of chlorovinyl alcohols to avoid possible *anti*−*syn* interference errors.

The calculation of $\Delta H^\circ_{\mathrm{f}\ 298}$ for the **s** form of $\mathrm{CH_2{=}COHCl}$ (**1s**) is similar but uses the **s** form of vinyl alcohol in the isodesmic reactions.

$$\textit{syn-}\mathit{CH_2{=}COHCl}\ (\mathbf{1s}) + \mathrm{C_2H_4} \rightarrow \textit{syn-}\mathrm{CH_2{=}CHOH} + \mathrm{C_2H_3Cl} \quad (\mathrm{R1_{\mathbf{1s}}})$$

$$\textit{syn-}\mathit{CH_2{=}COHCl}\ (\mathbf{1s}) + \mathrm{C_2H_3Cl} \rightarrow \textit{syn-}\mathrm{CH_2{=}CHOH} + \mathrm{CH_2{=}CCl_2} \quad (\mathrm{R2_{\mathbf{1s}}})$$

Anti and *syn* forms of (E)-CHCl═CHOH (**2a**, **2s**), (Z)-CHCl═CHOH (**3a**, **3s**), $\mathrm{CCl_2{=}CHOH}$ (**4a**, **4s**), (E)-CHCl═COHCl (**5a**, **5s**), (Z)-CHCl═COHCl (**6a**, **6s**), and $\mathrm{CCl_2{=}COHCl}$ (**7a**, **7s**) are determined in the same manner as for **1a** and **1s**.

2. $\boldsymbol{S^\circ_{298}}$**,** $\boldsymbol{C^\circ_p(T)}$ **(300 K ≤ *T* ≤ 1500 K), and the Contributions of Hindered Internal Rotations to the Thermodynamic Properties.** Contributions to S°_{298} and $C^\circ_p(T)$ from the translation, vibration, and external rotation (TVR) of each chlorinated vinyl alcohol (**1a**,**s**−**7a**,**s**) are obtained using the rigid-rotor-harmonic-oscillator approximation from the frequencies and the moments of inertia based on the optimized B3LYP/6-31G(d,p) structure. The torsion frequency (lowest frequency of each entry in Table 2) corresponding to the intramolecular rotor is not included in TVR.

Contributions to entropy and heat capacities from intramolecular rotation (C−OH) are determined using direct integration over energy levels of the internal rotation potential energy where barriers are determined at the B3LYP/6-31G(d,p) level. The "ROTATOR"[27] program is used for this integration. This technique employs the expansion of the hindrance potential in the Fourier series (eq 1), the calculation of the Hamiltonian matrix on the basis of wave functions of free internal rotation, and the subsequent calculation of energy levels by direct diagonalization of the Hamiltonian matrix.[28−30] The torsional potential calculated at discrete torsion angles is represented by a truncated Fourier series

$$V(\Phi) = a_0 + a_i \cos(i\Phi) + b_i \sin(i\Phi) \qquad (1)$$

where $i = 1, 2, 3, 4, 5$.

The values of the coefficient (a_0, a_i, and b_i) are calculated to provide the minimum and maximum of the torsional potentials with allowance for a shift of the theoretical extreme angular positions.

Results and Discussion

1. Geometries and Vibrational Frequencies. The fully optimized geometries at the DFT B3LYP/6-31G(d,p) level for all the chlorinated vinyl alcohols are shown in Table 1. For each species, the optimized geometry shows a planar structure for the vinyl moiety. The hydroxyl groups of **1s**, **2a**, **2s**, **3a**, **3s**, **4a**, **4s**, **5s**, **6s**, and **7s** are also in the plane of the vinyl group. For the *anti* forms of **1**, **5**, **6**, and **7** (all have OH bending to the Cl atom attached to the same carbon), the C−O bonds are 4−5° below the vinyl planes, and the O−H bonds are ca. 23° out of the vinyl plane. The C═C bond lengths optimized at the this level of calculation increase with the increasing degree of chlorine substitution from 1.329 and 1.333 Å in **1a** and **1s**, respectively, to 1.344 and 1.347 Å in **7a** and **7s**, respectively. The *syn* conformers tend to have shorter C−O bond lengths than the *anti* conformers for **2**, **3**, **4**, **5**, and **7**, but this trend is reversed in **1** and **6**.

Harmonic vibrational frequencies and moments of inertia are calculated for each chlorovinyl alcohol at the B3LYP/6-31G-(d,p) level on the basis of optimized geometries at this same level of theory (Table 2). One lowest frequency corresponding to the C−O bond torsion of each species is omitted in the calculation of entropies and heat capacities, but we replace its contributions with that from the internal rotation analysis (discussed above).

2. $\Delta H^\circ_{f\,298}$. Total energies for all the chlorovinyl alcohols and all benchmark species in isodesmic reactions are calculated at the B3LYP/6-31G(d,p) level and at B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d′), and CBS-Q levels based on the B3LYP/6-31G(d,p) structure (Table 3).

The *anti*-1-chlorovinyl alcohol (**1a**) is used as an example to illustrate the calculation for its standard enthalpy of formation via isodesmic reactions. Two bond-conserved isodesmic reactions, $R1_{\mathbf{1a}}$ and $R2_{\mathbf{1a}}$, are constructed for **1a** (Table 4). The enthalpy change of an isodesmic reaction can be calculated either from the total energies at a certain level of calculation (Table 3) or from the literature $\Delta H^\circ_{f\,298}$ (Table 5) of each species

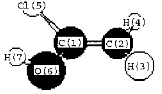
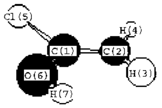
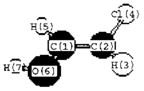
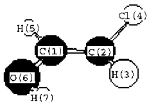
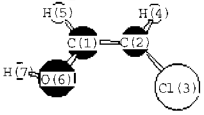
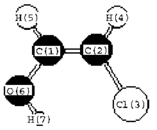
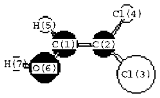
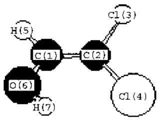
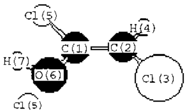
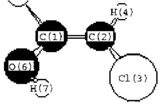
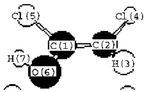
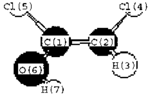
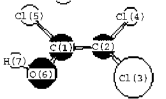
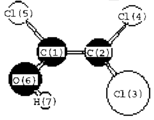
$$\begin{aligned}\Delta H_{\mathrm{rxn},298} &= \Sigma(\text{total energies at 298 K of products}) - \Sigma(\text{total energies at 298 K of reactants}) \\ &= \Sigma(\text{experimental } \Delta H^\circ_{f\,298} \text{ of products}) - \Sigma(\text{experimental } \Delta H^\circ_{f\,298} \text{ of reactants})\end{aligned}$$

We have the following equation for $R1_{\mathbf{1a}}$ at the B3LYP/6-31G(d,p) level of theory from Tables 3 and 5:

$$\begin{aligned}\Delta H_{\mathrm{rxn},298} &= [-153.7527644 + (-538.1437498) - (-613.3582432) - (-78.5396914)] \times 627.51 \\ &= -29.59 + 5.21 - \Delta H^\circ_{f\,298,\mathbf{1a}} - 12.55\end{aligned}$$

with $\Delta H^\circ_{f\,298,\mathbf{1a}} = -37.82$ kcal/mol.

TABLE 1: Geometries of Chlorovinyl Alcohols

Species (ID#)	Structure	Bond length	(angstrom)	Bond angle	(degree)	Dihedral angle	(degree)
anti-CH_2=COHCl (**1a**)		r21	1.329				
		r32	1.083	<321	118.96		
		r42	1.080	<421	121.35	ϕ4213	179.05
		r51	1.773	<512	121.79	ϕ5123	178.63
		r61	1.351	<612	124.04	ϕ6123	-4.02
		r76	0.967	<761	109.85	ϕ7612	157.15
syn-CH_2=COHCl (1s)		r21	1.333				
		r32	1.085	<321	120.40		
		r42	1.080	<421	121.15	ϕ4213	179.98
		r51	1.748	<512	122.31	ϕ5123	-179.96
		r61	1.353	<612	127.90	ϕ6123	0.00
		r76	0.969	<761	108.20	ϕ7612	0.09
anti-(*E*)-CHCl=CHOH (**2a**)		r21	1.333				
		r32	1.082	<321	123.65		
		r42	1.749	<421	121.38	ϕ4213	-179.99
		r51	1.087	<512	121.57	ϕ5123	179.99
		r61	1.366	<612	120.85	ϕ6123	0.00
		r76	0.964	<761	109.05	ϕ7612	179.97
syn-(*E*)-CHCl=CHOH (**2s**)		r21	1.335				
		r32	1.084	<321	124.27		
		r42	1.750	<421	121.76	ϕ4213	-180.00
		r51	1.085	<512	122.41	ϕ5123	180.00
		r61	1.359	<612	125.87	ϕ6123	0.00
		r76	0.968	<761	109.66	ϕ7612	0.00
anti-(*Z*)-CHCl=CHOH (**3a**)		r21	1.333				
		r32	1.743	<321	123.27		
		r42	1.081	<421	121.76	ϕ4213	179.99
		r51	1.088	<512	118.78	ϕ5123	-179.99
		r61	1.359	<612	123.56	ϕ6123	-0.04
		r76	0.964	<761	109.29	ϕ7612	179.82
syn-(*Z*)-CHCl=CHOH (**3s**)		r21	1.336				
		r32	1.758	<321	121.06		
		r42	1.079	<421	123.91	ϕ4213	179.99
		r51	1.085	<512	120.19	ϕ5123	180.00
		r61	1.350	<612	123.37	ϕ6123	0.00
		r76	0.971	<761	108.58	ϕ7612	0.00
anti-CCl_2=CHOH (**4a**)		r21	1.338				
		r32	1.734	<321	122.69		
		r42	1.745	<421	120.73	ϕ4213	179.88
		r51	1.086	<512	119.56	ϕ5123	-179.91
		r61	1.358	<612	121.99	ϕ6123	0.00
		r76	0.964	<761	109.11	ϕ7612	-179.96
syn-CCl_2=CHOH (**4s**)		r21	1.340				
		r32	1.751	<321	120.92		
		r42	1.736	<421	122.51	ϕ4213	179.99
		r51	1.084	<512	120.53	ϕ5123	180.00
		r61	1.349	<612	126.45	ϕ6123	0.00
		r76	0.971	<761	109.25	ϕ7612	0.00
anti-(*E*)-CHCl=CClOH (**5a**)		r21	1.335				
		r32	1.739	<321	121.89		
		r42	1.079	<421	122.35	ϕ4213	179.16
		r51	1.763	<512	119.53	ϕ5123	178.85
		r61	1.344	<612	124.66	ϕ6123	-4.12
		r76	0.967	<761	109.99	ϕ7612	155.92
syn-(*E*)-CHCl=CClOH (**5s**)		r21	1.338				
		r32	1.753	<321	119.93		
		r42	1.078	<421	124.21	ϕ4213	-180.00
		r51	1.739	<512	120.34	ϕ5123	-180.00
		r61	1.343	<612	127.75	ϕ6123	0.00
		r76	0.972	<761	108.07	ϕ7612	0.00
anti-(*Z*)-CHCl=CClOH (**6a**)		r21	1.336				
		r32	1.082	<321	119.45		
		r42	1.732	<421	125.00	ϕ4213	178.31
		r51	1.753	<512	123.67	ϕ5123	178.20
		r61	1.353	<612	120.79	ϕ6123	-5.09
		r76	0.969	<761	109.49	ϕ7612	144.79
syn-(*Z*)-CHCl=CClOH (**6s**)		r21	1.339				
		r32	1.084	<321	120.85		
		r42	1.735	<421	124.87	ϕ4213	179.98
		r51	1.751	<512	124.03	ϕ5123	-179.98
		r61	1.355	<612	125.16	ϕ6123	0.00
		r76	0.969	<761	109.06	ϕ7612	0.00
anti-CCl_2=CClOH (**7a**)		r21	1.344				
		r32	1.736	<321	120.19		
		r42	1.731	<421	123.67	ϕ4213	178.68
		r51	1.750	<512	122.30	ϕ5123	178.42
		r61	1.347	<612	121.87	ϕ6123	-4.87
		r76	0.968	<761	109.62	ϕ7612	148.47
syn-CCl_2=CClOH (**7s**)		r21	1.347				
		r32	1.754	<321	118.74		
		r42	1.726	<421	125.13	ϕ4213	179.99
		r51	1.729	<512	122.51	ϕ5123	180.00
		r61	1.345	<612	125.77	ϕ6123	0.00
		r76	0.972	<761	108.78	ϕ7612	-0.05

Similarly, we have the following equation for $R2_{\mathbf{1a}}$ at the B3LYP/6-31G(d,p) level of theory:

$$\begin{aligned}\Delta H_{\mathrm{rxn},298} &= [-153.7527644 + (-997.7403027) - (-613.3582432) - (-538.1437498)] \times 627.51 \\ &= -29.59 + 0.62 - \Delta H^\circ_{f\,298,\mathbf{1a}} - 5.21\end{aligned}$$

with $\Delta H^\circ_{f\,298,\mathbf{1a}} = -39.78$ kcal/mol.

Single-point energies are also determined at three additional calculation levels, B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G-

TABLE 2: B3LYP/6-31G(d,p) Harmonic Vibrational Frequencies (cm^{-1}) and Moments of Inertia ($amu\text{-}Bohr^2$) of Chlorovinyl Alcohols

species	freq	Ia	Ib	Ic
1a	217, 380, 430, 536, 644, 712, 825, 982, 1174, 1281, 1431, 1750, 3200, 3306, 3815	173.34	359.16	531.58
1s	325, 384, 441, 553, 682, 697, 793, 982, 1141, 1349, 1442, 1714, 3179, 3292, 3795	171.41	354.73	526.15
2a	148, 272, 299, 453, 777, 854, 937, 1174, 1198, 1319, 1351, 1748, 3184, 3251, 3861	34.96	724.83	759.79
2s	249, 274, 449, 455, 758, 864, 962, 1145, 1237, 1330, 1374, 1715, 3217, 3228, 3797	36.00	725.74	761.74
3a	201, 240, 473, 635, 719, 802, 886, 1103, 1247, 1304, 1382, 1760, 3171, 3261, 3860	108.98	492.76	601.74
3s	215, 408, 538, 627, 707, 802, 916, 1099, 1223, 1352, 1388, 1722, 3217, 3278, 3748	113.26	477.06	590.32
4a	184, 204, 286, 292, 452, 467, 642, 849, 927, 1189, 1273, 1352, 1752, 3201, 3853	451.13	737.74	1188.87
4s	215, 248, 283, 401, 472, 505, 629, 891, 944, 1179, 1291, 1383, 1719, 3237, 3752	446.04	741.69	1187.73
5a	176, 198, 229, 323, 439, 554, 756, 781, 835, 1118, 1257, 1329, 1748, 3277, 3812	203.49	1204.74	1407.09
5s	193, 207, 326, 379, 448, 584, 712, 795, 826, 1111, 1275, 1367, 1707, 3293, 3730	196.30	1195.10	1391.39
6a	172, 237, 275, 403, 485, 509, 624, 776, 882, 1196, 1218, 1300, 1734, 3249, 3788	353.67	876.84	1228.25
6s	174, 192, 303, 398, 484, 529, 653, 730, 894, 1159, 1245, 1358, 1698, 3217, 3788	347.84	878.65	1226.49
7a	116, 181, 234, 261, 309, 363, 411, 525, 556, 797, 952, 1214, 1259, 1724, 3797	738.89	1228.84	1965.15
7s	120, 183, 265, 287, 361, 363, 415, 531, 568, 804, 964, 1192, 1341, 1691, 3739	743.06	1223.69	1966.75

TABLE 3: Total Energies at 298 K[a,b]

	//B3LYP/6-31G(d,p)					
species	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	QCISD(T)/6-31+G(d′)	CBS-Q	ZPEV[c,d]	$H_{298} - H_0$[d]
1a	−613.3582432	−613.4526369	−612.3707585	−612.7209425	28.99	3.46
1s	−613.3568037	−613.4511004	−612.3696045	−612.7197326	29.11	3.35
2a	−613.3518606	−613.4460011	−612.3636620	−612.7131140	29.19	3.65
2s	−613.3538714	−613.4470259	−612.3650464	−612.7136620	29.52	3.45
3a	−613.3532525	−613.4477826	−612.3653792	−612.7145352	29.50	3.47
3s	−613.3598351	−613.4533151	−612.3711540	−612.7210303	29.78	3.30
4a	−1072.9477880	−1073.0763471	−1071.4109553	−1071.8701236	23.72	4.14
4s	−1072.9532738	−1073.0810576	−1071.4153430	−1071.8749779	24.04	3.96
5a	−1072.9549729	−1073.0827338	−1071.4172754	−1071.8756461	23.59	4.14
5s	−1072.9578454	−1073.0856944	−1071.4199904	−1071.8795779	23.77	3.99
6a	−1072.9536904	−1073.0812882	−1071.4165413	−1071.8746306	23.62	4.04
6s	−1072.9513001	−1073.0790595	−1071.4139416	−1071.8730325	23.58	4.05
7a	−1532.5457866	−1532.7081996	−1530.4606695	−1531.0289063	17.81	4.80
7s	−1532.5478045	−1532.7103543	−1530.4619937	−1531.0323365	17.98	4.70
C_2H_4	−78.5396914	−78.5669819	−78.2755540	−78.4116166	31.46	2.50
anti-CH_2CHOH	−153.7527644	−153.8146900	−153.3162306	−153.5579864	34.64	3.02
syn-CH_2CHOH	−153.7558425	−153.8163887	−153.3186909	−153.5596855	34.93	2.86
C_2H_3Cl	−538.1437498	−538.2042235	−537.3279935	−537.5718528	26.31	2.81
CH_2CCl_2	−997.7403027	−997.8353681	−996.3754201	−996.7296351	20.72	3.28
C_2HCl_3	−1457.3365867	−1457.4657984	−1455.4222310	−1455.8854531	15.27	3.96
C_2Cl_4	−1916.9269212	−1917.0916426	−1914.4651771	−1915.0406329	9.43	4.67
syn-(*E*)-$CHC_2H_5{=}CHOH$	−232.3337632	−232.4136569	−231.6317282	−232.0100286	70.03	4.50
syn-(*E*)-$CH(C_3H_7){=}CHOH$	−271.6212035	−271.7111813	−270.7876760	−271.2353450	87.60	5.33
1-butene	−157.1200436	−157.1671870	−156.5903991	−156.8637877	66.85	3.90
1-pentene	−196.4052813	−196.4625900	−195.7439096	−196.0875990	84.17	4.27

[a] All calculations are based on B3LYP/6-31g(d,p)-optimized structures. [b] Total energies (ZPVE and thermal corrections are included) in hartrees; 1 hartree = 627.51 kcal/mol. [c] Scaled by 0.9806.[25] [d] In kcal/mol.

(d′), and CBS-Q, for each species in these isodesmic reactions. So $\Delta H^\circ_{f\,298,\mathbf{1a}}$ is computed to be −37.82, −37.37, −38.24, and −38.64 for R1 and −39.78, −38.45, −38.64, and −37.43 for R2. The arithmetic mean of these eight values is −38.30 kcal/mol. The $\Delta H^\circ_{f\,298}$ of the **a** and **s** conformers for the remaining six chlorovinyl alcohols is obtained using this same methodology.

The accuracy of the $\Delta H^\circ_{f\,298}$ obtained theoretically is controlled by several factors: (i) the choice of the working chemical reactions used to cancel calculation errors; (ii) the level of sophistication (method + basis set) applied to calculate the electronic energy; (iii) the uncertainty of the ZPVE's and thermal corrections; and (iv) the reliability of the $\Delta H^\circ_{f\,298}$ of reference compounds.

The enthalpies of reaction in Table 4 are all within −5 to +8 kcal/mol of being thermoneutral; this signifies that both products and reactants have similar energies and that the chosen isodesmic reactions will likely have the optimal cancellation of the errors.

It can be seen from Table 4 that for most R2 reactions, the enthalpies of reaction decrease with an increase in calculation level, and the differences among four calculation levels can be as large as 4.8 kcal/mol ($R2_{\mathbf{7a}}$). To estimate which level is better for these chlorovinyl alcohol species, we evaluate ΔH_{rxn} on two reactions, R7 and R8, which are comprised of five standard vinyl species used in this work (Table 6). All calculated ΔH_{rxn} values in Table 6 are within the experimental error ranges of Table 5. The one exception is the B3LYP/6-31G(d,p) level calculation for R7, which is 0.55 out of the range. These data suggest that all four levels are applicable for our calculations.

ZPVE's and thermal corrections in Table 3 have small contributions to the errors on a relative base. Scott and Radom report rms errors after scaling (0.9806 for B3LYP/6-31G(d)) of 0.1 kcal/mol for ZPVE in their study on 39 molecules incorporating 1066 known vibrations. They also report rms error of ca. 0.01 kcal/mol for thermal correction from 0 to 298 K in DFT.[25] We assume that our calculations on species in the isodesmic reactions have the same error ranges, and we assign the cumulative uncertainties in $\Delta H^\circ_{f\,298}$ of chlorovinyl alcohols from ZPVE's and thermal corrections to be 0.44 kcal/mol. This ZPVE−thermal error and the statistical standard deviations from

TABLE 4: Calculated $\Delta H_{rxn,298}$ (kcal/mol) of the Isodesmic Reactions

	//B3LYP/6-31G(d,p)			
isodesmic reactions	B3LYP/ 6-31G(d,p)	B3LYP/ 6-311+G(3df,2p)	QCISD(T)/ 6-31+G(d′)	CBS-Q
(R$1_{\mathbf{1a}}$) **1a** + C_2H_4 → *anti*-C_2H_3OH + C_2H_3Cl	0.89	0.44	1.31	1.71
(R$2_{\mathbf{1a}}$) **1a** + C_2H_3Cl → *anti*-C_2H_3OH + CH_2CCl_2	5.60	4.27	4.46	3.25
(R$1_{\mathbf{1s}}$) **1s** + C_2H_4 → *syn*-C_2H_3OH + C_2H_3Cl	−1.94	−1.59	−0.96	−0.12
(R$2_{\mathbf{1s}}$) **1s** + C_2H_3Cl → *syn*-C_2H_3OH + CH_2CCl_2	2.77	2.24	2.19	1.42
(R$1_{\mathbf{2a}}$) **2a** + C_2H_4 → *anti*-C_2H_3OH + C_2H_3Cl	−3.11	−3.72	−3.14	−3.21
(R$2_{\mathbf{2a}}$) **2a** + C_2H_3Cl → *anti*-C_2H_3OH + CH_2CCl_2	1.60	0.10	0.00	−1.67
(R$1_{\mathbf{2s}}$) **2s** + C_2H_4 → *syn*-C_2H_3OH + C_2H_3Cl	−3.78	−4.14	−3.82	−3.93
(R$2_{\mathbf{2s}}$) **2s** + C_2H_3Cl → *syn*-C_2H_3OH + CH_2CCl_2	0.93	−0.32	−0.67	−2.39
(R$1_{\mathbf{3a}}$) **3a** + C_2H_4 → *anti*-C_2H_3OH + C_2H_3Cl	−2.24	−2.60	−2.07	−2.31
(R$2_{\mathbf{3a}}$) **3a** + C_2H_3Cl → *anti*-C_2H_3OH + CH_2CCl_2	2.47	1.22	1.08	−0.77
(R$1_{\mathbf{3s}}$) **3s** + C_2H_4 → *syn*-C_2H_3OH + C_2H_3Cl	−0.04	−0.20	0.01	0.70
(R$2_{\mathbf{3s}}$) **3s** + C_2H_3Cl → *syn*-C_2H_3OH + CH_2CCl_2	4.67	3.63	3.16	2.24
(R$1_{\mathbf{4a}}$) **4a** + C_2H_4 → *anti*-C_2H_3OH + CH_2CCl_2	−3.51	−4.22	−3.23	−3.69
(R$2_{\mathbf{4a}}$) **4a** + C_2H_3Cl → *anti*-C_2H_3OH + C_2HCl_3	1.37	0.05	0.31	−0.92
(R$1_{\mathbf{4s}}$) **4s** + C_2H_4 → *syn*-C_2H_3OH + CH_2CCl_2	−2.00	−2.33	−2.02	−1.71
(R$2_{\mathbf{4s}}$) **4s** + C_2H_3Cl → *syn*-C_2H_3OH + C_2HCl_3	2.88	1.94	1.52	1.06
(R$1_{\mathbf{5a}}$) **5a** + C_2H_4 → *anti*-C_2H_3OH + CH_2CCl_2	1.00	−0.21	0.74	−0.23
(R$2_{\mathbf{5a}}$) **5a** + C_2H_3Cl → *anti*-C_2H_3OH + C_2HCl_3	5.88	4.06	4.27	2.55
(R$1_{\mathbf{5s}}$) **5s** + C_2H_4 → *syn*-C_2H_3OH + CH_2CCl_2	0.87	0.58	0.90	1.18
(R$2_{\mathbf{5s}}$) **5s** + C_2H_3Cl → *syn*-C_2H_3OH + C_2HCl_3	5.75	4.85	4.43	3.95
(R$1_{\mathbf{6a}}$) **6a** + C_2H_4 → *anti*-C_2H_3OH + CH_2CCl_2	0.20	−1.12	0.28	−0.86
(R$2_{\mathbf{6a}}$) **6a** + C_2H_3Cl → *anti*-C_2H_3OH + C_2HCl_3	5.08	3.15	3.81	1.91
(R$1_{\mathbf{6s}}$) **6s** + C_2H_4 → *syn*-C_2H_3OH + CH_2CCl_2	−3.23	−3.59	−2.90	−2.93
(R$2_{\mathbf{6s}}$) **6s** + C_2H_3Cl → *syn*-C_2H_3OH + C_2HCl_3	1.64	0.69	0.64	−0.16
(R$1_{\mathbf{7a}}$) **7a** + C_2H_4 → *anti*-C_2H_3OH + C_2HCl_3	−2.43	−3.33	−1.40	−1.83
(R$2_{\mathbf{7a}}$) **7a** + C_2H_3Cl → *anti*-C_2H_3OH + C_2Cl_4	6.18	3.82	4.55	1.34
(R$1_{\mathbf{7s}}$) **7s** + C_2H_4 → *syn*-C_2H_3OH + C_2HCl_3	−3.10	−3.04	−2.12	−0.74
(R$2_{\mathbf{7s}}$) **7s** + C_2H_3Cl → *syn*-C_2H_3OH + C_2Cl_4	5.52	4.11	3.84	2.43
(R3) C_2HCl_3 + C_2H_4 → CH_2CCl_2 + C_2H_3Cl	−4.88	−4.27	−3.53	−2.77
(R4) C_2Cl_4 + C_2H_4 → 2 CH_2CCl_2	−8.78	−7.60	−6.34	−4.41
(R5) *syn-E-*$(C_2H_5)CH{=}CHOH$ + C_2H_4 → *syn*-C_2H_3OH + 1-butene	−1.53	−1.84	−1.13	−1.15
(R6) *syn-E-*$(n\text{-}C_3H_7)CH{=}CHOH$ + C_2H_4 → *syn*-C_2H_3OH + 1-pentene	−0.14	−0.51	0.39	−0.20

TABLE 5: Enthalpies of Formation for Reference Species (and Literature Citations)[a,b]

species	$\Delta H^\circ_{f\ 298}$ (kcal/mol)
C_2H_4	*12.55 ± 0.10*,[42] 12.54,[13,43] 12.50,[12,32] 12.52 ± 0.12[36]
anti-C_2H_3OH	*−29.59 ± 0.47*,[e] −29.02,[12] −29.95[44]
syn-C_2H_3OH	*−30.59 ± 0.55*,[e,40] −29.80 ± 2.0,[39] −30.86[12]
C_2H_3Cl	*5.21 ± 0.50*,[e,45] 5.00,[33] 4.70,[12] 5.5 ± 0.478,[46] 5.50 ± 0.50,[36] 5.0,[34] 6.81,[31] 8.40,[32] 8.91 ± 0.31,[42] 4.8 to 6.7[22]
CH_2CCl_2	*0.62 ± 0.31*,[42] 0.57,[31] −0.23,[33] 0.50,[35] 0.75,[12] 0.55 ± 0.33[36]
C_2HCl_3	*−2.86 ± 1.00*,[e] −2.29,[31] −3.9,[12] −1.88,[35] −1.94 ± 2.13,[42] −4.57 ± 0.74[36]
C_2Cl_4	*−4.53 ± 0.50*,[e] −2.63 ± 0.50,[36] −3.40,[32,47] −3.6,[34] −2.89,[31] −2.97,[43] −3.15,[35] −5.7,[12] −2.58 ± 2.01,[42] −6.3 to −0.1[22]
1-butene	*0.02 ± 0.24*,[42] −0.15 ± 0.19,[48] −0.13[31]
1-pentene	*−5.09 ± 0.24*,[42] −5.09[31]

[a] Italicized values are used in this work. [b] Superscript numbers correspond to the literature citation of the reference species. [c] Enthalpy of formation is calculated from *syn*-CH_2CHOH (−30.59 kcal/mol) and the relative enthalpies between the *anti* and *syn* conformers (4.2 kJ/mol[9]). Uncertainty is the standard deviation of three listed literature values. [d] Enthalpy of formation is from Turecek.[40] Uncertainty is the standard deviation of three listed literature values. [e] Because large discrepancies are found among literature data, the $\Delta H^\circ_{f\ 298}$ of C_2HCl_3 and C_2Cl_4 used in this study is calculated from isodesmic reactions R3 and R4 (see Table 4 and text). Uncertainty is estimated.

TABLE 6: Comparisons of Calculated $\Delta H_{rxn,298}$ with Literature Values (kcal/mol)

			calculations[b] (//B3LYP/6-31G(d,p))			
	$\Delta H_{rxn,298}$	literature[a]	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	QCISD(T)/6-31G(d′)	CBS-Q
R7	$2C_2H_3Cl = C_2H_4 + CH_2CCl_2$	2.75 ± 1.41	4.71[c]	3.83	3.15	1.54
R8	$2C_2HCl_3 = CH_2CCl_2 + C_2Cl_4$	1.81 ± 2.81	3.73	2.88	2.43	0.40

[a] From Table 5; errors for each species in the reaction are cumulated. [b] From Table 3. [c] Out of literature data error ranges.

the calculation results and uncertainties of reference species are reported in column 11 of Table 7.

Errors of $\Delta H^\circ_{f\ 298}$ for reference compounds in the isodesmic reactions R$1_{\mathbf{1a,1s}}$−R$2_{\mathbf{7a,7s}}$ will result in a systematic difference in reported thermodynamic parameters. The $\Delta H^\circ_{f\ 298}$ values of C_2H_3Cl, C_2Cl_3, and C_2Cl_4 have large discrepancies in the reported literature data.

(i) C_2H_3Cl. The two experimental values, 6.81[31] and 8.40,[32] are not used because the theoretical values determined by Melius's BAC-MP4 result (4.69[12]), Colegrove's G2 calculation (5.00[33]), Benson's recommendation (5.0[34]), and modified group additivity (5.06[35]) are in close agreement. Colegrove[33] and Petersson[22] suggest that the reported experimental enthalpies of C_2H_3Cl be re-examined. The uncertainties from literature values of reference compounds are listed in column 12 of Table 7.

(ii) C_2HCl_3. The literature value ranges from −1.88 (THERM[35]) to the −4.57 of Gurvich[36] (this value is lower than that of C_2Cl_4 in his book). To further evaluate the enthalpy of C_2HCl_3, we used isodesmic reaction R3 in Table 4 to calculate the $\Delta H^\circ_{f\ 298}$ of C_2HCl_3 in this study. The average of our four calculation levels is −2.86 ± 0.91, which is close to the average of literature values (−2.92).

(iii) C_2Cl_4. The literature values from either experiments or calculations range from −6.3 to 0.1 (see Table 5). Isodesmic reaction R4 in Table 4 is used to calculate the $\Delta H^\circ_{f\ 298}$ of C_2Cl_4

TABLE 7: $\Delta H^\circ_{f\ 298}$ (kcal/mol) of the Chlorovinyl Alcohols[a]

	//B3LYP/6-31G(d,p)												
	B3LYP/6-31G(d,p)		B3LYP/6-311+G(3df,2p)		QCISD(T)/6-31G(d′)		CBS-Q		avg		uncertainty		
species	R1	R2	R1	R2	R1	R2	R1	R2	[b]	[c]	SD[d]	expt[e]	Melius[12]
1a	−37.82	−39.78	−37.37	−38.45	−38.24	−38.64	−38.64	−37.43	−38.30	−37.97	0.78	1.28	−37.94
1s	−35.99	−37.95	−36.34	−37.42	−36.97	−37.37	−37.81	−36.60	−37.06	−37.04	0.70	1.36	−37.01
2a	−33.82	−35.78	−33.21	−34.28	−33.79	−34.18	−33.72	−32.51	−33.91	−33.43	0.94	1.28	−34.09
2s	−34.15	−36.11	−33.79	−34.86	−34.11	−34.51	−34.00	−32.79	−34.29	−33.86	0.95	1.36	−35.15
3a	−34.69	−36.65	−34.33	−35.40	−34.86	−35.26	−34.62	−33.41	−34.90	−34.44	0.94	1.28	−34.90
3s	−37.89	−39.85	−37.73	−38.81	−37.94	−38.34	−38.63	−37.42	−38.33	−38.15	0.77	1.36	−38.64
4a	−38.01	−38.46	−37.30	−37.14	−38.29	−37.40	−37.83	−36.17	−37.86	−37.40	0.67	1.97	
4s	−40.52	−40.97	−40.19	−40.03	−40.50	−39.61	−40.81	−39.15	−40.51	−40.33	0.53	2.05	
5a	−42.52	−42.97	−41.31	−41.15	−42.26	−41.36	−41.29	−39.64	−41.85	−41.13	0.99	1.97	−42.25
5s	−43.39	−43.84	−43.10	−42.94	−43.42	−42.52	−43.70	−42.04	−43.40	−43.23	0.53	2.05	−43.59
6a	−41.72	−42.17	−40.40	−40.24	−41.80	−40.90	−40.66	−39.00	−41.15	−40.36	0.98	1.97	−41.55
6s	−39.29	−39.73	−38.93	−38.78	−39.62	−38.73	−39.59	−37.93	−39.36	−39.09	0.53	2.05	−40.25
7a	−42.00	−43.61	−41.10	−41.25	−43.03	−41.98	−42.60	−38.77	−43.03	−42.17	1.46	1.57	−43.76
7s	−42.33	−43.95	−42.39	−42.54	−43.31	−42.27	−44.69	−40.86	−44.03	−43.85	1.14	1.65	−44.66

[a] All calculations are based on B3LYP/6-31G(d,p)-optimized structure. [b] Average of all levels. [c] Average of B3LYP/6-311+G(3df,2p) and CBS-Q levels. [d] Statistic standard deviations. [e] Cumulative uncertainties from reference species in isodesmic reactions (see also Table 4).

in this work. The average of our four calculation levels is −4.53 ± 1.87 kcal/mol. The experimental errors of reference compounds are one major source of uncertainty in our chlorovinyl alcohol results.

Columns 2−9 of Table 7 display the calculated enthalpies of formation for all chlorinated vinyl alcohols at the four calculation levels by two isodesmic reactions. The average values in column 10 are all within 1 kcal/mol of Melius's BAC-MP4 data.[12] Column 11 is the average of B3LYP/6-311+G(3df,2p) and CBS-Q calculation values. These two levels are considered to be higher levels and presumed to be more accurate methods. Within the standard deviations of calculation and uncertainties in reference species, there is no significant difference between the values of columns 10 and 11. We select the overall average (column 10) for report because our analysis relies on cancelling errors in the working reactions, and we do not show that this occurs to a higher extent in the higher-level calculations.

The recommended $\Delta H^\circ_{f\ 298}$ values (in kcal/mol) are −38.30 ± 2.50 and −37.06 ± 2.50 for *anti*- and *syn*-$CH_2{=}COHOH$, −33.91 ± 2.66 and −34.29 ± 2.75 for *anti*- and *syn*-(*E*)-$CHCl{=}CHOH$, −34.90 ± 2.66 and −38.33 ± 2.57 for *anti*- and *syn*-(*Z*)-$CHCl{=}CHOH$, −37.86 ± 3.08 and −40.51 ± 3.02 for *anti*- and *syn*-$CCl_2{=}CHOH$, −41.85 ± 3.40 and −43.40 ± 3.02 for *anti*- and *syn*-(*E*)-$CHCl{=}CClOH$, −41.15 ± 3.40 and −39.36 ± 3.02 for *anti*- and *syn*-(*Z*)-$CHCl{=}CClOH$, and −43.03 ± 3.47 and −44.03 ± 3.23 for *anti*- and *syn*-$CCl_2{=}CClOH$, respectively. The enthalpies of formation decrease with increased number of chlorine substituents from monochloride $CH_2{=}CClOH$ to trichloride C_2Cl_3OH.

3. Relative Energies of *Syn* and *Anti* Conformers. There are two relatively stable conformations, **a** (*anti*, ϕHO−CC = 150−180°) and **s** (*syn*, ϕHO−CC = 0°), in each chlorovinyl alcohol. Table 7 shows that the **s** conformer has the lowest enthalpy in five (**2**, **3**, **4**, **5**, and **7**) out of seven chlorovinyl alcohols, which is in agreement with trends observed on simple enols,[5,6] but the **a** conformers of **1** and **6** are lower in energy than the **s** conformers. The same observation is also found in Melius's data; therefore, we try to explain this nonuniformity.

It can be seen from the optimized structure in Table 1 that the distances between the hydroxyl H atom and the near Cl atom are 2.5−2.6 Å in **1a**, **3s**, **4s**, **5a**, **5s**, **6a**, **7a**, and **7s**. We assume (i) that there is hydrogen bonding between the hydroxyl hydrogen and the Cl atom when the Cl is on the same carbon as O (Figure 1a, *anti* conformer) or when a chlorine is on same side of the nonoxygenated carbon (Figure 1b, *syn* conformer) and (ii) that the hydrogen-bonding energies in both conformers are the same.

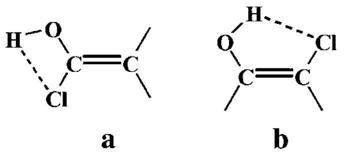


Figure 1. a. Intramolecular hydrogen bond in *anti* conformations. b. Intramolecular hydrogen bond in *syn* conformations.

The **1a**, **3s**, **4s**, and **6a** conformers are the lower-energy forms because they have H bonding; the other forms, **1s**, **3a**, **4a**, and **6s**, cannot have H bonding. Both the **a** and **s** forms have H bonding for **5** and **7**, so the **5s** and **7s** forms are lower in energy due to the effect of *syn* stabilization. (*Syn* forms tend to be in lower energy than the corresponding *anti* forms in simple enols. The electronic structural explanation for the *syn* preference is discussed by Leibold and Oberhammer.[8] They indicate a possible interaction between hydroxyl hydrogen orbitals and the π system as an explanation. Alternatively, the generalized anomeric effect, i.e., interactions between the n_σ(O) and σ^*-(C═C) orbitals, could explain the preference of the *syn* structure.) For **2**, either **s** or **a** can have H bonding with a chlorine, so **2s** is the lower-energy conformer due to *syn* stabilization. This hydrogen bonding postulate predicts the same energy trends of the calculations, and it suggests that intramolecular H bonding stabilization might be a larger component than *syn* stabilization in halogenated enols.

4. Internal Rotational Barriers. The potential barrier for internal rotation of hydroxyl group is calculated at the B3LYP/6-31G(d,p) level. Potential energy as a function of dihedral angle is determined by scanning the torsion angle of HO−CC from 0° (*syn* form) through 180° (*anti* form) to 360° (*syn* form) at 15° intervals and allowing the remaining molecular structural parameters to be optimized. Then geometries at all maximum and minimum values are fully optimized. The diagram for potential energy (ZPVE and thermal corrections included) versus torsion angle is shown in Figure 2, which reveals the results of the Fourier expansion (eq. 1). The values of the coefficients of the Fourier expansion, a_i and b_i in eq 1, are listed in Table 8.

Figure 2 illustrates that chlorovinyl alcohols **2**, **3**, and **4** have the symmetrical double-maximum patterns, while **1**, **5**, **6**, and **7** have an extra maximum around 180°. These four species (**1**, **5**, **6**, and **7**) happen to be the species whose **a** forms have the OH group slightly out of the vinyl plane as noted in Table 1, and they all have C_D/Cl/OH**a** (or C_D-(Cl)(OH**a**) in Benson's nomenclature) structures. The potential curves of *tert*-butyl vinyl

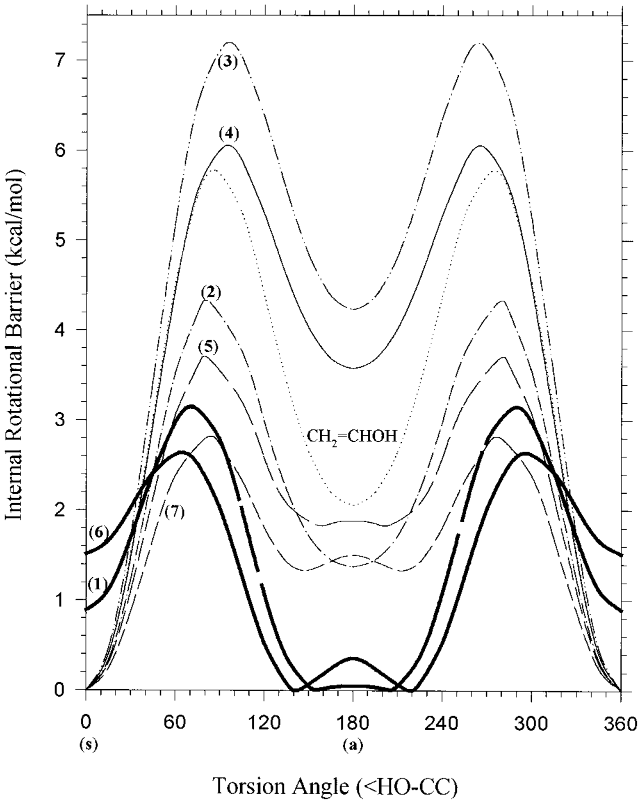


Figure 2. Potential barriers for internal rotations about C−OH bonds in chlorovinyl alcohols. Curves are results of Fourier expansions (eq 1), with the coefficients listed in Table 8.

ether and (*Z*)-methyl 1-propenyl ether, as calculated by Leibold and Oberhammer, are similar.[8] The nonplanar structures of some species result from several competing factors: (i) conjugation between the oxygen lone pair and the vinyl π bond, which is applicable to both **a** and **s** planar forms; (ii) H bonding between hydroxyl H and Cl atoms, which prefer the planar structure; (iii) repulsion between the two eclipsing single bonds, O−H and C−Cl, which prefer a nonplanar structure; and (iv) *syn* stabilization.

Figure 2 illustrates that the **a** forms (ϕHO−CC = 180°) of **1** and **6** are the low-energy conformers; while the **a** forms of **2**, **3**, **5**, and **7** have 0.4−3.4 kcal/mol higher energies than the **s** forms (ϕHO−CC = 0°), these values are comparable to the data of $\Delta H^\circ_{f\,298}$(*anti*−*syn*) = 0.3−3 kcal/mol for hydrocarbon enols.[8,9]

5. Standard Entropies and Heat Capacities. S°_{298} and $C^\circ_p(T)$ (300 K ≤ *T* ≤ 1500 K) calculation results using B3LYP/6-31G(d,p)-determined geometries and frequencies are summarized in Table 9. TVR represents the summation of the contributions from translation, external rotation, and vibration for S°_{298} and $C^\circ_p(T)$, and IR represents the contributions from hindered internal rotations.

If we consider each species as an equilibrium mixture of the *anti* and *syn* conformers, the ratio of the two conformers in the mixture can be calculated from their relative enthalpies of formation using the Boltzman distribution (Table 9). The entropy of the mixture is simply taken as the mean entropies of the two conformers. This estimation will not cause significant errors since the entropy differences between **a** and **s** conformers are no more than 1 cal mol^{-1} K^{-1}.

6. Group Additivity Values. Group additivity is straightforward and a reasonably accurate method for estimating the thermochemical properties of hydrocarbons and oxygenated hydrocarbons.[34] It is particularly useful for larger molecules where high-level ab initio or density functional calculations are not practical. Modifications have been reported which make this method useful for chlorinated and fluorinated hydrocarbons.[29,30,35,37,38] The selection of initial group values is critical to development of group additivity for accurate property estimation, and these criteria are fully discussed in refs 34 and 38.

7. O/C$_D$/H. C$_D$/H/O and O/C$_D$/H are two groups in every vinyl alcohol species. The $\Delta H^\circ_{f\,298}$ value of the C$_D$/H/O group, 8.6 kcal/mol, is assigned by Benson;[34] it is also used by Holmes,[39] Turecek,[40] and Cohen.[41] The $\Delta H^\circ_{f\,298}$ of the O/C$_D$/H group is calculated to be −44.6 kcal/mol by Holmes,[39] −48.28 by Turecek,[40] and −49.3 by Cohen.[41] These values are significantly lower than Benson's assignment of −37.9 kcal/mol for the O/C$_D$/H group.[34]

In this work, we independently calculate group values of the O/C$_D$/H (Table 10) using seven *syn* hydrocarbon vinyl alcohols, $CH_2{=}CHOH$, (*E*)-$(CH_3)CH{=}CHOH$, $CH_2{=}C(CH_3)OH$, $(CH_3)_2C{=}CHOH$, $(CH_3)_2C{=}C(CH_3)OH$, (*E*)-$(C_2H_5)CH{=}CHOH$, and (*E*)-$(C_3H_7)CH{=}CHOH$. The $\Delta H^\circ_{f\,298}$ values of first five are known, and those of the last two are calculated in this work using isodesmic reactions R5 and R6 in Table 4. Then according to group additivity

$$
\begin{aligned}
&\Delta H^\circ_{f\,298}(\mathrm{O/C_D/H})\\
&= \Delta H^\circ_{f\,298}(syn\text{-}\mathrm{CH_2{=}CHOH}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/H_2}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/H/O})\\
&= \Delta H^\circ_{f\,298}(syn\text{-}(E)\text{-}\mathrm{(CH_3)CH{=}CHOH}) - \Delta H^\circ_{f\,298}(\mathrm{C/C_D/H_3}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/C/H}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/H/O})\\
&= \Delta H^\circ_{f\,298}(syn\text{-}\mathrm{CH_2{=}C(CH_3)OH}) - \Delta H^\circ_{f\,298}(\mathrm{C/C_D/H_3}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/H_2}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/H/O})\\
&= \Delta H^\circ_{f\,298}(syn\text{-}\mathrm{(CH_3)_2C{=}CHOH}) - 2\Delta H^\circ_{f\,298}(\mathrm{C/C_D/H_3}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/C_2}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/H/O})\\
&= \Delta H^\circ_{f\,298}(syn\text{-}\mathrm{(CH_3)_2C{=}C(CH_3)OH}) - 3\Delta H^\circ_{f\,298}(\mathrm{C/C_D/H_3}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/C_2}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/H/O})\\
&= \Delta H^\circ_{f\,298}(syn\text{-}(E)\text{-}\mathrm{(C_2H_5)CH{=}CHOH}) - \Delta H^\circ_{f\,298}(\mathrm{C/C_D/H_2}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/C/H}) - \Delta H^\circ_{f\,298}(\mathrm{C/C/H_3}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/H/O})\\
&= \Delta H^\circ_{f\,298}(syn\text{-}(E)\text{-}(n\text{-}\mathrm{C_3H_7)CH{=}CHOH}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/C/H}) - \Delta H^\circ_{f\,298}(\mathrm{C/C/H_3}) - \Delta H^\circ_{f\,298}(\mathrm{C/C_2/H_2}) - \Delta H^\circ_{f\,298}(\mathrm{C/C/C_D/H_2}) - \Delta H^\circ_{f\,298}(\mathrm{C_D/H/O})
\end{aligned}
$$

All known or previously assigned values for the groups are summarized in Table 11. The $\Delta H^\circ_{f\,298}$ of the O/C$_D$/H group is calculated to be −46.30 kcal/mol, taken as the average results from the above seven nonchlorinated vinyl enols. This value is close to the data of Cohen,[41] Turecek,[40] and Holmes.[39]

The entropy and the heat capacity of O/C$_D$/H is calculated from *syn*-C_2H_3OH

$$X(\mathrm{O/C_D/H}) = X(syn\text{-}\mathrm{C_2H_3OH}) - X(\mathrm{C_D/H_2}) - X(\mathrm{C_D/H/O})$$

where $X = S^\circ_{298}$ or $C^\circ_p(T)$.

8. HB and *Anti* Groups. Groups are identified for the chlorovinyl alcohol species studied in this work and listed in Table 12. Here we introduce two new interaction groups, "HB"

TABLE 8: Coefficients (kcal/mol) of Truncated Fourier Series Representation Expansions for Internal Rotation Potentials[a,b]

coeff[c]	**1**	**2**	**3**	**4**	**5**	**6**	**7**	*syn*-C_2H_3OH
a_0	1.5062	2.3981	4.5685	3.8476	2.1935	1.3614	1.6445	3.3156
a_1	0.9347	−0.2733	−1.7945	−1.4646	−0.4479	1.1167	−0.2854	−0.6402
a_2	−1.1515	−1.7819	−2.5187	−2.1249	−1.3413	−0.5410	−0.9876	−2.3668
a_3	−0.4958	−0.4163	−0.3232	−0.3221	−0.4777	−0.5103	−0.4446	−0.3931
a_4	0.1165	0.0695	0.0678	0.0656	0.0871	0.1132	0.0915	0.0787
a_5	−0.0193	0.0000	0.0002	0.0003	−0.0172	−0.0278	−0.0212	3.5213×10^{-3}
b_1	2.2069×10^{-9}	2.4862×10^{-9}	8.0860×10^{-10}	-4.0464×10^{-4}	-1.2624×10^{-8}	4.9216×10^{-6}	1.7882×10^{-9}	1.2684×10^{-8}
b_2	2.5185×10^{-9}	1.8619×10^{-9}	-1.3946×10^{-9}	-7.2234×10^{-4}	3.446×10^{-08}	-1.1780×10^{-5}	1.7795×10^{-9}	-2.1424×10^{-8}
b_3	2.967×10^{-9}	1.4145×10^{-9}	2.0447×10^{-9}	-8.4528×10^{-4}	-4.4067×10^{-8}	1.6875×10^{-5}	2.6730×10^{-9}	3.6732×10^{-8}
b_4	2.3256×10^{-9}	2.6902×10^{-9}	-2.9202×10^{-9}	-7.2039×10^{-4}	5.5304×10^{-8}	-2.2356×10^{-5}	1.7510×10^{-9}	-4.1887×10^{-8}
b_5	2.0308×10^{-9}	2.3415×10^{-9}	3.6744×10^{-9}	-4.0485×10^{-4}	-6.458×10^{-8}	2.822×10^{-5}	2.2268×10^{-9}	5.8300×10^{-8}

[a] Values of rotational barriers computed at the B3LYP/6-31G(d,p) level of theory are used to calculate the coefficients. [b] See text for eq 1. [c] The b_i terms could be omitted, but entropies are slightly reduced to ca. 0.6 cal mol^{-1} K^{-1}.

TABLE 9: Calculated Ideal Gas Phase Thermodynamic Properties for Seven Chlorovinyl Alcohols and Vinyl Alcohols[a]

				$C_p^\circ(T)$							
chlorovinyl alcohol		$\Delta H_{f\,298}^\circ$	S_{298}°	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	%
anti-$CH_2{=}COHCl$ (**1a**)	TVR	−38.30	67.51	15.37	18.44	20.88	22.79	25.60	27.61	30.81	89
	IR		2.99	2.29	2.24	2.09	1.92	1.65	1.47	1.23	
	total	−38.30	70.50	17.66	20.68	22.97	24.71	27.25	29.08	32.04	
syn-$CH_2{=}COHCl$ (**1s**)	TVR	−37.06	67.38	15.30	18.39	20.84	22.76	25.59	27.62	30.83	11
	IR		2.99	2.29	2.24	2.09	1.92	1.65	1.47	1.23	
	total	−37.06	70.37	17.59	20.63	22.93	24.68	27.24	29.09	32.06	
anti-(*E*)-$CHCl{=}CHOH$ (**2a**)	TVR	−33.91	67.90	15.20	18.03	20.44	22.41	25.33	27.43	30.73	35
	IR		2.27	2.99	2.89	2.64	2.38	1.96	1.69	1.34	
	total	−33.91	70.17	18.19	20.92	23.08	24.79	27.29	29.12	32.07	
syn-(*E*)-$CHCl{=}CHOH$ (**2s**)	TVR	−34.29	67.29	14.85	17.78	20.26	22.27	25.26	27.39	30.72	65
	IR		2.27	2.99	2.89	2.64	2.38	1.96	1.69	1.34	
	total	−34.29	69.56	17.84	20.67	22.90	24.65	27.22	29.08	32.06	
anti-(*Z*)-$CHCl{=}CHOH$ (**3a**)	TVR	−34.90	67.67	14.77	17.80	20.31	22.32	25.29	27.40	30.72	0
	IR		0.94	1.67	2.30	2.86	3.23	3.37	3.08	2.21	
	total	−34.90	68.61	16.44	20.10	23.17	25.55	28.66	30.48	32.93	
syn-(*Z*)-$CHCl{=}CHOH$ (**3s**)	TVR	−38.33	66.64	14.30	17.48	20.09	22.16	25.20	27.35	30.71	100
	IR		0.94	1.67	2.30	2.86	3.23	3.37	3.08	2.21	
	total	−38.33	67.58	15.97	19.78	22.95	25.39	28.57	30.43	32.92	
anti-$CCl_2{=}CHOH$ (**4a**)	TVR	−37.86	74.90	18.43	21.26	23.49	25.23	27.72	29.42	31.98	1
	IR		1.12	1.97	2.72	3.21	3.40	3.16	2.71	1.88	
	total	−37.86	76.02	20.40	23.98	26.70	28.63	30.88	32.13	33.86	
syn-$CCl_2{=}CHOH$ (**4s**)	TVR	−40.51	73.89	17.96	20.91	23.23	25.04	27.61	29.35	31.97	99
	IR		1.12	1.97	2.72	3.21	3.40	3.16	2.71	1.88	
	total	−40.51	75.01	19.93	23.63	26.44	28.44	30.77	32.06	33.85	
anti-(*E*)-$CHCl{=}CClOH$ (**5a**)	TVR	−41.85	74.87	18.41	21.34	23.60	25.35	27.81	29.48	32.01	7
	IR		2.24	3.34	3.19	2.78	2.39	1.87	1.58	1.26	
	total	−41.85	77.11	21.75	24.53	26.38	27.74	29.68	31.06	33.27	
syn-(*E*)-$CHCl{=}CClOH$ (**5s**)	TVR	−43.40	73.82	18.08	21.13	23.47	25.25	27.77	29.47	32.02	93
	IR		2.24	3.34	3.19	2.78	2.39	1.87	1.58	1.26	
	total	−43.40	76.06	21.42	24.32	26.25	27.64	29.64	31.05	33.28	
anti-(*Z*)-$CHCl{=}CClOH$ (**6a**)	TVR	−41.15	74.07	18.28	21.29	23.59	25.35	27.83	29.51	32.03	95
	IR		3.16	2.16	2.16	2.00	1.83	1.56	1.39	1.19	
	total	−41.15	77.23	20.44	23.45	25.59	27.18	29.39	30.90	33.22	
syn-(*Z*)-$CHCl{=}CClOH$ (**6s**)	TVR	−39.36	74.24	18.26	21.26	23.56	25.33	27.82	29.51	32.04	5
	IR		3.16	2.16	2.16	2.00	1.83	1.56	1.39	1.19	
	total	−39.36	77.40	20.42	23.42	25.56	27.16	29.38	30.90	33.23	
anti-$CCl_2{=}CClOH$ (**7a**)	TVR	−43.03	80.55	21.87	24.66	26.70	28.20	30.23	31.50	33.28	16
	IR		2.99	3.08	2.55	2.12	1.83	1.49	1.32	1.14	
	total	−43.03	83.54	24.95	27.21	28.82	30.03	31.72	32.82	34.42	
syn-$CCl_2{=}CClOH$ (**7s**)	TVR	−44.03	79.85	21.58	24.44	26.53	28.08	30.15	31.46	33.28	84
	IR		2.99	3.08	2.55	2.12	1.83	1.49	1.32	1.14	
	total	−44.03	82.84	24.66	26.99	28.65	29.91	31.64	32.78	34.42	
syn-$CH_2{=}CHOH$	TVR		60.30	12.12	15.00	17.56	19.71	23.03	25.51	29.53	
	IR		1.45	2.68	3.13	3.16	3.01	2.57	2.19	1.62	
	total	−30.59[b]	61.75	14.80	18.13	20.72	22.72	25.60	27.70	31.15	

[a] $\Delta H_{f\,298}^\circ$ in kcal/mol; S_{298}° and $C_p^\circ(T)$ in cal mol^{-1} K^{-1}; TVR = translational + vibrational + rotational; IR = internal rotational. [b] From Table 5.

and "*anti*", using data in Tables 9 and 10. HB is to account for the hydrogen bonding described in Figure 1,b; *anti* is used for *anti* forms of enols for their instability relative to the *syn* forms. The values of these two groups in Table 10 show (i) that the $\Delta H_{f\,298}^\circ$ value of the *anti* group, 0.98, is comparable to the data of $\Delta H_{f\,298}^\circ$(*anti*−*syn*) = 0.3−3 kcal/mol for hydrocarbon enols calculated by other researchers[8,9] and (ii) that the hydrogen-bonding stabilization effect (i.e., the HB group) of −2.28 kcal/mol dominates the *anti* instability effect (i.e., the *anti* group). This means that an OH in the *anti* position with hydrogen bonding tends to have lower energy than the OH *syn* conformer without hydrogen bonding, such as **1a** and **6a** in this work.

With the knowledge of HB and *anti* groups, we find from Table 12 that the O/C_D/H group can be calculated alternatively from the **2a**,**s**−**4a**,**s** species. The average enthalpy of formation for O/C_D/H calculated from these six chlorovinyl alcohols is −46.00 kcal/mol, only 0.3 kcal/mol higher than the value of −46.30 kcal/mol derived from hydrocarbon vinyl alcohols. This comparison is one of many studies that support the value and

TABLE 10: Calculations of the O/C$_D$/H Group Using Seven Hydrocarbon Vinyl Alcohols

group	$\Delta H^\circ_{f\,298}$	S°_{298}	$C^\circ_p(T)$ 300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	
O/C$_D$/H	−46.30	26.14	5.50	6.77	7.41	7.72	7.93	8.03	8.36	recommended in this work[a,b]
	−44.60									Holmes (ref 39)
	−48.28									Turecek (ref 40)
	−49.30									Cohen (ref 41)
	−37.90									Benson (ref 34)
	−46.00	25.34	4.68	6.02	7.02	7.72	8.22	8.38	8.59	this work[c]

[a] $\Delta H^\circ_{f\,298}$ (in kcal/mol) is the average of values from seven nonchlorinated enols and known groups in Table 11. $\Delta H^\circ_{f\,298}$(*syn*-CH_2=CHOH) = −30.59,[40] $\Delta H^\circ_{f\,298}$(*syn*-(*E*)-(CH_3)CH=CHOH) = −40.39,[40] $\Delta H^\circ_{f\,298}$(*syn*-CH_2=C(CH_3)OH) = −39.91,[9] $\Delta H^\circ_{f\,298}$(*syn*-$(CH_3)_2$C=CHOH) = −49.47,[10] $\Delta H^\circ_{f\,298}$(*syn*-$(CH_3)_2$C=C(CH_3)OH) = −57.60,[10] $\Delta H^\circ_{f\,298}$(*syn*-(C_2H_5)CH=CHOH) = −41.70 and $\Delta H^\circ_{f\,298}$(*syn*-(C_3H_7)CH=CHOH) = −48.11 are calculated in this study using data in Tables 3−5. [b] S°_{298} and $C^\circ_p(T)$ (cal mol^{-1} K^{-1}) are calculated from *syn*-CH_2=CHOH in Table 9 and known groups in Table 11. [c] Calculated from average of chlorovinyl alcohols **2a**, **2s**, **3a**, **3s**, **4a**, and **4s** (see text).

TABLE 11: Group Values[a]

groups	$\Delta H^\circ_{f\,298}$	S°_{298}	$C^\circ_p(T)$ 300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	Benson's nomenclature
						Known Groups				
C/C/H$_3$[c]	−10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58	C-(H)$_3$
C/C$_2$/H$_2$[c]	−4.93	9.42	5.50	6.95	8.25	9.35	11.07	12.34	14.25	C-(C)$_2$(H)$_2$
C/C$_D$/H$_3$[c]	−10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58	C-(C$_D$)(H)$_3$
C/C/C$_D$/H$_2$[c]	−4.76	9.80	5.12	6.86	8.32	9.49	11.22	12.48	14.36	C-(C)(C$_D$)(H)$_2$
C$_D$/H$_2$[b]	6.26	27.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19	C$_D$-(H)$_2$
C$_D$/C/H[c]	8.59	7.97	4.16	5.03	5.81	6.50	7.65	8.45	9.62	C$_D$-(C)(H)
C$_D$/C$_2$[c]	10.34	−12.70	4.10	4.61	4.99	5.26	5.80	6.08	6.36	C$_D$-(C)$_2$
C$_D$/C/C$_D$[c]	8.88	−14.60	4.40	5.37	5.93	6.18	6.50	6.62	6.72	C$_D$-(C)(C$_D$)
C$_D$/C/O[c]	10.30	−14.60	4.40	5.37	5.93	6.18	6.50	6.62	6.72	C$_D$-(Cl)(H)
C$_D$/Cl/H[b]	−1.20	35.40	7.90	9.20	10.30	11.20	12.30	13.10	14.25	C$_D$-(Cl)(H)
C$_D$/Cl$_2$[b]	−5.76	40.77	10.97	12.42	13.33	13.92	14.63	15.01	15.44	C$_D$-(Cl)$_2$
C$_D$/H/O[c]	8.60	8.00	4.20	5.00	5.80	6.50	7.60	8.40	9.60	C$_D$-(H)(O)
int/C$_D$/Cl$_2$[b,d]	3.10	−0.13	0.16	0.15	0.03	−0.15	−0.02	0.02	0.13	
int/C$_D$/Cl$_3$[b,e]	5.08	1.50	0.39	0.18	0.04	−0.06	0.01	0.04	0.10	
int/C$_D$/Cl$_4$[b,f]	8.37	2.68	0.79	0.26	0.06	0.02	0.02	0.05	0.09	
						This Work				
O/C$_D$/H	−46.30	26.14	5.50	6.77	7.41	7.72	7.93	8.03	8.36	see table 10
HB	−2.28	−0.52	−0.21	−0.15	−0.10	−0.07	−0.04	−0.03	−0.01	
anti	0.98	0.79	0.32	0.23	0.16	0.12	0.06	0.03	0.00	
C$_D$/Cl/O	2.34	14.52	7.25	7.68	8.09	8.48	9.23	9.79	10.54	

[a] $\Delta H^\circ_{f\,298}$ in kcal/mol; S°_{298} and $C^\circ_p(T)$ in cal mol^{-1} K^{-1}. [b] Chen and Bozzelli.[35] [c] Benson;[34] also used by Holmes,[39] Turecek,[40] and Cohen.[41] [d] Interaction between two Cl atoms on two adjacent double-bond carbons.[35] [e] Interaction among three Cl atoms on two adjacent double-bond carbons.[35] [f] Interaction among four Cl atoms on tetrachloroethene.[35]

TABLE 12: Groups in the Chlorovinyl Alcohols[a]

species	C$_D$/ H$_2$	C$_D$/ Cl/H	C$_D$/ Cl$_2$	C$_D$/ H/O	O/ C$_D$/H[b]	HB[b]	*anti*[b]	C$_D$/ Cl/O[b]	Cl−Cl interactions[c]
1a	X				X	X	X	X	
1s	X				X			X	
2a		X		X	X		X		X (int/C$_D$/Cl$_2$)
2s		X		X	X				X (int/C$_D$/Cl$_2$)
3a		X		X	X		X		X (int/C$_D$/Cl$_2$)
3s		X		X	X	X			X (int/C$_D$/Cl$_2$)
4a			X	X	X		X		X (int/C$_D$/Cl$_3$)
4s			X	X	X	X			X (int/C$_D$/Cl$_3$)
5a		X			X	X	X	X	X (int/C$_D$/Cl$_3$)
5s		X			X	X		X	X (int/C$_D$/Cl$_3$)
6a		X			X	X	X	X	X (int/C$_D$/Cl$_3$)
6s		X			X			X	X (int/C$_D$/Cl$_3$)
7a			X		X	X	X	X	X (int/C$_D$/Cl$_4$)
7s			X		X	X		X	X (int/C$_D$/Cl$_4$)

[a] All species listed have symmetry number = 1 and number of internal rotor = 1. [b] Group which will be calculated in this work. [c] The repulsion between OH and Cl is treated as interaction between Cl and Cl due to the similar electronegativity of OH to Cl, i.e., int/C$_D$/Cl/OH = int/C$_D$/Cl$_2$, etc.

validity of group additivity. It also provides support for the accuracy of values for O/C$_D$/H and other groups in this work.

9. C$_D$/Cl/O. This group can be calculated from **1a**,**s** and **5a**,**s**−**7a**,**s**. The mean $\Delta H^\circ_{f\,298}$ value from these species is 2.34 kcal/mol, which is ca. 6 kcal/mol lower than that for the C$_D$/H/O group (8.6 kcal/mol) calculated by Benson.[34]

Summary

The geometries of *anti* and *syn* forms of C2 chlorovinyl alcohols are studied by B3LYP/6-31G(d,p) DFT calculation. The recommended $\Delta H^\circ_{f\,298}$ of each species is the average value of data using two isodesmic reactions calculated at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d′), and CBS-Q levels based on the B3LYP/6-31G(d,p)-optimized geometry. The S°_{298} and the $C^\circ_p(T)$ (300 K ≤ T ≤1500 K) are determined by B3LYP/6-31G(d,p)-optimized geometries and frequencies. The analysis of enthalpies and internal rotational barriers show that the *syn* forms of (*E*)- and (*Z*)-CHCl=CHOH, CCl_2=CHOH, (*E*)-CHCl=CClOH, and CCl_2=CClOH are more stable than the *anti* forms. CH_2=CClOH and (*Z*)-CHCl=CClOH are shown to prefer *anti* structures, and a stabilization effect via intramolecular hydrogen bonding is used to explain this phenomenon. Thermodynamic properties are determined for four groups, O/C$_D$/H, C$_D$/Cl/O, HB, and *anti*, which are useful for the group additivity estimation of higher chlorinated enol molecules.

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