Structures, Rotational Barriers, and Thermodynamic Properties of \( \text{C}_2 \) 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 \( C-\text{Cl} \) bonds (\( \beta \)-scission reactions), weaker relative to the newly formed \( C-\text{OH} \) bonds. Thermochemical properties, \( \Delta H_f^{\text{298}} \), \( S_f^{\text{298}} \), and \( C(T) \) (300 K \( \leq T \leq 1500 \text{ K} \)), 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: \( \text{C}_{2}\text{H}_{2}\text{Cl}=\text{COH Cl} \) (1), \( (E)-\text{CHCl}=\text{CHOH (2}, \text{)} \), \( (Z)-\text{CHCl}=\text{CHOH (3),} \text{)} \text{CCL}_{2}=\text{CHOH (4),} \text{)} \text{CH}-\text{ClCH}=\text{CHOH (5)}, \text{)} \text{CH}-\text{ClCH}=\text{CHOH (6),} \text{)} \text{and CCl}_{2}=\text{CClOCl (7).} \text{)} \text{Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) level of theory. Vibrat...
term, is calculated from available experimental data to be $8.1 \pm 0.6$ and $5.4 \pm 0.5$ 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)-CH(CH$_3$)=$CH$CH$_3$ and CH(O(CH$_3$)$_3$)=$CH$$_3$, are computed at ab initio HF/3-21G and MP2/6-31G* levels by Liebold et al.$^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 rotation 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-CH$_2$=CClOH, anti- and syn-(E)-CH$_2$=CHOH, anti- and syn-(Z)-CH$_2$=CHOH, anti- and syn-(Z)-CH(Cl)=CHOH, anti- and syn-$\text{ClCH}_2$=CClOH, and anti- and syn-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, $\Delta H^\text{298}$, $\Delta S^\text{298}$, and $\Delta C_p(T)$ for the anti (a) and syn (s) forms of seven chlorinated vinyl alcohols, CH$_2$=CHOH (1), (E)-CH$_2$=CHOH (2), (Z)-CH$_2$=CHOH (3), CCl$_2$=CHOH (4), (E)-CH$_2$=COCl (5), (Z)-CH$_2$=COCl (6), and CCl$_2$=COCl (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. $\Delta H^\text{298}$: 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 $H^\text{298}$ from $H^\text{0}$.$^{26}$

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

\[
\text{anti-CH}_2=\text{COHCl (1a)} + \text{C}_2\text{H}_4 \rightarrow \text{anti-CH}_2=\text{CHOH} + \text{C}_2\text{H}_2\text{Cl} \quad (R1a)
\]

\[
\text{anti-CH}_2=\text{COHCl (1a)} + \text{C}_2\text{H}_3\text{Cl} \rightarrow \text{anti-CH}_2=\text{CHOH} + \text{CH}_2=\text{CCl}_2 \quad (R2a)
\]

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 R1a and R2a, and the enthalpy change of each reaction is calculated. Since the $\Delta H^\text{298}$ values of all species but 1a in the above isodesmic reactions are known, the $\Delta H^\text{298}$ of the target species (in italics), i.e., anti-CH$_2$=COHCl (1a), is obtained from these data and the calculated $\Delta H^\text{exc,298}$. Eight $\Delta H^\text{298}$’s (from four different calculation levels on each of two isodesmic reactions, R1a and R2a) 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 $\Delta H^\text{298}$ for the s form of CH$_2$=COHCl (1s) is similar but uses the s form of vinyl alcohol in the isodesmic reactions.

\[
\text{syn-CH}_2=\text{COHCl (1s)} + \text{C}_2\text{H}_4 \rightarrow \text{syn-CH}_2=\text{CHOH} + \text{C}_2\text{H}_2\text{Cl} \quad (R1s)
\]

\[
\text{syn-CH}_2=\text{COHCl (1s)} + \text{C}_2\text{H}_3\text{Cl} \rightarrow \text{syn-CH}_2=\text{CHOH} + \text{CH}_2=\text{CCl}_2 \quad (R2s)
\]

Anti and syn forms of (E)-CH$_2$=CHOH (2a, 2s), (Z)-CH$_2$=CHOH (3a, 3s), CCl$_2$=CHOH (4a, 4s), (E)-CH$_2$=COCl (5a, 5s), (Z)-CH$_2$=COCl (6a, 6s), and CCl$_2$=COCl (7a, 7s) are determined in the same manner as for 1a and 1s.

2. $S^\text{298}$, $C_p(T)$ (300 K \leq T \leq 1500 K), and the Contributions of Hindered Internal Rotations to the Thermodynamic Properties. Contributions to $S^\text{298}$ and $C_p(T)$ 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.\textsuperscript{28–30} The torsional potential calculated at discrete torsion angles is represented by a truncated Fourier series

\[ V(\Phi) = a_0 + a_i \cos(i\Phi) + b_i \sin(i\Phi) \]  

(1)

where \( i = 1, 2, 3, 4, 5 \).

The values of the coefficient \((a_0, a_i, \text{ and } b_i)\) 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 \( \text{1a}, \text{2a}, \text{2s}, \text{3a}, \text{3s}, \text{4a}, \text{4s}, \text{5s}, \text{6s}, \text{and } 7s \) are also in the plane of the vinyl group. For the \textit{anti} forms of \( \text{1}, \text{5}, \text{6}, \text{and } 7 \) (all have OH bending to the Cl atom attached to the same carbon), the C=O bonds are 4–5\( ^\circ \) below the vinyl planes, and the O–H bonds are ca. 23\( ^\circ \) out of the vinyl plane. The C=C bond lengths optimized at the this level of calculation increase with the increasing degree of chlorination from 1.329 and 1.333 \( \AA \) in the vinyl plane. The C=C bond lengths optimized at this level of calculation increase with the increasing degree of chlorine substitution from 1.329 and 1.333 \( \AA \) in \( \text{1a} \) and \( \text{1s} \), respectively, to 1.344 and 1.347 \( \AA \) in \( \text{7a} \) and \( 7s \), respectively. The syn conformers tend to have shorter C–O bond lengths than the \textit{anti} conformers for \( \text{2}, \text{3}, \text{4}, \text{5}, \text{and } 7 \), but this trend is reversed in \( \text{1} \) and \( 6 \).

Harmonic vibrational frequencies and moments of inertia are calculated for each chlorovinyl alcohol at the B3LYP/6-31G(d,p) level (Table 2). Single-point energies are also determined at three additional calculation levels, B3LYP/6-311\( +G(3df,2p) \), QCISD(T)/6-31G(d,p), and CBS-Q levels based on the B3LYP/6-31G(d,p) structure (Table 3).

The \textit{anti}-1-chlorovinyl alcohol (\( \text{1a} \)) is used as an example to illustrate the calculation for its standard enthalpy of formation via isodesmic reactions. Two bond-conserved isodesmic reactions, \( \text{R1a} \) and \( \text{R2a} \), are constructed for \( \text{1a} \) (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 \( \Delta H_{\text{rxn},298} \) (Table 5) of each species

\[
\Delta H_{\text{rxn},298} = \Sigma(\text{total energies at 298 K of products}) - \\
\Sigma(\text{total energies at 298 K of reactants}) = \Sigma(\text{experimental } \Delta H_{\text{f},298} \text{ of products}) - \\
\Sigma(\text{experimental } \Delta H_{\text{f},298} \text{ of reactants})
\]

We have the following equation for \( \text{R1a} \) at the B3LYP/6-31G(d,p) level of theory from Tables 3 and 5:

\[
\Delta H_{\text{rxn},298} = [-153.7527644 + (-538.1437498) - (613.3582432) - (-78.5396914)] \times 627.51
\]

\[= -29.59 + 5.21 - \Delta H_{\text{f},298,\text{1a}} - 12.55 \]

with \( \Delta H_{\text{f},298,\text{1a}} = -37.82 \text{ kcal/mol} \).

\[
\Delta H_{\text{rxn},298} = [-153.7527644 + (-997.7403027) - (-613.3582432) - (-538.1437498)] \times 627.51
\]

\[= -29.59 + 6.2 - \Delta H_{\text{f},298,\text{1a}} - 5.21 \]

with \( \Delta H_{\text{f},298,\text{1a}} = -39.78 \text{ kcal/mol} \).

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·Bohr$^2$) of Chlorovinyl Alcohols

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<th>species</th>
<th>freq</th>
<th>B3LYP/6-31G(d,p)</th>
<th>B3LYP/6-31+1+G(3df,2p)</th>
<th>QCISD(T)/6-31+1+G(d,p)</th>
<th>CBS-Q</th>
<th>ZPEV,c</th>
<th>$H_{298}^c - H_d^c$</th>
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(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. (d) In kcal/mol.
the calculation results and uncertainties of reference species are reported in column 11 of Table 7.

Errors of \(\Delta H^f_{298}\) for reference compounds in the isodesmic reactions \(R^1a,ts\rightarrow R^2a,ts\) will result in a significant difference in reported thermodynamic parameters. The \(\Delta H^f_{298}\) values of \(\text{C}_2\text{H}_3\text{Cl}\), \(\text{C}_2\text{Cl}_3\), and \(\text{C}_2\text{Cl}_4\) have large discrepancies in the reported literature data.

(i) \(\text{C}_2\text{H}_2\text{Cl}\). The two experimental values, 6.81\(^{11}\) 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 (5.00\(^{33}\)), and modified group additivity (5.06\(^{35}\)) are in close agreement. Colegrove\(^{35}\) and Petersson\(^{22}\) suggest that the reported experimental enthalpies of \(\text{C}_2\text{H}_3\text{Cl}\) be re-examined. The uncertainties from literature values of reference compounds are listed in column 12 of Table 7.

(ii) \(\text{C}_2\text{HCl}_3\). The literature value ranges from \(-1.88\) (THERM\(^{5}\)) to the \(-4.57\) of Gurvich\(^{36}\) (this value is lower than that of \(\text{C}_2\text{Cl}_4\) in his book). To further evaluate the enthalpy of \(\text{C}_2\text{HCl}_3\), we used isodesmic reaction R3 in Table 4 to calculate the \(\Delta H^f_{298}\) of \(\text{C}_2\text{HCl}_3\) in this study. The average of our four calculation levels is \(-2.86 \pm 0.91\), which is close to the average of literature values \((-2.92\)\).

(iii) \(\text{C}_2\text{Cl}_4\). 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 \(\Delta H^f_{298}\) of \(\text{C}_2\text{Cl}_4\).
in this work. The average of our four calculation levels is $-4.53 \pm 1.87 \text{ kcal/mol}$. 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. Column 11 is the average of B3LYP/6-31+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 $\Delta H_f^{\text{298}}$ values (in kcal/mol) are $-38.30 \pm 2.50$ and $-37.06 \pm 2.50$ for anti- and syn-CH$_2$=CHOH, $-33.91 \pm 2.66$ and $-34.29 \pm 2.75$ for anti- and syn-(E)-CH$_2$=CHOH, $-34.90 \pm 2.66$ and $-38.33 \pm 2.57$ for anti- and syn-(Z)-CH$_2$=CHOH, $-37.86 \pm 3.08$ and $-40.51 \pm 3.02$ for anti- and syn-CCl$_2$=CHOH, $-41.85 \pm 3.40$ and $-43.40 \pm 3.02$ for anti- and syn-(E)-CCl$_2$=CHOH, $-41.15 \pm 3.40$ and $-39.36 \pm 3.02$ for anti- and syn-(Z)-CCl$_2$=CHOH, and $-43.03 \pm 3.47$ and $-44.03 \pm 3.23$ for anti- and syn-CCl$_2$=CClOH, respectively. The enthalpies of formation decrease with increased number of chlorine substituents from monochloride CH$_2$=CHOH to trichloride C$_2$Cl$_3$OH.

3. Relative Energies of Syn and Anti Conformers. There are two relatively stable conformations, a (anti, $\phi$HO–CC = 150–180$^\circ$) and s (syn, $\phi$HO–CC = 0$^\circ$), 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, 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, 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 the same side of the nonoxygenated carbon (Figure 1b, syn conformer) and (ii) that the hydrogen-bonding energies in both conformers are the same.

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. They indicate a possible interaction between hydroxyl hydrogen orbitals and the $\pi$ system as an explanation. Alternatively, the generalized anomic effect, i.e., interactions between the $\pi_a$(O) and $\sigma^*$- (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$^\circ$ (syn form) through 180$^\circ$ (anti form) to 360$^\circ$ (syn form) at 15$^\circ$ 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$^\circ$. 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$_2$HCl=OHa (or C$_2$H(OH)a) in Benson’s nomenclature) structures. The potential curves of tert-butyl vinyl
ether and (Z)-methyl 1-propenyl ether, as calculated by Leibold and Oberhammer, are similar. 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 ΔH° 298(anti−syn) = 0.3–3 kcal/mol for hydrocarbon enols.8,9

5. Standard Entropies and Heat Capacities. S°298 and C°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°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 Boltzmann 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. 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. 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/Cp/H. Cp/H/O and O/Cp/H are two groups in every vinyl alcohol species. The ΔH° 298 value of the Cp/H/O group, 8.6 kcal/mol, is assigned by Benson; it is also used by Holmes,39 Turecek,40 and Cohen.41 The ΔH° 298 of the O/Cp/H group is calculated to be −44.6 kcal/mol by Holmes,39 −48.2 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/Cp/H group.

In this work, we independently calculate group values of the O/Cp/H (Table 10) using seven syn hydrocarbon vinyl alcohols, CH₂=CHOH, (E)-(CH₃)CH=CHOH, CH₃=C(CH₃)OH, (CH₃)₂C=CHOH, (CH₃)₂C=C(CH₃)OH, (E)-(CH₃)₂CH=CHOH, and (E)-(CH₃)₂CH=CHOH. The ΔH° 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

\[ \Delta H°_{298}(O/C_p/H) = \Delta H°_{298}(syn-CH₃=CHOH) - \Delta H°_{298}(C_p/H_2) - \Delta H°_{298}(C/D/H_2) - \Delta H°_{298}(C/D/H/O) \]

\[ = \Delta H°_{298}(syn-(E)-(CH₃)CH=CHOH) - \Delta H°_{298}(C/C/D/H_2) - \Delta H°_{298}(C/D/H/O) \]

\[ = \Delta H°_{298}(syn-CH₂=C(CH₃)OH) - \Delta H°_{298}(C/D/H) - \Delta H°_{298}(C/D/H/O) \]

\[ = \Delta H°_{298}(syn-(CH₃)₂C=CHOH) - 2\Delta H°_{298}(C/D/H) - \Delta H°_{298}(C/D/H/O) \]

\[ = \Delta H°_{298}(syn-(CH₃)₂C=C(CH₃)OH) - 3\Delta H°_{298}(C/C/D/H) - \Delta H°_{298}(C/D/H/O) \]

\[ = \Delta H°_{298}(syn-(E)-(CH₃)₂CH=CHOH) - \Delta H°_{298}(C/D/H/O) \]

\[ = \Delta H°_{298}(C/D/H) - \Delta H°_{298}(C/D/H/O) \]

All known or previously assigned values for the groups are summarized in Table 11. The ΔH° 298 of the O/Cp/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/Cp/H is calculated from syn-C₂H₂OH

\[ X(O/C_p/H) = X(syn-C₂H₂OH) - X(C/D/H_2) - X(C/D/H/O) \]

where X = S°298 or C°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”
and “anti”, using data in Tables 9 and 10. HB is to account for the hydrogen bonding described in Figure 1b; 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 $\Delta H^\circ_{298}$ value of the anti group, 0.98, is comparable to the data of $\Delta H^\circ_{298}$(anti-syn) = 0.3 – 3 kcal/mol for hydrocarbon enols calculated by other researchers and (ii) that the hydrogen-bonding stabilization effect (i.e., the HB group) of $\Delta H^\circ_{298}$ 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 conformation 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 =H group can be calculated alternatively from the 2a–4a species. The average enthalpy of formation for O/C=H calculated from these six chlorovinyl alcohols is $-46.0$ kcal/mol, only 0.3 kcal/mol higher than the value of $-46.3$ kcal/mol derived from hydrocarbon vinyl alcohols. This comparison is one of many studies that support the value and
C2 Vinyl and Chlorovinyl Groups

The repulsion between OH and Cl is treated as interaction between Cl and

Table 10: Calculations of the O/Cp/H Group Using Seven Hydrocarbon Vinyl Alcohols

<table>
<thead>
<tr>
<th>group</th>
<th>$\Delta H^\circ_{298}$</th>
<th>$S^\circ_{298}$</th>
<th>300 K</th>
<th>400 K</th>
<th>500 K</th>
<th>600 K</th>
<th>800 K</th>
<th>1000 K</th>
<th>1500 K</th>
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</thead>
<tbody>
<tr>
<td>O/Cp/H</td>
<td>-46.30</td>
<td>26.14</td>
<td>5.50</td>
<td>6.77</td>
<td>7.41</td>
<td>7.72</td>
<td>7.93</td>
<td>8.03</td>
<td>8.36</td>
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</tr>
</tbody>
</table>

Treated in this work: Holmes (ref 39), Turecek (ref 40), Cohen (ref 41), and Benson (ref 34).

Table 11: Group Values

<table>
<thead>
<tr>
<th>groups</th>
<th>$\Delta H^\circ_{298}$</th>
<th>$S^\circ_{298}$</th>
<th>300 K</th>
<th>400 K</th>
<th>500 K</th>
<th>600 K</th>
<th>800 K</th>
<th>1000 K</th>
<th>1500 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/C/H</td>
<td>-10.20</td>
<td>30.41</td>
<td>6.19</td>
<td>7.84</td>
<td>9.40</td>
<td>10.79</td>
<td>13.02</td>
<td>14.77</td>
<td>17.58</td>
</tr>
<tr>
<td>C/C/H</td>
<td>-10.20</td>
<td>30.41</td>
<td>6.19</td>
<td>7.84</td>
<td>9.40</td>
<td>10.79</td>
<td>13.02</td>
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<td>9.40</td>
<td>10.79</td>
<td>13.02</td>
<td>14.77</td>
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</tr>
<tr>
<td>C/C/H</td>
<td>-10.20</td>
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<td>6.19</td>
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<td>9.40</td>
<td>10.79</td>
<td>13.02</td>
<td>14.77</td>
<td>17.58</td>
</tr>
</tbody>
</table>

$\Delta H^\circ_{298}$ (in kcal/mol) is the average of values from seven nonchlorinated enols and known groups in Table 11. $\Delta H^\circ_{298}(\text{CH}_{3}OH) = -30.59$, $\Delta H^\circ_{298}(\text{syn-CH}_{2}OH) = -40.39$, $\Delta H^\circ_{298}(\text{syn-CH}_{2}OH) = -39.91$, $\Delta H^\circ_{298}(\text{anti-CH}_{2}OH) = -49.47$, $\Delta H^\circ_{298}(\text{anti-CH}_{2}OH) = -48.11$ are calculated in this study using data in Tables 3–5. $S^\circ$ and $C^\circ(T)$ are calculated from $\text{syn-CH}_{2}OH$ in Table 9 and known groups in Table 11. Calculated from average of chlorovinyl alcohols 2a, 2s, 3a, 3s, 4a, and 4s (see text).

Table 12: Groups in the Chlorovinyl Alcohols

| species   | C/C/O | C/C/H | C/C/H | O/Cp/H | HB | anti | C/C/O | Cl–Cl | interactions
|-----------|-------|-------|-------|--------|----|------|-------|-------|-----------
| 1a        | X     | X     | X     | X      | X  |      |       |       |           |
| 1s        | X     | X     | X     | X      | X  |      |       |       |           |
| 2a        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |
| 2s        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |
| 3s        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |
| 3a        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |
| 4s        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |
| 4s        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |
| 5a        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |
| 5s        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |
| 6a        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |
| 6s        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |
| 7a        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |
| 7s        | X     | X     | X     | X      | X  | (int/Cp/Cl) |       |       |           |

* All species listed have symmetry number = 1 and number of internal rotor = 1.

Summary

The geometries of anti and syn forms of C2 vinyl alcohol are studied by B3LYP/6-31G(p,d) DFT calculation. The recommended $\Delta H^\circ_{298}$ of each species is the average value of data using two isosmotic reactions calculated at the B3LYP/6-31G(d,p), B3LYP/6-31+G(3df,2p), QCISD(T)/6-31G(d’,p), and CBS-Q levels based on the B3LYP/6-31G(d,p)-optimized geometry. The $S^\circ_{298}$ and $C^\circ(T)$ (300 K ≤ T ≤ 1500 K) are determined by B3LYP/6-31G(d,p)-optimized geometries and frequencies. The analyses of enthalpies and internal rotational barriers show that the syn forms of (E)- and (Z)-CHCl=CHOH, CCS=CHOH, (E)-CHCl=CClOH, and (Z)-CHCl=CClOH are more stable than the anti forms. CHCl=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/Cp/H, C/C/H/O, HB, and anti, which are useful for the group additivity estimation of higher chlorinated enol molecules.

mol, which is ca. 6 kcal/mol lower than that for the C/Cp/H group (8.6 kcal/mol) calculated by Benson.  

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

9. C/Cp/C/O. This group can be calculated from 1a.s and 5a.s–7a.s. The mean $\Delta H^\circ_{298}$ value from these species is 2.34 kcal/mol.
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