Thermodynamic Properties (Enthalpy, Bond Energy, Entropy, and Heat Capacity) and Internal Rotor Potentials of Vinyl Alcohol, Methyl Vinyl Ether, and Their Corresponding Radicals

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Vinyl alcohols (enols) have been discovered as important intermediates and products in the oxidation and combustion of hydrocarbons, while methyl vinyl ethers are also thought to occur as important combustion intermediates. Vinyl alcohol has been detected in interstellar media, while poly(vinyl alcohol) and poly(methyl vinyl ether) are common polymers. The thermochemical property data on these vinyl alcohols and methyl vinyl ethers is important for understanding their stability, reaction paths, and kinetics in atmospheric and thermal hydrocarbon−oxygen systems. Enthalpies ($\Delta_f H^\circ_{298}$), entropies (S°_{298}), and heat capacities ($C_p(T)$) are determined for $CH_2{=}CHOH$, $C^\bullet H{=}CHOH$, $CH_2{=}C^\bullet OH$, $CH_2{=}CHOCH_3$, $C^\bullet H{=}CHOCH_3$, $CH_2{=}C^\bullet OCH_3$, and $CH_2{=}CHOC^\bullet H_2$. Molecular structures, vibrational frequencies, S°_{298}, and $C_p(T)$ are calculated at the B3LYP/6-31G(d,p) density functional calculation level. Enthalpies are also determined using the composite CBS-Q, CBS-APNO, and G3 methods using isodesmic work reactions to minimize calculation errors. Potential barriers for internal rotors are calculated at the B3LYP/6-31G(d,p) level and used to determine the hindered internal rotational contributions to entropy and heat capacity. The recommended ideal gas phase $\Delta_f H^\circ_{298}$ values calculated in this study are the following (in kcal mol^{-1}): −30.0, −28.9 (syn, anti) for $CH_2{=}CHOH$; −25.6, −23.9 for $CH_2{=}CHOCH_3$; 31.3, 33.5 for $C^\bullet H{=}CHOH$; 27.1 for *anti*-$CH_2{=}C^\bullet OH$; 35.6, 39.3 for $C^\bullet H{=}CHOCH_3$; 33.5, 32.2 for $CH_2{=}C^\bullet OCH_3$; 21.3, 22.0 for $CH_2{=}CHOC^\bullet H_2$. Bond dissociation energies (BDEs) and group additivity contributions are also determined. The BDEs reveal that the O−H, O−CH_3, C−OH, and C−OCH_3 bonds in vinyl alcohol and methyl vinyl ether are similar in energy to those in the aromatic molecules phenol and methyl phenyl ether, being on average around 3 kcal mol^{-1} weaker in the vinyl systems. The keto−enol tautomerization enthalpy for the interconversion of vinyl alcohol to acetaldehyde is determined to be −9.7 kcal mol^{-1}, while the activation energy for this reaction is calculated as 55.9 kcal mol^{-1}; this is the simplest keto−enol tautomerization and is thought to be important in the reactions of vinyl alcohol. Formation of the formyl methyl radical (vinoxy radical/vinyloxy radical) from both vinyl alcohol and methyl vinyl ether is also shown to be important, and its reactions are discussed briefly.

Introduction

Vinyl alcohols and methyl vinyl ethers are intermediates in low-temperature combustion processes, such as in the initial and intermediate stages of combustion[1] and in the atmospheric photochemical oxidation of hydrocarbons. The importance of vinyl alcohols as combustion intermediates has been discovered only recently,[2] highlighting the absence of vinyl alcohols and their radicals from combustion mechanisms. Vinyl alcohol has also been detected recently in interstellar media,[3] and there is interest in the mechanism by which it is formed.[4] Additionally, both poly(vinyl alcohol) and poly(methyl vinyl ether) are widely used polymers. Knowledge of the thermodynamic parameters for these species is thus central to understanding and predicting their reaction pathways, rate constants, and equilibrium constants in flames, in the atmosphere, and in interstellar space, among other areas.

The rapid interconversion of conformers and the instability of vinyl alcohols and methyl vinyl ethers relative to their keto (aldehyde) forms leads to complexities in the study of their thermochemistry. Experimental and theoretical studies on heats of formation ($\Delta_f H^\circ_{298}$) of vinyl alcohols have been reported by several research groups. Turecek et al.[5] reported $\Delta_f H^\circ_{298}$ of $CH_2{=}CHOH$ to be −30.59 kcal mol^{-1} by an experimental ion method study. Holmes et al.[6] reported $\Delta_f H^\circ_{298}$ of $CH_2{=}CHOH$ to be −26.59 kcal mol^{-1} by electron impact method in 1976. Holmes and Lossing[7] measured $\Delta_f H^\circ_{298}$ of $CH_2{=}CHOH$ to be −29.87 kcal mol^{-1} by mass spectrometry in 1982. Traeger and Djordjevic[8] measured the enthalpy of vinyl alcohol to be −27.3 kcal mol^{-1}. Yamada, Bozzelli, and Lay[9] have determined $\Delta_f H^\circ_{298}$ of $CH_2{=}CHOH$ to be −29.95 kcal mol^{-1} from CBS-Q calculations. Zhu, Chen, and Bozzelli[10] have reported $\Delta_f H^\circ_{298}$ of *syn*-$CH_2{=}CHOH$ to be −30.59 kcal mol^{-1} and *anti*-$CH_2{=}CHOH$ to be −29.59 kcal mol^{-1} by using CBS-Q calculations. Turecek et al.[11] reported the $\Delta_f H^\circ_{298}$ of *syn*-vinyl alcohol as −29.39 kcal mol^{-1} using ab initio calculations at the G2MP2 level of theory. Smith et al.[12] reported the $\Delta_f H^\circ_{298}$ of *syn*-vinyl alcohol as −27.8 kcal mol^{-1} using G1 ab initio calculations. The experimental results above show a span of around 4 kcal mol^{-1} for the enthalpy of $CH_2{=}CHOH$.

In cases such as this, where experimental measurements are difficult and imprecise, the most accurate means of obtaining thermochemical properties can be from ab initio calculations.

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Through the use of highly accurate compound theoretical methods (such as G3 and CBS-APNO) in conjunction with well-chosen isodesmic work reactions, enthalpies of formation can be calculated with accuracy of ±0.5 kcal mol^{-1} or below. This was demonstrated recently in a study of the enthalpy of formation of formaldehyde,[13] which for a long time was not known to within an accuracy of 1 kcal mol^{-1}. Our above evaluation of previous measurements of the vinyl alcohol enthalpy reveals a similar level of inaccuracy. Furthermore, no accurate thermochemical information is available for methyl vinyl ether, or the radicals of vinyl alcohol and methyl vinyl ether.

In this work, enthalpies ($\Delta_f H^\circ_{298}$), entropies (S°_{298}) and heat capacities ($C_p(T)$) are determined for vinyl alcohol, methyl vinyl ether, and the radicals corresponding to loss of a hydrogen atom from these two parent molecules, using density functional and ab initio calculation methods. The enthalpies of formation are evaluated at four calculation levels using isodesmic work reactions. Entropies and heat capacities are calculated using the rigid-rotor-harmonic-oscillator approximation based on frequencies and moments of inertia of the optimized B3LYP/6-31G(d,p) structures. Contributions to entropy and heat capacity from internal rotation are estimated from rotor energy profiles calculated at the B3LYP/6-31G(d,p) level of theory. We also derive group additivity and hydrogen bond increment (HBI) groups[14] from the data that we obtain.

Calculation Methods

Structural parameters for each molecule are optimized for structure at the B3LYP/6-31G(d,p) level of theory,[15] and the harmonic vibrational frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. The compound methods CBS-Q,[16] CBS-APNO,[16] and G3[17] are also used to determine accurate enthalpies of formation. The CBS-Q and G3 methods perform initial geometry optimization and frequency calculations with HF theory (and the 6-31G(d′) and 6-31G(d) basis sets, respectively), followed by higher-level geometry optimizations using MP2 theory (again with the same basis sets). The CBS-APNO method involves initial geometry optimization and frequency calculations at the HF/6-311G(d,p) level of theory, followed by a higher-level QCISD/6-311G(d,p) optimization. All calculations are performed using Gaussian 03.[18]

Enthalpies of Formation. Standard enthalpies of formation are estimated using total enthalpies obtained by the four calculation methods with a series of working reactions that are bond isodesmic. The method of isodesmic reactions relies on the similarity of bonding environment in the reactants and products that leads to cancellation of systematic errors in the calculations. Calculations are performed for all components in each reaction, and the enthalpy of reaction ($\Delta_{rxn} H^\circ_{298}$) is calculated. The enthalpy of formation of the target species is then determined from the calculated $\Delta_{rxn} H^\circ_{298}$ with experimental $\Delta_f H^\circ_{298}$ values for reference species. Enthalpies for all reference species in our isodesmic reactions have been measured experimentally to within a low uncertainty.

Entropies, Heat Capacities, and Hindered Rotation Contribution to Thermodynamic Parameters. Entropies and heat capacities are calculated using the geometry, symmetry, frequencies, and moments of inertia of the B3LYP/6-31G(d,p) optimized structures using the SMCPS program. Symmetry and electronic degeneracy of radical species are incorporated. Contributions to entropy and heat capacity from internal rotations are determined with the program ROTATOR, using rotation potential curves from B3LYP/6-31G(d,p) calculations.

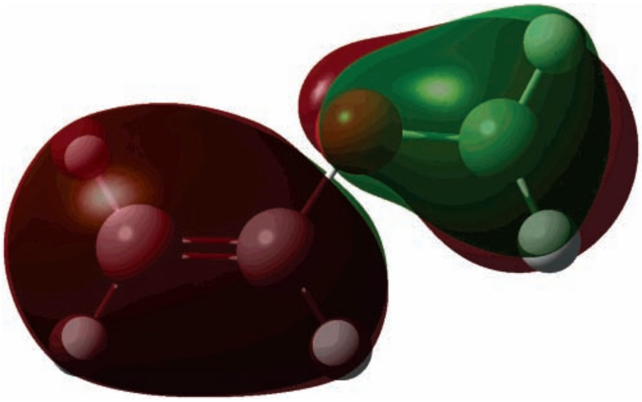

Figure 1. HOMO −1 molecular orbital diagram for *anti*-$CH_2{=}CHOC^{\bullet}H_2$.

A technique for the calculation of thermodynamic functions from hindered rotations with arbitrary potentials is used to calculate hindered internal rotor contributions to the entropy and heat capacity of vinyl alcohol and methyl vinyl ether.[19] This technique employs expansion of the hindrance potential in a Fourier series, calculation of the Hamiltonian matrix on the basis of wave functions of the free internal rotor, and subsequent calculation of energy levels by direct diagonalization of the Hamiltonian matrix. In this work, the torsional potential calculated at discrete torsional angles is represented by a truncated seven-parameter Fourier series of the following form:

$$V(\phi) = a_0 + \sum_{i=1}^{7} a_i \cos(i\phi) + \sum_{j=1}^{7} b_j \cos(j\phi) \qquad (1)$$

The values of the coefficients a_i and b_j are calculated to provide the minima and maxima of the torsional potentials with allowance for a shift of the theoretical extreme angular positions.

Results and Discussion

Geometries and Frequencies. Illustrations of the optimized geometries at the B3LYP/6-31G(d,p) density functional calculation level for $CH_2{=}CHOH$, $C^{\bullet}H{=}CHOH$, $CH_2{=}C^{\bullet}OH$, $CH_2{=}CHOCH_3$, $C^{\bullet}H{=}CHOCH_3$, $CH_2{=}C^{\bullet}OCH_3$, and $CH_2{=}CHOC^{\bullet}H_2$ are presented in the Supporting Information, along with their Cartesian coordinates, vibrational frequencies, and moments of inertia. Trends in bond lengths are illustrated in Table 1. Also included in Table 1 are bond lengths for QCISD/6-311G(d,p) optimized geometries, taken from the CBS-APNO calculations. From Table 1 we find that the B3LYP calculations yield similar geometries to the higher-level QCISD calculations, and the B3LYP geometries and frequencies are therefore suitable for the calculation of entropies and heat capacities. Also, in Table 1 we observe that the removal of a hydrogen atom from the vinyl backbone of either vinyl alcohol or methyl vinyl ether results in relatively little change to the molecular structure, indicating that the radical electron is left predominantly localized on the carbon atom. However, formation of the $CH_2{=}CHOC^{\bullet}H_2$ radical results in contraction of the $O{-}CH_2$ bond by around 0.06 Å, indicating resonance stabilization of the radical electron between the oxygen atom and the methylene carbon atom. This is demonstrated in Figure 1, which shows the HOMO −1 of *anti*-$CH_2{=}CHOC^{\bullet}H_2$. Here we observe π bonding between the vinyl carbon atoms and, to a lesser extent, between the ether oxygen atom and the methylene carbon atom.

Enthalpies of Formation. The isodesmic reaction schemes used to determine $\Delta_f H^\circ_{298}$ of vinyl alcohol, methyl vinyl ether,

TABLE 1: Important Bond Lengths for syn and anti Conformations of Vinyl Alcohol and Methyl Vinyl Ether, and Their Corresponding Radicals, at the B3LYP/6-31G(d,p) and QCISD/6-311G(d,p) Levels of Theory

	bond lengths (Å)					
	B3LYP[a]	QCISD[b]	B3LYP[a]	QCISD[b]	B3LYP[a]	QCISD[b]
vinyl alcohol species	$C{=}C$		$C{-}O$		$O{-}H$	
syn-$CH_2{=}CHOH$	1.334	1.339	1.362	1.363	0.968	0.960
syn-$C^{\bullet}H{=}CHOH$	1.316	1.323	1.368	1.367	0.969	0.961
syn-$CH_2{=}C^{\bullet}OH$	N/A	N/A	N/A	N/A	N/A	N/A
antii-$CH_2{=}CHOH$	1.332	1.336	1.369	1.370	0.964	0.956
anti-$C^{\bullet}H{=}CHOH$	1.315	1.315	1.373	1.373	0.964	0.964
anti-$CH_2{=}C^{\bullet}OH$	1.322	1.326	1.340	1.343	0.968	0.961
methyl vinyl ether species	$C{=}C$		$C{-}O$		$O{-}CH_3$	
syn-$CH_2{=}CHOCH_3$	1.355	1.342	1.430	1.357	1.430	1.417
syn-$C^{\bullet}H{=}CHOCH_3$	1.320	1.327	1.359	1.358	1.424	1.421
syn-$CH_2{=}C^{\bullet}OCH_3$	1.325	1.331	1.318	1.321	1.445	1.436
syn-$CH_2{=}CHOC^{\bullet}H_2$	1.334	1.318	1.369	1.348	1.362	1.356
anti-$CH_2{=}CHOCH_3$	1.316	1.337	1.367	1.364	1.422	1.418
anti-$C^{\bullet}H{=}CHOCH_3$	1.316	1.323	1.367	1.366	1.422	1.419
anti-$CH_2{=}C^{\bullet}OCH_3$	1.323	1.328	1.331	1.333	1.437	1.433
anti-$CH_2{=}CHOC^{\bullet}H_2$	1.332	1.334	1.367	1.370	1.364	1.368

[a] B3LYP/6-31G(d,p). [b] QCISD/6-311G(d,p).

TABLE 2: Isodesmic Reactions and Calculated Enthalpies of Reaction ($\Delta_{rxn}H^{\circ}_{298}$, kcal mol^{-1}) with Four Theoretical Methods for syn Conformations of Vinyl Alcohol, Methyl Vinyl Ether, and the Corresponding Radicals

	$\Delta_{rxn}H^{\circ}_{298}$ (kcal mol^{-1})			
isodesmic reaction	B3LYP[a]	CBS-Q	CBS-APNO	G3
syn-$CH_2{=}CHOH + CH_4 \rightarrow CH_3OH + CH_2{=}CH_2$	14.38	12.13	12.33	12.09
syn-$CH_2{=}CHOH + C_2H_6 \rightarrow CH_3CH_2OH + CH_2{=}CH_2$	9.17	6.25	6.58	6.17
syn-$CH_2{=}CHOH + C_3H_8 \rightarrow CH_3CH_2OH + CH_2{=}CHCH_3$	5.28	3.52	3.74	3.51
syn-$C^{\bullet}H{=}CHOH + CH_4 \rightarrow CH_3OH + CH_2{=}C^{\bullet}H$	11.58	9.25	9.52	9.26
syn-$C^{\bullet}H{=}CHOH + C_2H_6 \rightarrow CH_3CH_2OH + CH_2{=}C^{\bullet}H$	6.37	3.37	3.78	3.35
syn-$CH_2{=}CHOCH_3 + C_2H_6 \rightarrow CH_2{=}CHCH_3 + CH_3OCH_3$	7.26	6.65	6.74	6.71
syn-$CH_2{=}CHOCH_3 + C_3H_8 \rightarrow CH_2{=}CHCH_3 + CH_3CH_2OCH_3$	3.77	3.28	3.45	3.33
syn-$C^{\bullet}H{=}CHOCH_3 + C_2H_6 \rightarrow CH_2{=}C^{\bullet}H + CH_3CH_2OCH_3$	5.27	3.26	3.63	3.36
syn-$C^{\bullet}H{=}CHOCH_3 + CH_4 \rightarrow CH_2{=}C^{\bullet}H + CH_3OCH_3$	10.38	9.37	9.59	9.45
syn-$CH_2{=}C^{\bullet}OCH_3 + C_2H_6 \rightarrow CH_2{=}C^{\bullet}H + CH_3CH_2OCH_3$	8.34	5.37	5.92	5.07
syn-$CH_2{=}C^{\bullet}OCH_3 + CH_4 \rightarrow CH_2{=}C^{\bullet}H + CH_3OCH_3$	13.46	11.48	11.87	11.16
syn-$CH_2{=}CHOC^{\bullet}H_2 + C_2H_6 \rightarrow CH_2{=}C^{\bullet}H + CH_3CH_2OCH_3$	20.25	17.35	18.37	17.48
syn-$CH_2{=}CHOC^{\bullet}H_2 + CH_4 \rightarrow CH_2{=}C^{\bullet}H + CH_3OCH_3$	25.37	23.46	24.33	23.57

[a] B3LYP/6-31G(d,p).

TABLE 3: Isodesmic Reactions and Calculated Enthalpies of Reaction ($\Delta_{rxn}H^{\circ}_{298}$, kcal mol^{-1}) with Four Theoretical Methods for anti Conformations of Vinyl Alcohol, Methyl Vinyl Ether, and the Corresponding Radicals

	$\Delta_{rxn}H^{\circ}_{298}$ (kcal mol^{-1})			
isodesmic reaction	B3LYP[a]	CBS-Q	CBS-APNO	G3
anti-$CH_2{=}CHOH + CH_4 \rightarrow CH_3OH + CH_2{=}CH_2$	12.46	11.09	11.19	10.99
anti-$CH_2{=}CHOH + C_2H_6 \rightarrow CH_3CH_2OH + CH_2{=}CH_2$	7.25	5.21	5.44	5.07
anti-$CH_2{=}CHOH + C_3H_8 \rightarrow CH_3CH_2OH + CH_2{=}CHCH_3$	3.36	2.48	2.60	2.41
anti-$C^{\bullet}H{=}CHOH + CH_4 \rightarrow CH_3OH + CH_2{=}C^{\bullet}H$	8.32	7.11	7.26	7.06
anti-$C^{\bullet}H{=}CHOH + C_2H_6 \rightarrow CH_3CH_2OH + CH_2{=}C^{\bullet}H$	3.12	1.23	1.51	1.15
anti-$CH_2{=}C^{\bullet}OH + CH_4 \rightarrow CH_3OH + CH_2{=}C^{\bullet}H$	16.41	13.58	14.03	13.16
anti-$CH_2{=}C^{\bullet}OH + C_2H_6 \rightarrow CH_3CH_2OH + CH_2{=}C^{\bullet}H$	11.21	7.70	8.29	7.25
anti-$CH_2{=}CHOCH_3 + C_2H_6 \rightarrow CH_2{=}CHCH_3 + CH_3OCH_3$	5.34	5.09	4.96	5.05
anti-$CH_2{=}CHOCH_3 + C_3H_8 \rightarrow CH_2{=}CHCH_3 + CH_3CH_2OCH_3$	1.84	1.72	1.67	1.67
anti-$C^{\bullet}H{=}CHOCH_3 + C_2H_6 \rightarrow CH_2{=}C^{\bullet}H + CH_3CH_2OCH_3$	1.55	−0.32	−0.15	−0.35
anti-$C^{\bullet}H{=}CHOCH_3 + CH_4 \rightarrow CH_2{=}C^{\bullet}H + CH_3OCH_3$	6.66	5.79	5.81	5.74
anti-$CH_2{=}C^{\bullet}OCH_3 + C_2H_6 \rightarrow CH_2{=}C^{\bullet}H + CH_3CH_2OCH_3$	9.66	6.61	7.32	6.39
anti-$CH_2{=}C^{\bullet}OCH_3 + CH_4 \rightarrow CH_2{=}C^{\bullet}H + CH_3OCH_3$	14.77	12.72	13.27	12.48
anti-$CH_2{=}CHOC^{\bullet}H_2 + C_2H_6 \rightarrow CH_2{=}C^{\bullet}H + CH_3CH_2OCH_3$	20.14	16.24	17.86	16.72
anti-$CH_2{=}CHOC^{\bullet}H_2 + CH_4 \rightarrow CH_2{=}C^{\bullet}H + CH_3OCH_3$	25.25	22.35	23.82	22.81

[a] B3LYP/6-31G(d,p).

and their corresponding radicals are shown in Tables 2 and 3 for the syn and anti conformers, respectively. Tables 2 and 3 include calculated reaction enthalpies for each of the isodesmic reactions with the four computational methods used in this study. We find that reaction enthalpies for all of the isodemic reactions are small, indicating good cancellation of bond energy across the reactions.

Enthalpies of formation and their respective uncertainties for standard species used in the working reactions are adopted from evaluation of literature data; values for the standard species are listed in Table 4. Analysis of Table 4 shows that all reference species have accurately known enthalpies.

Enthalpies of formation are determined using the calculated reaction enthalpies of Tables 2 and 3 and the experimental

TABLE 4: Experimental Enthalpies of Formation ($\Delta_f H^\circ_{298}$, kcal mol^{-1}) with Uncertainties for Reference Species in Isodesmic Reactions

species	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	ref
CH_4	−17.89 ± 0.08	20
C_2H_6	−20.04 ± 0.07	21
C_3H_8	−24.82 ± 0.14	20
CH_3OH	−48.07 ± 0.05	22
CH_3CH_2OH	−56.23 ± 0.12	22
$CH_2{=}CH_2$	12.54 ± 0.07	23
$CH_2{=}CH^\bullet$	70.9 ± 0.3	24
$CH_2{=}CHCH_3$	4.88 ± 0.08	25
CH_3OCH_3	−43.99 ± 0.12	26
$CH_3CH_2OCH_3$	−51.73 ± 0.16	26

TABLE 5: Calculated Enthalpies of Formation ($\Delta_f H^\circ_{298}$) Uncertainties, and Standard Deviations for Vinyl Alcohol and Methyl Vinyl Ether Species[a]

	$\Delta_f H^\circ_{298}$	uncertainty	deviation
	vinyl alcohol species		
syn-$CH_2{=}CHOH$	−29.98	±0.5	±0.16
syn-$C^\bullet H{=}CHOH$	31.29	±0.5	±0.20
anti-$CH_2{=}CHOH$	−28.88	±0.5	±0.13
anti-$C^\bullet H{=}CHOH$	33.50	±0.5	±0.15
anti-$CH_2{=}C^\bullet OH$	27.05	±0.5	±0.48
	methyl vinyl ether species		
syn-$CH_2{=}CHOCH_3$	−25.58	±0.5	±0.07
syn-$C^\bullet H{=}CHOCH_3$	35.56	±0.5	±0.15
syn-$CH_2{=}C^\bullet OCH_3$	33.53	±0.5	±0.39
syn-$CH_2{=}CHOC^\bullet H_2$	21.25	±0.5	±0.51
anti-$CH_2{=}CHOCH_3$	−23.91	±0.5	±0.05
anti-$C^\bullet H{=}CHOCH_3$	39.25	±0.5	±0.07
anti-$CH_2{=}C^\bullet OCH_3$	32.21	±0.5	±0.45
anti-$CH_2{=}CHOC^\bullet H_2$	22.04	±0.5	±0.79

[a] Average values from CBS-Q, CBS-APNO, and G3 calculations with isodesmic work reactions. All values in kcal mol^{-1}.

enthalpies of formation of Table 4. The determined enthalpies are presented in Table A1 (Appendix) for the syn and anti conformers of vinyl alcohol, methyl vinyl ether, and their corresponding alcohols. From Table A1 we see that the enthalpies determined with the three compound methods are all in agreement to within about 0.5 kcal mol^{-1} (or typically less). The B3LYP enthalpies, however, differ from the other values by around 2 kcal mol^{-1}, indicating the importance of using high-level computational methods when trying to determine thermodynamic properties of these unsaturated vinyl-oxy hydrocarbons accurately.

Table 5 gives the average value of the CBS-Q, CBS-APNO, and G3 enthalpies of formation for each vinyl alcohol and methyl vinyl ether species, along with an estimated uncertainty and the standard deviation for the three values. The computational errors of the CBS-Q, CBS-APNO, and G3 methods for atomization reactions with the G2 test set are 1.3, 0.7, and 0.9 kcal mol^{-1}, respectively. When using isodesmic reactions, the accuracy of the CBS-APNO and G3 methods have been evaluated as 0.30 and 0.32 kcal mol^{-1}, respectively.[13] However, for radical species these calculations will be less accurate because of spin contamination, and we estimate an average computational error of ±0.5 kcal mol^{-1}. Our calculated enthalpy for *syn*-vinyl alcohol is compared to previous literature values in Table 6. We find that our value agrees well with the experimental value of Holmes and Lossing.[7] We also observe in Table 5 that the syn conformers of vinyl alcohol and methyl vinyl ether are more stable than their anti conformers by around 1 to 2 kcal mol^{-1}. The stability of the syn confirmations of vinyl alcohol and methyl vinyl ether, with respect to their anti confirmations, has been attributed to steric effects.[27]

TABLE 6: Comparison of Literature Enthalpies of Formation ($\Delta_f H^\circ_{298}$) for Vinyl Alcohol

$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	ref
−29.98[a]	this work
−30.59	5
−26.59	6
−29.87	7
−27.3	8
−29.95	9
−30.59[a]	10
−29.39[a]	11
−27.8[a]	12

[a] Syn conformation.

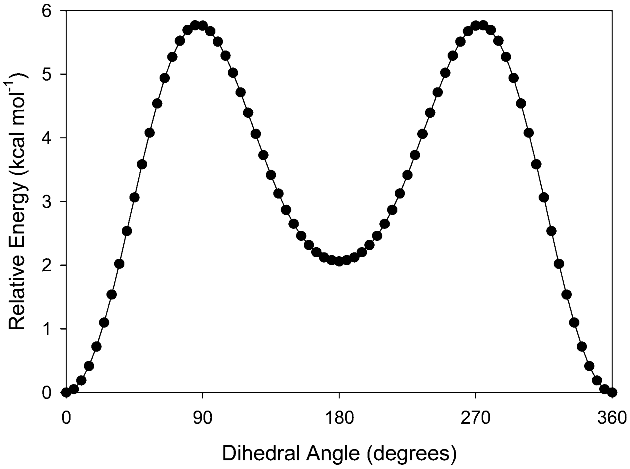

Figure 2. Potential energy profile of the C−OH internal rotor for $CH_2{=}CHOH$ (dot points). The solid line indicates Fourier series expansion.

Internal Rotor Potentials. Potential energy profiles for internal rotations in each molecule are calculated at the B3LYP/6-31G(d,p) density functional level. The potential energy as a function of dihedral angle is determined by scanning the torsion angles from 0° to 360° at 5° intervals, while allowing the molecule's remaining structural parameters to be optimized. Seven-parameter Fourier series expansions have been calculated for each of the internal rotors, according to Equation 1. Figure 2 shows an example of an internal rotor potential energy profile (for $CH_2{=}CHOH$) and its Fourier series expansion. The remaining profiles are included in the Supporting Information (Figures S8−S18).

Figures 2, S8, and S9 show the potential energy profiles of the C−OH internal rotors in $CH_2{=}CHOH$, $C^\bullet H{=}CHOH$, and $CH_2{=}C^\bullet OH$; these rotors correspond to interconversion of the syn and anti conformations of these molecules. The $CH_2{=}CHOH$ and $C^\bullet H{=}CHOH$ rotors are observed to be relatively similar, with the syn conformer being more stable than the anti conformer by 2−4 kcal mol^{-1}; the total barrier for rotation is between 5 and 7 kcal mol^{-1}. For $CH_2{=}C^\bullet OH$ we find that *anti*-$CH_2{=}C^\bullet OH$ is the only stable conformer, while the barrier for internal rotation is around half that calculated for $CH_2{=}CHOH$ and $C^\bullet H{=}CHOH$. Also, unlike $CH_2{=}CHOH$ and $C^\bullet H{=}CHOH$, the C=C−O−H atoms for $CH_2{=}C^\bullet OH$ do not lie in the same plane.

Potential energy profiles for the $C{-}OCH_3$ rotors in methyl vinyl ether and its radicals are illustrated in Figures S10−S12. The internal rotors are similar to those observed for vinyl alcohol and its radicals, with the anti conformations of $CH_2{=}CHOCH_3$ and $C^\bullet H{=}CHOHCH_3$ being more stable than the syn conformations by around 2−4 kcal mol^{-1}. For $CH_2{=}C^\bullet OHCH_3$ the syn

TABLE 7: Bond Dissociation Energies (BDEs) for Vinyl Alcohol and Methyl Vinyl Ether

species	BDE (kcal mol^{-1})
$\mathrm{H{-}CH{=}CHOH}$	113.4
$\mathrm{CH_2{=}C(OH){-}H}$	109.1
$\mathrm{CH_2{=}CHO{-}H}$	85.2
$\mathrm{CH_2{=}CH{-}OH}$	110.3
$\mathrm{H{-}CH{=}CHOCH_3}$	113.2
$\mathrm{CH_2{=}C(OCH_3){-}H}$	109.9
$\mathrm{CH_2{=}CHOCH_2{-}H}$	98.9
$\mathrm{CH_2{=}CH{-}OCH_3}$	100.6
$\mathrm{CH_2{=}CHO{-}CH_3}$	63.5

and anti conformations are both stable, although the potential energy well for *syn*-$\mathrm{CH_2{=}C^{\bullet}OHCH_3}$ is very shallow (0.2 kcal mol^{-1}).

Figures S13−S15 give the internal $\mathrm{O{-}CH_3}$ rotor energy profiles for the syn and anti conformations of $\mathrm{CH_2{=}CHOCH_3}$ and its radicals corresponding to loss of a hydrogen atom. All three species exhibit symmetric threefold barriers. For the anti conformers, the barrier to rotation is around 1 kcal mol^{-1}. For *syn*-$\mathrm{CH_2{=}CHOCH_3}$ and *syn*-$\mathrm{C^{\bullet}H{=}CHOCH_3}$ the barrier to rotation of the methyl group is 2−4 kcal mol^{-1}. With *syn*-$\mathrm{CH_2{=}C^{\bullet}OCH_3}$ we were not able to calculate the energy profile for rotation of the methyl group because the molecule became unstable in the syn conformation and unfolded to the more stable anti configuration. This is a consequence of the very shallow potential energy well for *syn*-$\mathrm{CH_2{=}C^{\bullet}OCH_3}$ seen in Figure S12. In our entropy and heat capacity calculations we use the *syn*-$\mathrm{CH_2{=}CHOCH_3}$ methyl rotor to model the *syn*-$\mathrm{CH_2{=}C^{\bullet}OCH_3}$ rotor.

The potential energy profiles for rotation of the $\mathrm{O{-}C^{\bullet}H_2}$ group in *syn*- and *anti*-$\mathrm{CH_2{=}CHOC^{\bullet}H_2}$ are shown in Figures S16 and S17, and the $\mathrm{C{-}OC^{\bullet}H_2}$ rotor for this same molecule is shown in Figure S18. From Figures S16 and S17 we find that the $\mathrm{O{-}C^{\bullet}H_2}$ rotors in *syn*- and *anti*-$\mathrm{CH_2{=}CHOC^{\bullet}H_2}$ show twofold barriers with well depths of about 5 kcal mol^{-1}, which results from stabilization (overlap) between the radical and the oxygen orbitals (see Figure 1). Figure S18 demonstrates that the syn and anti conformations are of similar energy, with *syn*-$\mathrm{CH_2{=}CHOC^{\bullet}H_2}$ being more stable by around 0.5 kcal mol^{-1}.

Entropy and Heat Capacity. The entropy and heat capacity results using B3LYP/6-31G(d,p) geometries and frequencies are summarized in Table A2 (Appendix). TVR represents the sum of the contributions from translations, vibrations, and external rotations, and IR indicates the contribution from hindered internal rotation. The torsion frequencies for these internal rotors are not included in TVR. The final standard entropies also include correction terms for rotational conformers. This correction is calculated by the following formula for 1 mol of mixture

$$\Delta S_{\text{mixing}} = -R \sum n_i \ln(n_i) \tag{2}$$

Where n_i is the equilibrium mole fraction of the ith form. ΔS_{mixing} represents the entropy of mixing of rotational conformations or optical conformations.

Bond Dissociation Energies. The bond dissociation energies of the $\mathrm{H{-}CH{=}CHOH}$, $\mathrm{CH_2{=}C(OH){-}H}$, $\mathrm{CH_2{=}C(OH){-}H}$, $\mathrm{CH2{=}CHO{-}H}$, $\mathrm{H{-}CH{=}CHOCH_3}$, $\mathrm{CH_2{=}C(OCH_3){-}H}$, and $\mathrm{CH_2{=}CHOCH_2{-}H}$ bonds are presented in Table 7. They are estimated using the $\Delta_f H^{\circ}_{298}$ values of vinyl alcohol and methyl vinyl ether, their corresponding radicals from this work, the enthalpy of the $\mathrm{CH_2{=}CHO^{\bullet}}$ radical calculated by Lee and Bozzelli (3.08 kcal mol^{-1}),[28] and the experimental enthalpy of formation of the methyl radical (34.821 kcal mol^{-1}).[23] For molecules with both syn and anti conformations, the enthalpy of the most stable conformation is used. Also included in Table 7 are bond dissociation energies for cleavage of the $\mathrm{C{=}C{-}O}$ bonds in vinyl alcohol and methyl vinyl ether, that is, $\mathrm{CH_2{=}CH{-}OH}$ and $\mathrm{CH_2{=}CH{-}OCH_3}$. These values are calculated using literature enthalpies for $\mathrm{CH_2{=}C^{\bullet}H}$, $\mathrm{HO^{\bullet}}$ and $\mathrm{CH_3O^{\bullet}}$.

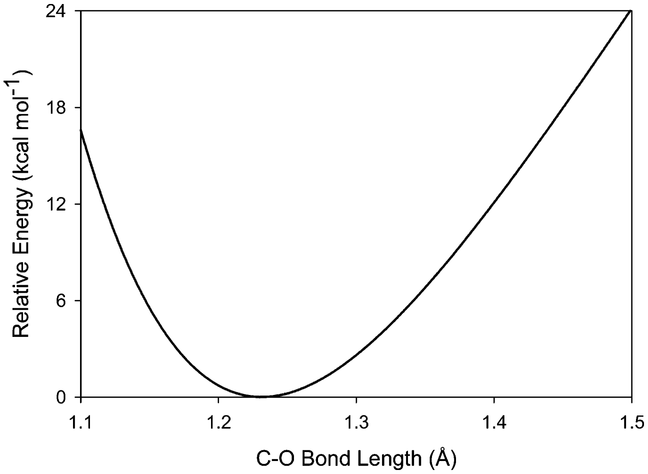

Figure 3. Relaxed potential energy scan of the C−O bond in the $\mathrm{CH_2CHO}$ radical at the B3LYP/6-311++G(3df,3pd) level of theory.

Analysis of Table 7 shows that the weakest bond in vinyl alcohol is the $\mathrm{CH_2{=}CHO{-}H}$ bond, with a BDE of 85.2 kcal mol^{-1}, while the weakest bond in methyl vinyl ether is the $\mathrm{CH_2{=}CHO{-}CH_3}$ bond, with a BDE of 63.5 kcal mol^{-1}. The $\mathrm{CH_2{=}CHO{-}H}$ and $\mathrm{CH_2{=}CHO{-}CH_3}$ bonds are weak because the homolytic cleavage of these bonds results in formation of the resonantly stabilized $\mathrm{CH_2CHO}$ radical. In this radical the carbonyl bond, which is stronger than the olefin bond, is formed. As a result, the formyl methyl radical $\mathrm{C^{\bullet}H_2{-}CH{=}O}$ structure is favored by around 10 kcal mol^{-1} over that of the vinoxy (or vinyloxy) radical $\mathrm{CH_2{=}CH{-}O^{\bullet}}$ structure, with the equilibrium geometry close to that of the formyl methyl radical.[29] We refer to this $\mathrm{C^{\bullet}H_2CH{=}O}$ species as the formyl methyl radical in the remainder of this article.

In Figure 3 the energy of the formyl methyl radical at the B3LYP/6-311++G(3df,3pd) level of theory is plotted as a function of the C−O bond length, with all other geometrical parameters optimized. The optimized C−C bond length as a function of the C−O bond length is given in the Supporting Information (Figure S19). From Figure 3 we find that the molecule's energy minimum occurs at a bond length of 1.23 Å, which is very close to the C=O bond length in acetaldehyde (1.20 Å at the B3LYP/6-311++G(3df,3pd) level). However, at the optimum C−O bond length the C−C bond is 1.42 Å, which is somewhere between a standard single and double C−C bond, indicating that there is still a significant degree of resonance stabilization in the formyl methyl radical.

It is likely that the cleavage of the $\mathrm{CH_2{=}CHO{-}H}$ and $\mathrm{CH_2{=}CHO{-}CH_3}$ bonds will constitute important decomposition pathways during the combustion of vinyl alcohol and methyl vinyl ether. The very weak $\mathrm{C{=}CO{-}H}$ bonds in vinyl alcohols (85.2 kcal mol^{-1}) make these species more reactive to abstraction by the radical pool than their corresponding aldehydes, where the $\mathrm{RC({=}O){-}H}$ bond energies are around 89 kcal mol^{-1}. Similarly, the $\mathrm{CH({=}O){-}CH_3}$ bonds in vinyl ethers (63.5 kcal mol^{-1}) are significantly weaker than the $\mathrm{CH({=}O){-}CH_3}$ bond energies in the aldehydes (ca. 86 kcal mol^{-1}) and will dissociate at much lower temperatures.

Loss of the weakly bound hydroxyl hydrogen in vinyl alcohol via the abstraction reaction $\mathrm{CH_2{=}CHOH + X \rightarrow C^{\bullet}H_2CH{=}O}$

TABLE 8: Enthalpies of Reaction ($\Delta_{rxn}H°$, kcal mol^{-1}) for Vinyl Alcohol Formation from OH Addition Reactions

reaction	$\Delta_{rxn}H^{\circ}_{298}$
$CH_2{=}CH_2 + OH \rightarrow CH_2{=}CHOH + H^{\bullet}$	1.3
$CH_2{=}CHCH_3 + OH \rightarrow CH_2{=}CHOH + C^{\bullet}H_3$	−8.3
$CH_2{=}CHC_2H_5 + OH \rightarrow CH_2{=}CHOH + C^{\bullet}H_2CH_3$	−9.7
$CH_2{=}CHF + OH \rightarrow CH_2{=}CHOH + F^{\bullet}$	13.2
$CH_2{=}CHCl + OH \rightarrow CH_2{=}CHOH + Cl^{\bullet}$	−16.2
$CH_2{=}CHBr + OH \rightarrow CH_2{=}CHOH + Br^{\bullet}$	−30.4

+ HX and the facile loss of methyl in methyl vinyl ether by unimolecular bond cleavage both result in formation of the formyl methyl radical. The reactions of formyl methyl radicals are known to be important in combustion and thermal reaction systems.[28,30−33] Unimolecular dissociation of the formyl methyl radical has been shown to result primarily in the products CH_3 + CO by Lee and Bozzelli,[28] where the CH_3 radical can further react to abstract a hydrogen atom from hydrocarbons or other hydrogenated species. This has been reported as an important path for the formation of methane by Kaiser.[34] A second major pathway for reaction of the formyl methyl radical is reaction with molecular oxygen in the atmosphere and in combustion processes.[30,31] The major products of this reaction have been studied by Lee and Bozzelli[30] as a function of both pressure and temperature, showing the importance of peroxy radical formation at low temperatures and moderate to high pressures, and formation of CO, HCO, and OH as major products at higher temperatures and at low temperature and pressure conditions. A third reaction of the formyl methyl radical in thermal systems is ketene + H atom formation via beta scission of the aldehydic hydrogen,[28,32] which proceeds with an activation energy of around 46 kcal mol^{-1}; the reactions of ketenes and ketene radicals are a very important component of combustion models.

Vinyl Alcohol Formation. Vinyl alcohol can form from the addition of OH radicals to ethylene, alkyl olefins, vinyl halides, and other substituted olefins,[2c,9,35] especially at low to moderate temperatures where competing reaction pathways are less important. Our newly calculated enthalpy of formation for vinyl alcohol allows us to calculate the enthalpies of some of these reactions. Table 8 lists the reaction enthalpies for the reaction of OH with ethylene, propene, 1-butene, vinyl fluoride, vinyl chloride, and vinyl bromide. The enthalpies of formation used to calculate $\Delta_{rxn}H°$ are provided as Supporting Information. From Table 8 we see that all of the reactions proceed with small or negative reaction enthalpies. Additionally, the activation energies for these reactions are relatively small.[35,36]

Hydrogen Bond Increment Group Values for Radicals. A method to estimate thermochemical properties for radicals from the corresponding properties of the parent molecule with a H atom bonded to the radical site using a single group to modify the parent properties (hydrogen bond increment (HBI) group) has been reported by Lay et al.[14] HBI group values are derived for the vinyl alcohol and methyl vinyl ether radicals in this study using the thermodynamic property data of radicals corresponding to loss of a H atom from the parent vinyl alcohol and methyl vinyl ether. ΔS°_{298} and $\Delta C_p(T)$ are determined as the differences in respective properties of the parent molecule versus the radical so that the HBI values for S°_{298} and $C_p(T)$ are added to the parent values to yield the thermochemical properties of the radical. The contributions corresponding to change in symmetry between the radical and parent are not included in the HBI group but are included in evaluation of the entropy of each species separately, along with the degeneracy of the radical electronic state. The HBI group, therefore, remains an intrinsic value.[37] The data of HBI groups for vinyl alcohols and methyl vinyl ethers are listed in Table 9. The $C_p(T)$ and S°_{298} values in the HBI group correspond to contributions from the loss of three vibrational frequencies, loss of a H atom, plus changes in moments of inertia and internal rotors. HBI groups in Table 9 are for the most stable conformation of each species, and the thermodynamic properties of the $CH2{=}CHO^{\bullet}$ radical are taken from the CBS-APNO calculations of Lee and Bozzelli.[28]

Group Additivity Values. Group additivity is a straightforward and reasonably accurate method for estimating the thermochemical properties of hydrocarbons and oxygenated hydrocarbons. It is particularly useful for large molecules where high-level ab intio or density functional calculations are not practical. Group additivity represents a molecule's thermochemical properties as the sum of the thermochemical properties of a series of groups. For example, the group additivity contributions for vinyl alcohol and methyl vinyl ether are as follows:

$$CH_2{=}CHOH = C_D/H_2 + C_D/H/O + O/C_D/H$$

$$CH_2{=}CHOCH_3 = C_D/H_2 + C_D/H/O + C/H_3/O + O/C/CD$$

The additivity contributions for groups C_D/H_2, $C/H_3/O$, and $C_D/H/O$ and well-known and are summarized in Table 10. Groups $O/C_D/H$ and $O/C/C_D$ are less well-known, however, and have been calculated here, with the results provided in Table 10. Group additivity calculations were made for the syn conformers of vinyl alcohol and methyl vinyl ether. The $\Delta_f H^{\circ}_{298}$ value of the $O/C_D/H$ group has been calculated previously as −44.6 kcal mol^{-1} by Holmes,[7] −48.28 by Turecek,[5] −46.30 by Zhu et al.,[10] and −49.3 by Cohen.[38] These values are significantly lower than Benson's[37] assignment of −37.9 kcal mol^{-1} based on $O/C_D/H$ in alcohols. Both Cohen[38] and Benson[37] have assigned the $O/C/C_D$ group an enthalpy value of −30.5 kcal mol^{-1}.

The enthalpy values of the $O/C_D/H$ and $O/C/C_D$ groups are calculated to be −44.8 kcal mol^{-1} and −30.4 kcal mol^{-1}, respectively. This $O/C_D/H$ value is close to the data of Holmes[7] but 4−5 kcal mol^{-1} higher than the values reported by Turecek[5] and Cohen,[38] and about 1 kcal mol^{-1} higher than value of Zhu

TABLE 9: Hydrogen Bond Increment (HBI) Group Values (ΔH°_{298}, S°_{298}, and $C_p(T)$) for Vinyl Alcohol and Methyl Vinyl Ether Radicals[a]

species	ΔH°_{298}	ΔS°_{298}	$\Delta C_{p,300}$	$\Delta C_{p,400}$	$\Delta C_{p,500}$	$\Delta C_{p,600}$	$\Delta C_{p,800}$	$\Delta C_{p,1000}$	$\Delta C_{p,1500}$
$C^{\bullet}HCHOH$	113.4	2.20	−0.61	−0.87	−1.05	−1.29	−1.99	−2.75	−4.09
$CH_2C^{\bullet}OH$	109.1	1.34	−0.70	−1.82	−2.64	−3.20	−3.87	−4.27	−4.89
$CH_2CHO^{\bullet}$	85.2	−3.52	−6.75	−8.63	−10.19	−11.47	−13.45	−14.92	−17.36
$C^{\bullet}HCHOCH_3$	113.2	6.41	−0.81	−1.16	−1.22	−1.33	−1.+0	−2.61	−3.98
$CH_2C^{\bullet}OCH_3$	109.9	10.93	−1.50	−3.01	−3.84	−4.27	−4.67	−4.90	−5.39
$CH_2CHOC^{\bullet}H_2$	98.9	10.13	−1.12	−1.70	−2.09	−2.41	−3.03	−3.59	−4.65

[a] ΔH°_{298} in kcal mol^{-1}; ΔS°_{298} and $C_p(T)$ in cal mol^{-1} K^{-1}. With the exception of enthalpy, these represent values that are added to the corresponding value of the parent molecule to result in the entropy and heat capacity of the radical. The values do not include effects of symmetry or electron degeneracy. Enthalpy increments correspond to the respective C−H and O−H bond dissociation energies.

TABLE 10: Literature and Calculated Group Additivity Values for Vinyl Alcohol and Methyl Vinyl Ether[a]

group	$\Delta_f H^\circ_{298}$	S°_{298}	$C_{p,300}$	$C_{p,400}$	$C_{p,500}$	$C_{p,600}$	$C_{p,800}$	$C_{p,1000}$	$C_{p,1500}$
				literature:					
C_D/H_2[39]	6.26	27.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19
$C/H_3/O$[37]	−10.08	30.41	6.19	7.84	9.40	10.79	13.03	14.77	17.58
$C_D/H/O$[10]	8.60	8.00	4.20	5.00	5.80	6.50	7.60	8.40	9.60
				calculated:					
$O/C_D/H$	−44.84	26.15	5.51	6.77	7.41	7.72	7.93	8.03	8.36
$O/C_D/H$ anti[b]	1.10	−0.03	0.02	0.03	0.03	0.02	0.01	0.00	−0.01
$O/C/C_D$	−30.36	−0.58	4.31	5.19	5.51	5.54	5.39	5.13	4.68
$O/C/C_D$ anti[b]	1.67	6.11	−0.35	−0.58	−0.64	−0.6	−0.47	−0.34	−0.17

[a] Enthalpies in kcal mol^{-1}, entropies and heat capacities in cal mol^{-1} K^{-1}. [b] Anti group = values added to syn group to obtain values of anti conformer.

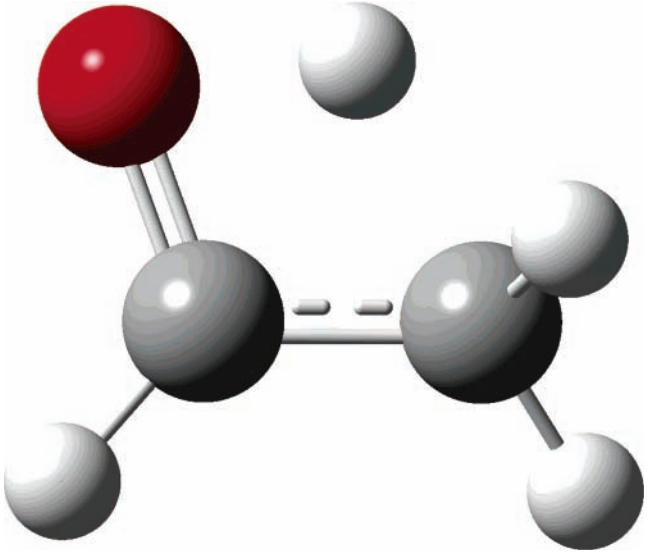

Figure 4. Transition-state structure for the interconversion of vinyl alcohol and acetaldehyde at the QCISD/6-311G(d,p) level of theory.

and Bozzelli.[10] The enthalpy value of the $O/C/C_D$ group (−30.36 kcal mol^{-1}) agrees well with the values of Cohen[38] and Benson[37] (−30.5 kcal mol^{-1}).

Keto−Enol Tautomerism. Vinyl alcohol will readily undergo keto−enol tautomerization to yield acetaldehyde. Keto−enol tautomerizations are important reactions in organic chemistry, and the interconversion of vinyl alcohol and acetaldehyde represents the simplest such reaction. It is also suggested that this tautomerization is a major decomposition pathway for enols during combustion, following their formation via the reaction of alkenes with OH.[2] Using our calculated enthalpy for *syn*-vinyl alcohol and the experimental enthalpy of acetaldehyde (−39.70 kcal mol^{-1})[40] we calculate the enthalpy of this tautomerization reaction to be −9.7 kcal mol^{-1}. Comparatively, the tautomerization enthalpy of 1-propenol ($\Delta_f H^\circ_{298} = -41.6$ kcal mol^{-1})[41] to propanal ($\Delta_f H^\circ_{298} = -45.09$ kcal mol^{-1})[42] is −3.5 kcal mol^{-1}, while the tautomerization enthalpy of 2-propenol ($\Delta_f H^\circ_{298} = -42.1$ kcal mol^{-1})[5] to acetone ($\Delta_f H^\circ_{298} = -52.23$ kcal mol^{-1})[42] is −10.1 kcal mol^{-1}. In all cases the keto form is more stable than the enol form.

Methyl vinyl ether will isomerize to form the more stable propanal by transfer of the methyl group. Utilizing an experimental enthalpy of −45.09 kcal mol^{-1} for propanal,[42] we calculate the *syn*-methyl vinyl ether to propanal reaction enthalpy as −19.5 kcal mol^{-1}. Methyl vinyl ether is therefore found to be considerably higher in enthalpy than vinyl alcohol, with respect to their aldehyde isomers, although in both cases the saturated aldehyde form is more stable than the unsaturated enol/ether form.

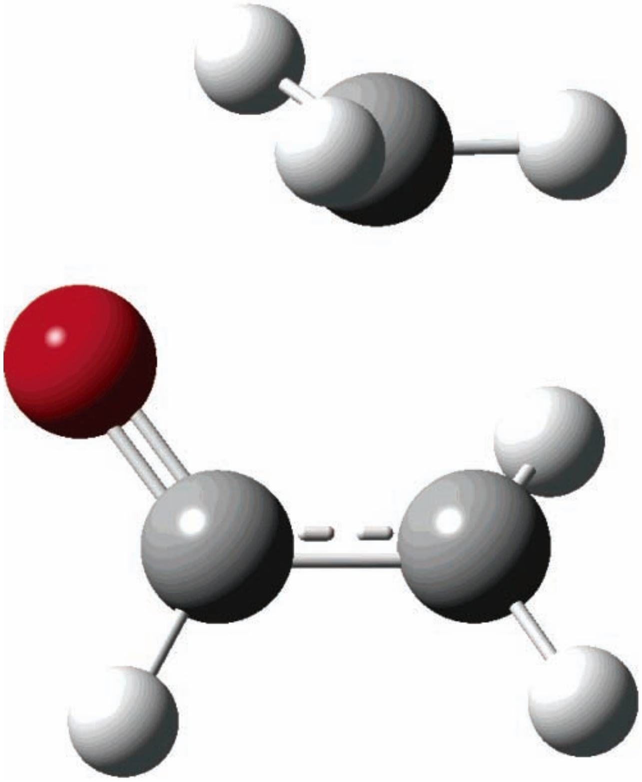

Figure 5. Transition-state structure for the interconversion of methyl vinyl ether and propanal at the QCISD/6-311G(d,p) level of theory.

The transition state structure for the keto−enol tautomerization of vinyl alcohol at the QCISD/6-311G(d,p) level of theory (from CBS-APNO calculations) is depicted in Figure 4. The calculated rate parameters for the forward and reverse reaction at the CBS-APNO level are provided in Table 11, where the pre-exponential (A) factor is determined as a function of temperature in the form of eq 3. The parameters A' and n were determined using entropy and heat capacity (300−2000 K) values. The CBS-APNO method provides an activation energy for this reaction of 55.9 kcal mol^{-1}. The activation barrier to the keto−enol tautomerization of vinyl alcohol is known to be greater in the gas phase than in aqueous media because of the presence of solvent catalysis in solution.[43] The transition state for the interconversion of methyl vinyl ether and propanal at the QCISD/6-311G(d,p) level of theory is provided in Figure 5, with the rate parameters included in Table 11. At the CBS-APNO level, the activation energy is calculated as 72.8 kcal mol^{-1}. Accordingly, the isomerization of methyl vinyl ether to propanal is probably less important than the tautomerization of vinyl alcohol to acetaldehyde because of the higher activation energy barrier for the methyl vinyl ether reaction.

$$A(T) = A'T^n \qquad (3)$$

TABLE 11: Kinetic Parameters for the Conversion of Vinyl Alcohol to Acetaldehyde and Methyl Vinyl Ether to Propanal, Calculated at the CBS-APNO Level of Theory[a]

	E_a (kcal mol^{-1})	A'	n	A (298 K) (s^{-1})
vinyl alcohol → acetaldehyde	55.9	8.59×10^{11}	0.318	5.25×10^{12}
acetaldehyde → vinyl alcohol	66.3	1.05×10^{9}	1.202	9.87×10^{11}
methyl vinyl ether → propanal	72.8	1.36×10^{10}	0.879	2.03×10^{12}
propanal → methyl vinyl ether	92.3	7.67×10^{8}	1.366	1.85×10^{12}

[a] E_a value is at 298 K.

TABLE 12: Comparison of Bond Dissociation Energies (BDEs) in Vinyl and Benzene Molecules

	BDE (kcal mol^{-1})			
bond	vinyl alcohol	methyl vinyl ether	phenol	methyl phenyl ether
O−H	85.2	N/A	89.0	N/A
C−OH	110.3	N/A	113	N/A
O−CH_3	N/A	63.5	N/A	66
C−OCH_3	N/A	100.6	N/A	103.4

Comparison of Bond Energies in Vinyl and Aromatic Systems. Bonds in vinyl compounds are known to provide good models for bonds in analogous aromatic compounds. The similarity in these bonds is useful in developing isodesmic work reactions for accurate thermochemical calculations. Furthermore, small vinyl compounds can replace large aromatic molecules in time-saving preliminary ab initio calculations. In this study we calculated the BDE of the vinyl alcohol O−H bond as 85.2 kcal mol^{-1}. This value is very similar to the O−H BDE for phenol, which is 89.0 kcal mol^{-1}.[44] In comparison, BDEs for aliphatic alcohols are of the order of 105 kcal mol^{-1}. The O−H bonds in vinyl alcohol and phenol are around 20 kcal mol^{-1} weaker than those in aliphatic alcohols because of resonance stabilization of the respective phenoxy and vinoxy radicals. The structure of the vinoxy radical resembles the formyl methyl radical ($C^{\bullet}H_2CH{=}O$) more closely, whereas the phenoxy radical structure is closer to the 2,5-cyclohexadienyl-1-one radical. This is a result of the C=O π bond being considerably stronger than the C=C π bond.

Our study of vinyl alcohol and methyl vinyl ether affords further comparisons with phenol. The BDE of the phenol Ph−OH bond is 113 kcal mol^{-1} (calculated using formation enthalpies of -23.03 ± 0.14 kcal mol^{-1} for phenol[45] and 81 ± 2 kcal mol^{-1} for the phenyl radical).[46] We have determined the vinyl alcohol C−OH BDE as 110.2 kcal mol^{-1}, which again shows good agreement with the corresponding benzene bond energy. The O−CH_3 BDE in methyl vinyl ether is 63.5 kcal mol^{-1}, and the O−CH_3 BDE in methyl phenyl ether is 66 kcal mol^{-1}, calculated using enthalpies of formation of -18.33 ± 0.22 kcal mol^{-1} for methyl phenyl ether[40] and 13 ± 1 kcal mol^{-1} for the phenoxy radical.[46] Finally, the Ph−OCH_3 BDE can be determined as 103.4 kcal mol^{-1} from the enthalpies of formation of methyl phenyl ether and the methoxy radical (4.1 ± 1 kcal mol^{-1}).[46] This BDE compares favorably with the C−OCH_3 BDE in methyl vinyl ether (100.6 kcal mol^{-1}). BDEs for vinyl and benzene systems are compared in Table 12, and we find that in all cases the bonds in the benzene compounds are slightly stronger than those in the vinyl compounds; on average, these bonds are stronger by 3 kcal mol^{-1}. We find that the C−H, C−O, and O−H bond energies in vinyl alcohol and methyl vinyl ether are similar to the corresponding bond energies in phenol and methyl phenyl ether. We also find that the trends with bond energy change with OH and OCH_3 substitution on ethylene and benzene are very similar.

Summary

Thermodynamic properties of vinyl alcohol and methyl vinyl ether and related radicals corresponding to loss of a H atom from a carbon are calculated using density functional and ab initio methods with isodesmic reaction schemes for cancellation of errors. Standard enthalpies of formation, $\Delta_f H^{\circ}_{298}$, are determined from B3LYP/6-31G(d,p), CBS-Q, CBS-APNO, and G3 calculations. Entropies (S°_{298}) and heat capacity ($C_p(T)$) are determined with B3LYP/6-31G(d,p) optimized geometries and frequencies. Hindered internal rotation contributions to entropy and heat capacity are calculated by intramolecular torsion

TABLE A1: Calculated Enthalpies of Formation ($\Delta_f H^{\circ}$, kcal mol^{-1}) with Four Theoretical Methods for syn and anti Conformations of Vinyl Alcohol, Methyl Vinyl Ether, and the Corresponding Radicals

		$\Delta_f H^{\circ}$ (kcal mol^{-1})							
		B3LYP		CBS-Q		CBS-APNO		G3	
species	isodesmic reaction	syn	anti	syn	anti	syn	anti	syn	anti
$CH_2{=}CHOH$	1	−32.02	−30.10	−29.77	−28.73	−29.97	−28.83	−29.73	−28.63
$CH_2{=}CHOH$	2	−32.82	−30.90	−29.90	−28.86	−30.23	−29.09	−29.82	−28.72
$CH_2{=}CHOH$	3	−31.81	−29.89	−30.05	−29.01	−30.27	−29.14	−30.05	−28.95
$CH_2{=}CHOH$	average	−32.22	−30.30	−29.91	−28.87	−30.16	−29.02	−29.87	−28.77
$C^{\bullet}H{=}CHOH$	1	29.14	32.40	31.47	33.61	31.20	33.46	31.46	33.66
$C^{\bullet}H{=}CHOH$	2	28.34	31.59	31.34	33.48	30.93	33.20	31.36	33.56
$C^{\bullet}H{=}CHOH$	average	28.74	32.00	31.41	33.55	31.07	33.33	31.41	33.61
$CH_2{=}C^{\bullet}OH$	1	N/A	24.31	N/A	27.14	N/A	26.69	N/A	27.56
$CH_2{=}C^{\bullet}OH$	2	N/A	23.50	N/A	27.01	N/A	26.42	N/A	27.46
$CH_2{=}C^{\bullet}OH$	average	N/A	23.91	N/A	27.08	N/A	26.56	N/A	27.51
$CH_2{=}CHOCH_3$	1	−26.33	−24.41	−25.72	−24.16	−25.81	−24.03	−25.78	−24.13
$CH_2{=}CHOCH_3$	2	−25.80	−23.87	−25.31	−23.75	−25.48	−23.70	−25.36	−23.70
$CH_2{=}CHOCH_3$	average	−26.07	−24.14	−25.52	−23.96	−25.65	−23.87	−25.57	−23.92
$C^{\bullet}H{=}CHOCH_3$	1	33.94	37.66	35.95	39.53	35.58	39.36	35.85	39.56
$C^{\bullet}H{=}CHOCH_3$	2	34.42	38.14	35.43	39.01	35.21	38.99	35.35	39.06
$C^{\bullet}H{=}CHOCH_3$	average	34.18	37.90	35.69	39.27	35.40	39.18	35.60	39.31
$CH_2{=}C^{\bullet}OCH_3$	1	30.87	29.55	33.84	32.60	33.29	31.89	34.14	32.82
$CH_2{=}C^{\bullet}OCH_3$	2	31.34	30.03	33.32	32.08	32.93	31.53	33.64	32.32
$CH_2{=}C^{\bullet}OCH_3$	average	31.11	29.79	33.58	32.34	33.11	31.71	33.89	32.57
$CH_2{=}CHOC^{\bullet}H_2$	1	18.96	19.07	21.86	22.97	20.84	21.35	21.73	22.49
$CH_2{=}CHOC^{\bullet}H_2$	2	19.43	19.55	21.34	22.45	20.47	20.98	21.23	21.99
$CH_2{=}CHOC^{\bullet}H_2$	average	19.20	19.31	21.60	22.71	20.66	21.17	21.48	22.24

TABLE A2: Calculated Entropies (S°_{298}) and Heat Capacities ($C_p(T)$) for Vinyl Alcohol and Methyl Vinyl Ether Species, from B3LYP/6-31G(d,p) Geometries, Frequencies, Moments of Inertia, and Internal Rotors[a]

species		S°_{298}	$C_{p,300}$	$C_{p,400}$	$C_{p,500}$	$C_{p,600}$	$C_{p,800}$	$C_{p,1000}$	$C_{p,1500}$
syn-CH_2CHOH	TVR	60.31	12.12	15.00	17.56	19.71	23.03	25.51	29.53
σ (symmetry) = 2	IR	1.45	2.69	3.13	3.16	3.01	2.57	2.19	1.62
	total	61.76	14.81	18.13	20.72	22.72	25.60	27.70	31.15
syn-$C^{\bullet}HCHOH$	TVR	62.89	12.24	14.55	16.48	18.06	20.45	22.23	25.15
σ (symmetry) = 1	IR	1.07	1.96	2.70	3.19	3.37	3.16	2.72	1.91
	total	63.96	14.20	17.25	19.67	21.43	23.61	24.95	27.06
anti-CH_2CHOH	TVR	60.28	12.14	15.03	17.59	19.73	23.04	25.51	29.52
σ (symmetry) = 2	IR	1.45	2.69	3.13	3.16	3.01	2.57	2.19	1.62
	total	61.73	14.83	18.16	20.75	22.74	25.61	27.70	31.14
anti-$C^{\bullet}HCHOH$	TVR	62.80	12.26	14.57	16.50	18.07	20.46	22.24	25.15
σ (symmetry) = 1	IR	1.07	1.96	2.70	3.19	3.37	3.16	2.72	1.91
	total	63.87	14.22	17.27	19.69	21.44	23.62	24.96	27.06
anti-$CH_2C^{\bullet}OH$	TVR	59.85	11.95	14.22	16.18	17.79	20.26	22.10	25.11
σ (symmetry) = 2	IR	3.26	2.16	2.08	1.90	1.73	1.47	1.32	1.15
	total	63.11	14.11	16.30	18.08	19.52	21.73	23.42	26.26
syn-CH_2CHOCH_3	TVR	62.48	14.35	18.68	22.74	26.25	31.81	35.94	42.43
σ (symmetry) = 6	IR 1 ($C-OCH_3$)	3.68	3.44	3.68	3.53	3.24	2.66	2.18	1.38
	IR 2($O-CH_3$)	4.42	2.01	2.03	1.95	1.84	1.62	1.46	1.24
	total	65.44	19.80	24.39	28.22	31.33	36.09	39.57	45.05
syn-$C^{\bullet}HCHOCH_3$	TVR	64.06	14.54	18.29	21.72	24.65	29.27	32.71	38.08
σ (symmetry) = 3	IR 1 ($C-OCH_3$)	3.02	2.36	3.00	3.53	3.75	3.53	2.98	1.87
	IR 2($O-CH_3$)	4.77	2.08	1.94	1.76	1.60	1.40	1.27	1.13
	total	71.85	18.99	23.23	27.00	30.01	34.19	36.96	41.07
syn-$CH_2C^{\bullet}OCH_3$	TVR	64.29	14.53	18.22	21.62	24.55	29.18	32.63	38.04
σ (symmetry) = 6	IR 1 ($C-OCH_3$)	5.99	2.48	2.08	1.78	1.57	1.31	1.16	0.88
	IR 2($O-CH_3$)	4.42	2.01	2.03	1.95	1.84	1.62	1.46	1.24
	total	74.69	19.01	22.33	25.35	27.96	32.11	35.24	40.15
syn-$CH_2CHOC^{\bullet}H_2$	TVR	64.57	14.79	18.79	22.27	25.16	29.60	32.87	38.07
σ (symmetry) = 4	IR 1 ($C-OC^{\bullet}H_2$)	5.37	1.92	1.99	2.01	1.98	1.83	1.64	1.21
	IR 2($O-C^{\bullet}H_2$)	5.63	1.97	1.91	1.85	1.79	1.63	1.48	1.12
	total	75.56	18.67	22.69	26.13	28.93	33.06	35.98	40.39
anti-CH_2CHOCH_3	TVR	62.41	14.54	18.82	22.84	26.33	31.87	36.00	42.48
σ (symmetry) = 6	IR 1 ($C-OCH_3$)	3.68	3.44	3.68	3.53	3.24	2.66	2.18	1.38
	IR 2($O-CH_3$)	5.46	1.47	1.31	1.21	1.15	1.09	1.06	1.02
	total	71.55	19.45	23.81	27.58	30.73	35.62	39.23	44.88
anti-$C^{\bullet}HCHOCH_3$	TVR	65.06	14.64	18.36	21.76	24.68	29.29	32.74	38.11
σ (symmetry) = 3	IR 1 ($C-OCH_3$)	3.02	2.36	3.00	3.53	3.75	3.53	2.98	1.87
	IR 2($O-CH_3$)	5.39	1.52	1.35	1.24	1.18	1.10	1.07	1.03
	total	73.47	18.52	22.71	26.53	29.61	33.92	36.78	41.00
anti-$CH_2C^{\bullet}OCH_3$	TVR	63.70	14.28	17.96	21.38	24.34	29.03	32.52	37.98
σ (symmetry) = 6	IR 1 ($C-OCH_3$)	5.99	2.48	2.08	1.78	1.57	1.31	1.16	0.88
	IR 2($O-CH_3$)	6.68	1.54	1.34	1.23	1.16	1.07	1.00	0.81
	total	76.36	18.30	21.38	24.38	27.06	31.42	34.68	39.66
anti-$CH_2CHOC^{\bullet}H_2$	TVR	64.62	15.15	19.05	22.45	25.29	29.68	32.93	38.11
σ (symmetry) = 4	IR 1 ($C-OC^{\bullet}H_2$)	5.37	1.92	1.99	2.01	1.98	1.83	1.64	1.21
	IR 2($O-C^{\bullet}H_2$)	5.74	1.66	1.69	1.71	1.70	1.64	1.52	1.16
	total	75.73	18.73	22.73	26.17	28.98	33.15	36.08	40.48

[a] All values in cal mol^{-1} K^{-1}.

potential curves at the B3LYP/6-31G(d,p) level, with an entropy correction for mixing of rotational conformers.

The isomerization reactions of vinyl alcohol and methyl vinyl ether to form acetaldehyde and propanal, respectively, are exothermic, with reaction enthalpies of −9.7 and −19.5 kcal mol^{-1}. The activation energies for these tautomerization reactions were calculated as 54.8 kcal mol^{-1} for vinyl alcohol and 72.8 kcal mol^{-1} for methyl vinyl ether, at the CBS-APNO level of theory. Bond dissociation energies (BDEs) were calculated for several bonds in vinyl alcohol and methyl vinyl ether, and compared to corresponding BDEs for aromatic systems. In all cases the BDEs were found to be of similar magnitude, with the bonds in the corresponding aromatic systems being stronger by around 3 kcal mol^{-1}, on average. Vinyl alcohol and methyl vinyl ether are shown to be very similar in bond energies to phenol and methyl phenyl ether. The weakest bonds in vinyl alcohol and methyl vinyl ether are the $CH_2{=}CHO-H$ and $CH_2{=}CHO-CH_3$ bonds, respectively. Cleavage of these two bonds results in formation of the formyl methyl radical, which is known to be an important intermediate in atmospheric and combustion chemistry.

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Supporting Information Available: Geometries, moments of inertia, and vibrational frequencies for all species at the B3LYP/6-31+G(d) level of theory; internal rotor potential energy profiles; experimental enthalpies of formation used to calculate enthalpies of reaction for vinyl alcohol formation; and optimized C−C bond lengths from a relaxed potential energy scan of the C−O bond in the CH_2CHO radical. This material is available free of charge via the Internet at http://pubs.acs.org.

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