J. Phys. Chem. A **2005,** *109,* 2233−2253

Thermochemical Properties, Rotation Barriers, and Group Additivity for Unsaturated Oxygenated Hydrocarbons and Radicals Resulting from Reaction of Vinyl and Phenyl Radical Systems with O_2

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Received: August 17, 2004; In Final Form: December 8, 2004

Oxidation of unsaturated and aromatic hydrocarbons in atmospheric and combustion processes results in formation of linear and cyclic unsaturated, oxygenated-hydrocarbon intermediates. The thermochemical parameters $\Delta_f H^\circ_{298}$, S°_{298}, and $C_{pf298}(T)$ for these intermediates are needed to understand their stability and reaction paths in further oxidation. These properties are not available for a majority of these unsaturated oxy-hydrocarbons and their corresponding radicals, even via group additivity methods. Enthalpy, entropy, and heat capacity of a series of 40 oxygenated and non-oxygenated molecules, or radicals corresponding to hydrogen atom loss from the parent stable molecules are determined in this study. Enthalpy ($\Delta_f H^\circ_{298}$ in kcal mol^{-1}) is derived from the density function calculations at the B3LYP/6-311g(d,p) calculated enthalpy of reaction ($\Delta H^\circ_{\mathrm{rxn},298}$) and by use of isodesmic (work) reactions. Estimation of error in enthalpy ($\Delta_f H^\circ_{298}$), from use of computational chemistry coupled with work reactions analysis, is presented using comparisons between the calculated and literature enthalpies of reaction. Entropies (S°_{298}) and heat capacities ($C_{pf298}(T)$) were calculated using the B3LYP/6-311G(d,p) determined frequencies and geometries. Potential barriers for internal rotors in each molecule were determined and used (in place of torsion frequencies) to calculate contributions to S and $C_p(T)$ from the hindered rotors. Twenty-six groups for use in group additivity (GA) are also developed.

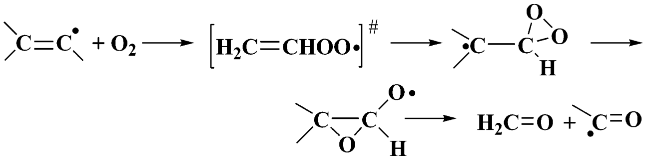
Introduction

The initial steps in reaction of aromatic, poly-aromatic and other cyclic and linear unsaturated hydrocarbons in the atmosphere or in combustion involve radical formation and then reaction with molecular oxygen. The subsequent reactions of these peroxy radicals result in unsaturated linear or cyclic, oxygenated or multi-oxygenated hydrocarbon intermediates. Thermochemistry for these unsaturated−oxygenated species is needed to evaluate their stability and likely reaction paths in the environment, in combustion and in other thermal and oxidative processes.

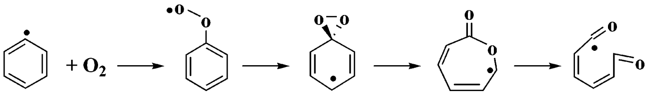
Carpenter[1−3] has shown that the important reaction of vinyl radical with O_2 has a low barrier to formation of a dioxetane formyl radical, which then undergoes isomeration to oxetane−oxy radical, then to $C^\bullet H_2OCH{=}O$ and finally to $CH_2O + HC^\bullet{=}O$ (see Scheme 1).

Carpenter has also indicated a similar low barrier in phenyl leading to ring opening through a 2-oxepinoxy radical intermediate, where ring opening has a low barrier (ca. 20 kcal mol^{-1}), and results in the formation of an unsaturated dicarbonyl radical, as shown in Scheme 2.

SCHEME 1



SCHEME 2



Though one may readily visualize a series of β scission reactions (unzipping of the above ring opening product Y($O{=}COC^\bullet HCH{=}CHCH{=}CH-$) to yield $CO + HC^\bullet{=}O + 2CH{\equiv}CH$, the reactions of substituted aromatics and the reactions of stabilized, unsaturated intermediates with O_2 and the radical pool are more complex. Figure 1 illustrates one such reaction path for an unsaturated oxy-aromatic species, a benzofuran carbonyl radical. We estimate that this radical is formed by reaction of a phenyl radical in dibenzofuran with oxygen.

The thermochemical parameters or groups for use in group additivity (GA) estimations[4,5] are not available for a many of the unsaturated, oxy-hydrocarbon intermediates in this reaction path.

There are some data on unsaturated oxygen species in the literature. The research group of Turecek[6] has worked on enthalpy groups for vinyl alcohols in addition to unsaturated

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10.1021/jp046285+ CCC: $30.25

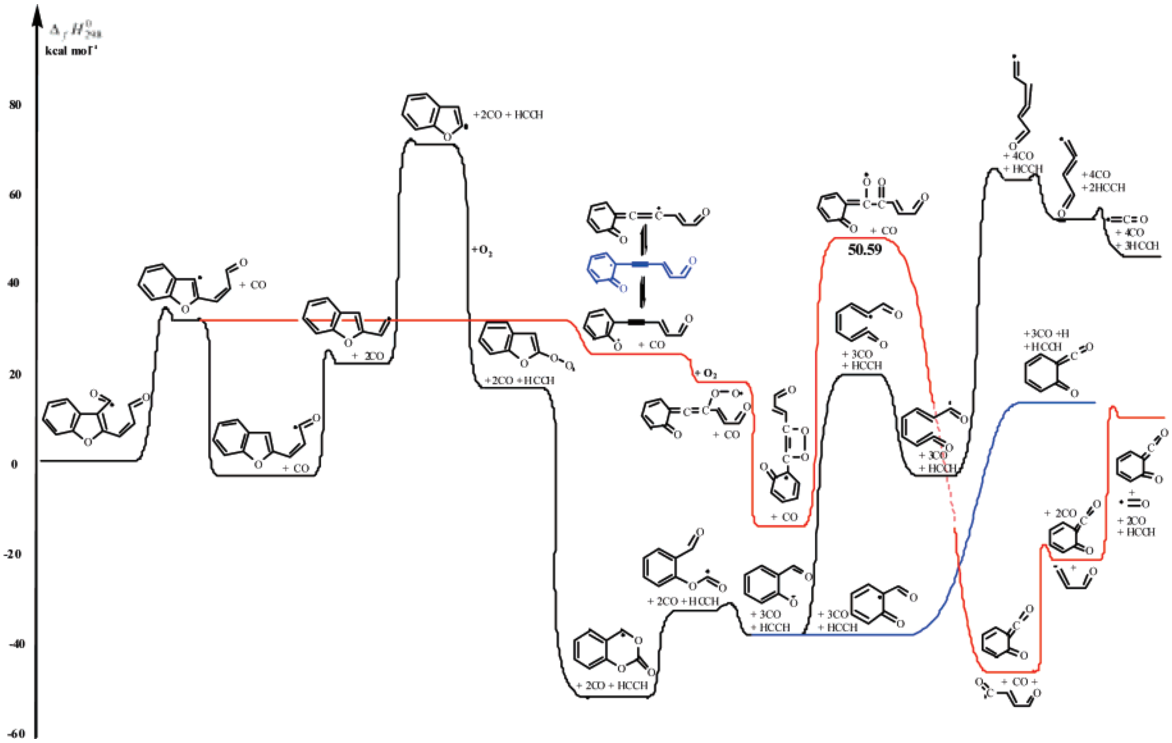


Figure 1. Potential energy diagram of the destruction (oxidation) of dibenzofuran radical.

nitrogen and sulfur species. Sumathi and Green have recently observed the thermochemical properties of sp^3 and sp^2 carbon groups with multiple bonds to unsaturated carbon groups in their modeling of hydrocarbon combustion and developed GA values using G2 and CBS-Q calculations.[7] They compare the data from the two calculation levels, selected G2 enthalpies as their recommended values. In a second study they reported a consistent set of 12 Benson groups together with 20 hydrogen bond increment (HBI) group values for saturated hydrocarbons and oxygenated hydrocarbons.[8] Recently Janoschek and Rossi[9] have reported thermochemical properties of a set of 32 selected oxygenated hydrocarbon free radicals ($C_1$$-$$C_6$).

This study estimates thermochemical properties for a number of unsaturated oxy-hydrocarbons using density functional calculations (DFT) combined with isodesmic work reactions to determine enthalpy of formation, entropy, and heat capacity values. Enthalpy values for molecules used as reference species in the work reactions are evaluated from the literature when available, but sometimes a reference molecule enthalpy value is determined from our calculation methods. A method is also presented to estimate the error from the calculations used in the work reaction analysis of $\Delta_f H^\circ_{298}$.

The molecules in this study are selected to contain a specific group needed in the unsaturated oxygenated intermediates resulting from aromatic species decomposition. We develop the thermochemical properties for the molecules containing the target groups and then use the thermochemistry along known groups to calculate new groups for use in group additivity on large molecules system, where direct calculation techniques are not as feasible.

Values of group contributions to enthalpies, $\Delta_f H^\circ_{298}$, entropies, S°_{298} and heat capacities $C_{pf298}(T)$ are developed for some 26 molecules and 14 radical species in this class of molecules.

Methodology

All calculations are performed using the Gaussian 98 program suite.[10−12] Structural parameters for all molecules are optimized using density functional calculations at the B3LYP/6-311G(d,p) level of theory. Harmonic vibration frequencies and zero-point vibration energies (ZPVE) are computed at the same level. Total electronic energies are from the optimized geometry.[13−15] The B3LYP density functional theory[16,17] (DFT) is a Hartree−Fock-based methodology. In density functional theory, the exact exchange (HF) for a single determinant is replaced by a more general expression, the exchange-correlation functional, which includes terms accounting for both exchange energy and the electron correlation, which is omitted from Hartree−Fock theory.

Appendix I includes comparison and reference data that illustrate B3LYP/6-11G(d,p) calculations combined with work reactions provide enthalpy of formation values on oxygenated hydrocarbons with good accuracy.

A computer code, SMCPS (Statistical Mechanics for Heat Capacity and Entropy), is used to calculate $H - H_0$, C_p, S, and zero-point vibrational energy (ZPVE) of molecular species from computation chemistry results. SMCPS[18] calculates the contributions from the mass, structure (moments of inertia), and vibration frequencies for translation, external rotation, and vibration contributions to S°_{298} and $C_{pf298}(T)$. The method of calculation is based on principles of statistical mechanics. Contributions from symmetry, number of optical isomers, and unpaired electrons are included.

The SMCPS code is coupled to the Rotator[18−20] code, which is used for determining enthalpy, entropy and heat capacity contributions from internal rotors.

1. Enthalpy of Formation $\Delta_f H^\circ_{298}$. Total energies at 298 K are calculated for each species (given in Supporting Information, Table SM1) to obtain the enthalpy change across the work reactions. The total energies were corrected by zero-point vibration energies (ZPVE), which are scaled by 0.97, as recommended by Scott and Radom.[21] Thermal correction, 0−298.15 K, was calculated to estimate $\Delta_f H^\circ_{298}$ at 298.15 K.[22] Standard enthalpies of formation ($\Delta_f H^\circ_{298}$), for the oxygenated and non-oxygenated hydrocarbons were calculated, using the isodesmic work reactions described below.

2. Entropy (S°_{298}), Heat Capacities $C_{pf298}(T)$, and Hindered Rotation Contribution to Thermodynamic Parameters. Entropies S°_{298} and heat capacities $C_{pf298}(T)$ are calculated using the harmonic-oscillator approximation for vibrations, on the basis of frequencies and moments of inertia of the optimized B3LYP/6-311G(d,p) structures. Torsional frequencies are not included in the contributions to entropy and heat capacities; instead, they are replaced with values from a separate analysis on each internal rotor analysis.

Potential barriers for internal rotations about the C—C, C—OH, C—O, C—CH=O, C_d—C, C_d—C_d, C_d—O, C_d—OH, C_d—CH=O, C_b—C, C_b—C_d, C_b—O, C_b—CH=O, and O—CH(=O) bonds in the stable molecules are determined at the B3LYP/6-31G(d,p) calculation level. The same level calculations were also performed for radicals about $RC^\bullet$—OH, C—$C^\bullet$=O, $RC^\bullet$—C=O, C—C($O^\bullet$)=O, C_d—$C^\bullet$R, $RC_d^\bullet$—CH=O, C_d—$C^\bullet$=O, C_b—$C^\bullet$=O, and RO—$C^\bullet$(=O). A technique for the calculation of the thermodynamic functions from hindered rotations with arbitrary potentials is used to calculate the hindered internal rotor contributions to S°_{298} and $C_{pf298}(T)$.[23−25] This method employs expansion of the hindrance potential in the Fourier series, calculation of the Hamiltonian matrix on the basis of wave functions of free internal rotation, and subsequent calculation of energy levels by direct diagonalization of the Hamiltonian matrix. In this work, a truncated Fourier series is used to represent the torsional potential calculated at the discrete torsional angles.

$$V(\Phi) = a_0 + \sum a_i \cos(i\Phi) + \sum b_i \sin(i\Phi) \qquad \text{(I)}$$

where $i = 1-7$.

The values of the coefficients (a_0, a_i, and a_b) are calculated to provide the minimum and maximum of the torsional potentials with allowance of shift of the theoretical extreme angular positions. Further descriptions of this method to calculate contributions from the internal rotors are reported by Lay et al.[26] A Fortran program, "Rotator" is used for calculation of the energy levels, the partition coefficient, and the corresponding contributions to $S(T)$ and $C_p(T)$. The Rotator program takes into account the entropy of mixing and the optical isomer corrections for systems, where isomers are connected by a hindered rotor.

Contributions to S°_{298} and $C_{pf298}(T)$ from translation, scaled vibration frequencies, and external rotation (TVR) of each species considered in this study are obtained using the rigid-rotor−harmonic-oscillator approximation for the frequencies along with moments of inertia based on the optimized B3LYP/6-311G(d,p) structures. Entropies S°_{298} and heat capacities $C_{pf298}(T)$ are calculated using the SMCPS[18] code (Statistical Mechanics for Heat Capacity and Entropy), which is also used to calculate $H - H_0$ and the zero-point vibration energy (ZPVE) of molecular species. Symmetry, number of optical isomers, and unpaired electrons are included.

Results and Discussions

1. Geometries and Vibration Frequencies. Optimized geometries at the B3LYP/6-311G(d,p) density function calculation level for the oxygenated and non-oxygenated species are listed in Table SM2 of the Supporting Information. Vibration frequencies and moments of inertia for the studied molecules and radicals are listed in Tables SM3 and SM4 of the Supporting Information.

2. Enthalpies of formation ($\Delta_f H^\circ_{298}$) Evaluated enthalpy values for standard reference species used in the work reactions are listed in Table 1 along with literature references. The prop-2-enoic acid radical CH_2=CHC($O^\bullet$)=O is used for illustration with the isodesmic reactions:

$$R'{-}C(O^\bullet){=}O + R{-}OH \rightarrow R'{-}C(OH){=}O + RO^\bullet$$

where R ≡ CH_3−, CH_3CH_2−, and HC(=O)− and R′ ≡ CH_2=CH−.

2-Propenyl radical CH_2=$C^\bullet CH_3$ is estimated according to the reactions below:

$$CH_2{=}C{\cdot}CH_3 + R \rightarrow CH_2{=}CHCH_3 + R^\bullet$$

where R ≡ CH_2=CH_2 and C_6H_6.

2*H*-Pyran, Y(C_5H_6O), is estimated with the following reactions:

$$Y(C_5H_6O) + CH_4 \rightarrow CH_2{=}CHCH{=}O + CH_3CH{=}CH_2$$

$$Y(C_5H_6O) + CH_4 \rightarrow \text{Furan } (Y(C_4H_4O) + CH_3CH_3)$$

$\Delta_f H^\circ_{298}$ of the target compounds are estimated by using up to five isodesmic reaction schemes for each stable molecule or radical. The density functional energy, *E*, the ZPVE and the thermal correction to 298.15 K are calculated for each molecule and $\Delta H^\circ_{rxn,298}$ calculated. Thermal corrections account for translation, external rotation, and vibrations, and include the torsion frequencies, for all molecules in the work reaction. This provides consistency in the working reaction, as all species in the reaction do not have detailed analysis for the internal rotors. Selection of the work reaction with similar internal rotors on both sides allows for cancellation of this error.

The evaluated literature enthalpy ($\Delta_f H^\circ_{298}$) for each reference species (Table 1) in the reaction along with the calculated $\Delta H^\circ_{rxn,298}$ is then used to calculate $\Delta_f H^\circ_{298}$ of the target species. The isodesmic reactions used to determine $\Delta_f H^\circ_{298}$ and the corresponding $\Delta H^\circ_{rxn,298}$ values for each reaction are illustrated in Table 2 for the linear, unsaturated oxygenated hydrocarbons and in Table 3 for aromatic and related unsaturated oxyhydrocarbons. The isodesmic work reactions for radical species from Tables 2 and 3 corresponding to loss of H atoms from a carbon, carbonyl, or a hydroxy−oxygen site along with the calculated $\Delta_f H^\circ_{298}$ values are listed in Table 4. The first column of Tables 2−4 also lists the target group to be estimated using the enthalpy of the calculated species. Fourteen unsaturated C_2−C_6 species are listed in Table 2; they all contain an oxygenate functionality (alcohol, peroxide, and aldehyde). There is one non-oxygenated species, CH_2=CHCH(CH_3)CH=CH_2, in Table 2. Table 3 lists nine unsaturated oxygenated species; all of which contain a phenyl group.

The several work reaction calculations for each species show good precision, which provides an internal data check.

The calculated data are used to estimate corresponding R—H bond dissociation enthalpies (BDE) at 298 K. The first column of Table 4 lists the BDE group identifying the parent and radical.

Several of our previous papers on thermochemistry of oxygenated hydrocarbons[27−30] show good agreement between enthalpy from density functional calculations on stable molecules and radicals with enthalpies calculated using higher level methods. We have recently compared enthalpy of these oxygenated hydrocarbons and radicals using the G3MP2B3 composite method, with results from B3LYP/6-311g(d,p) density functional

TABLE 1: Enthalpies of Formation for Reference Species Used in Work Reactions

species	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	group additivity	source
CH_4	−17.89 ± 0.07		49
CH_3CH_3	−20.24 ± 0.12	−20.40	50
$CH_2{=}CH_2$	12.55 ± 0.1	12.52	49
$CH_3CH{=}CH_2$	4.88 ± 0.16	4.65	51
$HC{\equiv}CH$	54.19 ± 0.19	53.86	49
$CH_3C{\equiv}CH$	44.32 ± 0.21	44.28	52
$CH{\equiv}CCH_2CH_3$	39.48 ± 0.21	39.55	53
$CH_2{=}CHCH_2CH_2CH_3$	−5.33 ± 0.31	−5.04	54
$CH_2{=}CHCH_2CH{=}CH_2$	25.41 ± 0.31	25.41	55
$CH_2{=}CHCH_2CH_3$	−0.15 ± 0.19	−0.11	49
$CH_2{=}CHCH{=}CH_2$	26 ± 0.19	26	52
$CH_3CH_2CH_3$	−24.82 ± 0.14	−25.33	50
$CH_2{=}CHCH{=}CHCH{=}CH_2$	40.1 ± 0.6	39.48	56
$CH_3CH{=}CHCH_3$	−1.83 ± 0.30	−3.22	53
C_6H_6	19.82 ± 0.12	19.8	57
$C_6H_5CH_3$	11.95 ± 0.15	11.81	53
$C_6H_5CH_2CH_3$	7.12 ± 0.20	6.95	53
$C_6H_5CH{=}CH_2$	35.11 ± 0.24	35.11	58
$Y(C_5H_6)$	31.89	31.89	59
CO	−26.41 ± 0.041		60
$CH_2{=}O$	−27.7		49
$CH_3CH{=}O$	−40.80 ± 0.35	−39.18	61
$CH_3CH_2CH{=}O$	−45.09 ± 0.18	−44.50	49
$CH_2{=}CHC({=}O)OH$	−80.51 ± 0.55	−79.62	62
$CH_3CH_2C({=}O)OH$	−108.4 ± 0.5	−108.6	54
$CH_2(OH)_2$	−91.03		therm
$OHCH{=}O$	−90.5 ± 0.4/−90.49	−90.20	63/64
$CH_3C({=}O)OH$	−103.26	−103.28	54
CH_3OH	−48.08 ± 0.05	−47.9	65
CH_3CH_2OH	−56.23 ± 0.12	−56.2	63
CH_3OCH_3	−43.99 ± 0.12	−43.2	66
$CH_3CH_2OCH_3$	−51.73 ± 0.16	−51.5	63
$CH_3OCH{=}O$	−84.97/−83.39 ± 1.19	−84.29	67/this work
$CH_2{=}CHCH_2OH$	−29.55 ± 0.35	−29.81	68
$CH_2{=}C(CH_3)OH$	−42.1	−38	69
$CH_2{=}C(OH)CH{=}CH_2$	−18 ± 1	-18.04	70
$CH_2{=}CHOH$	−29.8 ± 2.0	−31.44	71
C_6H_5OH	−23.03 ± 0.14	−22.8	72
$C_6H_5CH_2OH$	−22.6 ± 0.72	−22.65	73
$C_6H_5OCH_3$	−17.27 ±0.93		63
$C_6H_5OCH{=}O$	−51.55 ± 0.74/−51.49 ± 0.26		74/this work
furan	−8.29		75
furan−$CH{=}O$	−36.1	36.89	76
$Y(C_5H_6O)$	−1.37 ± 0.23	−1.6	this work
$CH_3^\bullet$	34.82 ± 0.2		49
$CH_3CH_2^\bullet$	28.4 ± 0.5	28.6	77
$CH_2{=}CH^\bullet$	71.0 ± 1.0	71.62	77
$CH_2{=}CHCH_2^\bullet$	40.9 ± 0.7	40.75	77
$CH_2{=}C^\bullet CH_3$	58.42 ± 0.16	61.55	this work
$C_6H_5^\bullet$	81 ± 2		77
$HC{\equiv}C^\bullet$	133.0 ± 2.0		77
$CH_3O^\bullet$	4.1 ± 1.0		77
$CH_3C^\bullet{=}O$	−2.9 ± 0.7	−2.13	77
$CH_2{=}CHO^\bullet$	4.44 ± 0.31	4.46	30
$CH_2^\bullet OH$	−2 ± 1		77
$CH^\bullet{=}O$	10.40		49
$CH_2^\bullet CH{=}O$	3.52 ± 0.38	4.47	27
$CH_2{=}CHC(O^\bullet){=}O$	−22.47	−21.71	this work
$Y(C_5H_5^\bullet)$	62	61.59	78

calculated values.[31] The result for 27 oxygenated and non-oxygenated stable species and 12 radicals show a deviation between G3MP2B3 and B3LYP methods under ±0.5 kcal mol^{-1} for nine species, eighteen species differ by less than ±1 kcal mol^{-1}, and eleven species differ by about 1.5 kcal mol^{-1}. The eleven radicals derived from the above-oxygenated hydrocarbons also show good agreement between G3MP2B3 and B3LYP methods.

Error Analysis. We estimate error limits on the target $\Delta_f H^\circ_{298}$ by considering the errors reported for the reference species in the work reactions plus the error due to the calculation method. For the reference species we add the absolute value of the reported errors. We choose not to take the square root of the sum of squared errors, because these reported errors may not include unknown and non random errors.

The error resulting from the B3LYP/6-311g(d,p) work reaction computation method, where the total energy includes zero-point vibration energy (ZPVE) and the thermal energy, is estimated by comparing the calculated enthalpy of reaction for a series of work reactions with $\Delta H^\circ_{rxn,298}$ from accepted literature data. The reactions are chosen to be representative of species in this study. The enthalpies ($\Delta H^\circ_{rxn,298}$) for a series of 27 work reactions, where each species in the reaction has a literature value, are determined and compared to the experi-

TABLE 2: Calculated $\Delta_f H^\circ_{298}$ for Linear Species in kcal mol^{-1} and Reference Reactions

groups to be calculated	reaction series	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	error limit[a]
C/CD/CO/CO/H	$\boldsymbol{CH_2{=}CHCH(CH{=}O)CH{=}O} + CH_3CH_3 \rightarrow CO + CH_2{=}O + CH_2{=}CHCH_2CH_2CH_3$	−40.38	± 2.14
	$\boldsymbol{CH_2{=}CHCH(CH{=}O)CH{=}O} + CH_3CH_3 \rightarrow 2CH_2{=}O + CH_2{=}CHCH_2CH{=}CH_2$	−40.08	± 2.1
	$\boldsymbol{CH_2{=}CHCH(CH{=}O)CH{=}O} + CH_4 \rightarrow CO + CH_2{=}O\ CH_2{=}CHCH_2CH_3$	−38.93	± 1.97
	$\boldsymbol{CH_2{=}CHCH(CH{=}O)CH{=}O} + CH_4 \rightarrow CO + CH_3CH{=}O + CH_2{=}CHCH_3$	−38.85	± 2.27
		av **−39.56 ± 0.78**	
C/CD/CO/CT/H	$\boldsymbol{CH_2{=}CHCH(CH{=}O)C{\equiv}CH} + CH_3CH_3 \rightarrow CO + CH{\equiv}CH + CH_2{=}CHCH_2CH_2CH_3$	45.07	± 1.77
	$\boldsymbol{CH_2{=}CHCH(CH{=}O)C{\equiv}CH} + CH_4 \rightarrow CO + CH_3C{\equiv}CH + CH_2{=}CHCH_3$	45.39	± 1.59
		av **45.23 ± 0.22**	
C/CO/O2/H	$\boldsymbol{CH(OH)_2CH{=}O} + CH_4 \rightarrow 2CH_3OH + CO$	−119.4	± 1.54
	$\boldsymbol{CH(OH)_2CH{=}O} + CH_3CH_3 \rightarrow CH_3CH_2OH + CH_3OH + CO$	118.77	± 1.66
		av **−119.08 ± 0.44**	
C/C/CO/O2	$\boldsymbol{CH_3C(OH)_2CH{=}O} + 2CH_4 \rightarrow CH_3CH_2CH{=}O + 2CH_3OH$	−131.55	± 2.73
	$\boldsymbol{CH_3C(OH)_2CH{=}O} \rightarrow CH_3C({=}O)OH + CH_2{=}O$	−129.08	± 2.08
	$\boldsymbol{CH_3C(OH)_2CH{=}O} + 2CH_3CH_3 \rightarrow CH_3CH_2CH{=}O + 2CH_3CH_2OH$	−131.09	± 2.97
		av **−130.57 ± 1.31**	
C/CD2/CO/H	$\boldsymbol{CH_2{=}CHCH(CH{=}O)CH{=}CH_2} + CH_2CH_2 \rightarrow CH_2{=}CHCH{=}O + CH_2{=}CHCH_2CH{=}CH_2$	−1.74	± 3.43
	$\boldsymbol{CH_2{=}CHCH(CH{=}O)CH{=}CH_2} + 2CH_4 \rightarrow CH_3CH{=}O + 2CH_2{=}CHCH_3$	−0.049	± 2.66
	$\boldsymbol{CH_2{=}CHCH(CH{=}O)CH{=}CH_2} + CH_4 \rightarrow CH_3CH{=}O + CH_2{=}CHCH_2CH{=}CH_2$	−0.69	± 2.36
		av **−0.83 ± 0.85**	
C/CD2/O2	$\boldsymbol{CH_2{=}CHC(OH)_2CH{=}CH_2} + CH_4 \rightarrow 2CH_2{=}CHCH_2OH$	−61.01	± 1.96
	$\boldsymbol{CH_2{=}CHC(OH)_2CH{=}CH_2} + 2CH_4 \rightarrow CH_2(OH)_2 + 2CH_2{=}CHCH_3$	−61.59	± 1.31
		av **−61.30 ± 0.41**	
CD/O2	$\boldsymbol{CH_2{=}C(OH)_2} + CH_4 \rightarrow CH_2(OH)_2 + CH_2{=}CH_2$	−74.42	± 1.6
	$\boldsymbol{CH_2{=}C(OH)_2} + CH_2CH_2 \rightarrow 2CH_2{=}CHOH$	−73.49	± 5.53
		av **−73.95 ± 0.65**	
C/CD/CO/H2	$\boldsymbol{CH_2{=}CHCH_2CH{=}O} + CH_4 \rightarrow CH_2{=}CHCH_3 + CH_3CH{=}O$ −19.96		± 2.1
	$\boldsymbol{CH_2{=}CHCH_2CH{=}O} + CH_4 \rightarrow CH_2{=}CHCH_2CH_3 + CH_2{=}O$	−20.04	± 1.78
	$\boldsymbol{CH_2{=}CHCH_2CH{=}O} + CH_2{=}CH_2 \rightarrow CH_2{=}CHCH_3 + CH_2{=}CHCH{=}O$	−21.01	± 2.73
	$\boldsymbol{CH_2{=}CHCH_2CH{=}O} + CH_3CH_3 \rightarrow CH_2{=}CHCH_2CH_2CH_3 + CH_2{=}O$	−21.19	± 1.95
		av **−20.62 ± 0.74**	
$C/CD_2/C/H$	$\boldsymbol{CH_2{=}CHCH(CH_3)CH{=}CH_2} + CH_2CH_2 \rightarrow CH_2{=}CHCH_3 + CH_2{=}CHCH_2CH{=}CH_2$	17.75	± 1.55
	$\boldsymbol{CH_2{=}CHCH(CH_3)CH{=}CH_2} + CH_3CH_3 \rightarrow CH_3CH_2CH_3 + CH_2{=}CHCH_2CH{=}CH_2$	18.10	± 1.55
	$\boldsymbol{CH_2{=}CHCH(CH_3)CH{=}CH_2} + CH_4 \rightarrow CH_3CH_3 + CH_2{=}CHCH_2CH{=}CH_2$	18.09	± 1.48
		av **17.98 ± 0.20**	
CD/CD/CO	$\boldsymbol{CH_2{=}C(CH{=}O)CH{=}CH_2} + CH_2CH_2 \rightarrow CH_2{=}CHCH{=}O + CH_2{=}CHCH{=}CH_2$	−2.93	± 2.67
	$\boldsymbol{CH_2{=}C(CH{=}O)CH{=}CH_2} + CH_3CH_3 \rightarrow CH_3CH_2CH{=}CH_2 + CH_2{=}CHCH{=}O$	−2.83	± 2.59
	$\boldsymbol{CH_2{=}C(CH{=}O)CH{=}CH_2} + CH_4 \rightarrow CH_3CH{=}O + CH_2{=}CHCH{=}CH_2$	−1.93	± 1.94
		av **−2.56 ± 0.55**	
CD/CO/CT	$\boldsymbol{CH_2{=}C(CH{=}O)C{\equiv}CH} + CH_3CH_3 \rightarrow CH_3CH_2C{\equiv}CH + CH_2{=}CHCH{=}O$	38.33	± 3.15
	$\boldsymbol{CH_2{=}C(CH{=}O)C{\equiv}CH} + CH_2CH_2 \rightarrow CH_2{=}C(CH{=}O)CH{=}CH_2 + CH{\equiv}CH$	40.04	± 2.73
		av **39.18 ± 1.21**	
C/CD2/H/O	$\boldsymbol{CH_2{=}CHCH(OH)CH{=}CH_2} + CH_4 \rightarrow CH_2{=}CHCH_2OH + CH_3CH{=}CH_2$	−13.18	± 2.14
	$\boldsymbol{CH_2{=}CHCH(OH)CH{=}CH_2} + CH_2{=}O \rightarrow CH_2{=}CHCH_2OH + CH_2{=}CHCH{=}O$	−12.25	± 2.86
	$\boldsymbol{CH_2{=}CHCH(OH)CH{=}CH_2} + CH_3CH_3 \rightarrow CH_2{=}CHCH_2OH + CH_2{=}CHCH_2CH_3$	−11.63	± 2.22
		av **−12.35 ± 0.78**	
O/CD2	$\boldsymbol{CH_2{=}CHOCH{=}CH_2} + CH_4 \rightarrow CH_3CH{=}O + CH_3CH{=}CH_2$	−6.19	± 1.64
	$\boldsymbol{CH_2CH_2{=}CHOCH{=}CH_2} + CH_2{=}O \rightarrow CH_2{=}CHOH + CH_2{=}CHCH{=}O$	−6.45	± 4.04
	$\boldsymbol{CH_2{=}CHOCH{=}CH_2} + CH_3CH_3 \rightarrow CH_2{=}CHOH + CH_2{=}CHCH_2CH_3$	−5.83	± 3.4
		av **−6.15 ± 0.31**	
CO/CD/H	$\boldsymbol{CH2{=}CHCH{=}O} + CH_3CH_3 \rightarrow CH_2{=}CHCH_2CH_3 + CH_2{=}O$	−18.03	± 2.04
	$\boldsymbol{CH2{=}CHCH{=}O} + CH_2{=}CH_2 \rightarrow CH_2{=}CHCH{=}CH_2 + CH_2{=}O$	−18.16	± 2.02
	$\boldsymbol{CH2{=}CHCH{=}O} + CH_4 \rightarrow CH_2{=}CHCH_3 + CH_2{=}O$	−19.75	± 1.96
		av **−18.65 ± 0.95**	

[a] Sum of reported errors for each of the standard species (when available), plus absolute average error from work reactions calculation method (see Table in Appendix II).

mental enthalpy of reaction $\Delta H^\circ_{\mathrm{rxn},298}$ (see Appendix II). The difference $\Delta H^\circ_{\mathrm{rxn},298}(\mathrm{cal}) - \Delta H^\circ_{\mathrm{rxn},298}(\mathrm{exp})$ on these work reactions provides a reasonable evaluation of the error of the calculation method. The mean absolute average from the 27 calculated difference values for B3LYP computation method (0.78 kcal mol^{-1}) is considered as the error in the calculation method for this study.

A hypothetical standard deviation S_h determined for each method for the differences, $\Delta H^\circ_{\mathrm{rxn},298}(\mathrm{cal}) - \Delta H^\circ_{\mathrm{rxn},298}(\mathrm{exp})$, using 27 different work reactions are given in Appendix II. We note that each reaction is different, and we do not wish to imply that this S_h be used to represent an error bound.

3. Entropy (S°_{298}) and Heat Capacities ($C_{pf298}(T)$). The S°_{298} and $C_{pf298}(T)$ for the target molecules and radicals are obtained from the calculated vibration frequencies along with moments of inertia (Table SM3 of supporting material) and are based on the B3LYP/6-311G(d,p) geometries and frequencies. The contributions from translation, vibrations, and external rotations (TVR) are given in Table 5. TVR represents the sum of these contributions to S°_{298} and $C_{pf298}(T)$. The frequencies representing internal rotor torsions are not included in TVR. Instead, a more exact contribution from hindered rotations is calculated.

The final standard entropies also include corrections for rotational conformers. This correction is usually calculated by the following formula for 1 mol of mixture:[4]

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

where n_i is the equilibrium mole fraction of the ith form. $\Delta S_{\mathrm{mixing}}$

TABLE 3: Calculated $\Delta_f H^\circ_{298}$ for Phenyl Containing Species in kcal mol^{-1} and Reference Reactions

groups to be calculated	reactions series	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	error limit[b]
C/C/CB/O2	$\boldsymbol{C_6H_5C(OH)_2CH_3} + CH_4 \rightarrow C_6H_5CH_2CH_3 + CH_2(OH)_2$	−80.10	± 1.86
	$\boldsymbol{C_6H_5C(OH)_2CH_3} + 2CH_4 \rightarrow C_6H_5CH_3 + CH_2(OH)_2 + CH_3CH_3$	−78.95	± 2.0
		av **−79.52 ± 0.81**	
CD/CB/CD	$\boldsymbol{C_6H_5C(CH_2)CH{=}CH_2} + CH_2CH_2 \rightarrow C_6H_5CH{=}CH_2 + CH_2{=}CHCH{=}CH_2$	53.62	± 2.03
	$\boldsymbol{C_6H_5C(CH_2)CH{=}CH_2} + CH_3CH_3 \rightarrow C_6H_5\ CH_2CH_3 + CH_2{=}CHCH{=}CH_2$	52.70	± 1.96
	$\boldsymbol{C_6H_5C(CH_2)CH{=}CH_2} + CH_4 \rightarrow C_6H_5CH{=}CH_2 + CH_3CH{=}CH_2$	52.20	± 1.94
		av **52.84 ± 0.72**	
C/CB/C2/CO	$\boldsymbol{C_6H_5C(CH_3)_2CH{=}O} + 2CH_4 \rightarrow C_6H_5CH_3 + CH_3CH{=}O + CH_3CH_2CH_3$	−21.33	± 2.76
	$\boldsymbol{C_6H_5C(CH_3)_2CH{=}O} + CH_3CH_3 + CH_4 \rightarrow C_6H_5CH_2CH_3 + CH_3CH{=}O + CH_3CH_2CH_3$	−22.59	± 2.96
		av **−21.96 ± 0.98**	
CB/CO	$\boldsymbol{C_6H_5CH{=}O} \rightarrow C_6H_6 + CO$	−7.27	± 1.1
	$\boldsymbol{C_6H_5CH{=}O} + CH_3CH_3 \rightarrow C_6H_6 + CH_3CH_2CH{=}O$	−7.66	± 1.47
		av **−7.46 ± 0.27**	
CB/CO	$\boldsymbol{CH_3C_6H_4CH{=}O} \rightarrow C_6H_5CH_3 + CO$	−15.78	± 1.3
	$\boldsymbol{CH_3C_6H_4CH{=}O} + CH_3CH_3 \rightarrow C_6H_6 + CH_3CH_2CH_3 + CO$	−16.32	± 1.75
	$\boldsymbol{CH_3C_6H_4CH{=}O} + CH_4 \rightarrow C_6H_6 + CH_3CH_3 + CO$	−16.53	± 1.68
	$\boldsymbol{CH_3C_6H_4CH{=}O} + CH_3CH_3 \rightarrow C_6H_5CH{=}O + CH_3CH_2CH_3$	−16.84	± 1.75
		av **−16.37 ± 0.44**	
CD/CB/CO	$\boldsymbol{C_6H_5C({=}CH_2)CH{=}O} + CH_4 \rightarrow C_6H_5CH_3 + CO + CH_2{=}CH_2$	12.48	± 1.83
	$\boldsymbol{C_6H_5C({=}CH_2)CH{=}O} + CH_4 \rightarrow C_6H_6 + CO + CH_2{=}CHCH_3$	11.34	± 1.86
	$\boldsymbol{C_6H_5C({=}CH_2)CH{=}O} \rightarrow C_6H_5CH{=}CH_2 + CO$	12.14	± 1.53
		av **11.98 ± 0.58**	
O/CB/CO	$\boldsymbol{C_6H_5OCH{=}O} + CH_3CH_3 \rightarrow C_6H_5OH + CH_3CH_2CH{=}O$	−51.68	± 1.48
	$\boldsymbol{C_6H_5OCH{=}O} \rightarrow C_6H_5OH + CO$	−51.30	± 1.11
		av **−51.49 ± 0.26**	
CD/C/CB	$\boldsymbol{C_6H_5C({=}CH_2)CH_3} + 2CH_3CH_3 \rightarrow C_6H_6 + CH_3CH_2CH_2CH{=}CH_2$	28.37	± 2.07
	$\boldsymbol{C_6H_5C({=}CH_2)CH_3} + CH_4 \rightarrow C_6H_6 + CH_2{=}CHCH_2CH_3$	29.82	± 1.67
	$\boldsymbol{C_6H_5C({=}CH_2)CH_3} + CH_4 \rightarrow C_6H_5CH{=}CH_2 + CH_3CH_3$	29.01	± 1.72
	$\boldsymbol{C_6H_5C({=}CH_2)CH_3} + CH_4 \rightarrow C_6H_5CH_3 + CH_3CH{=}CH_2$	29.01	± 1.67
	$\boldsymbol{C_6H_5C({=}CH_2)CH_3} + CH_3CH_3 \rightarrow C_6H_5CH{=}CH_2 + CH_3CH_2CH_3$	29.02	± 1.79
		av **29.05 ± 0.51**	
CD/CB/O	$\boldsymbol{C_6H_5C({=}CH_2)OH} + CH_3CH_3 \rightarrow C_6H_5CH_2CH_3 + CH_2{=}CHOH$	−8.49	± 3.89
	$\boldsymbol{C_6H_5C({=}CH_2)OH} + CH_3CH_3 \rightarrow C_6H_5CH{=}CH_2 + CH_3CH_2OH$	−8.71	± 2.05
	$\boldsymbol{C_6H_5C({=}CH_2)OH} + CH_4 \rightarrow C_6H_6CH_3 + CH_2{=}CHOH$	−7.23	± 3.79
		av **−8.14 ± 0.79**	

[a] Sum of reported errors for each of the standard species (when available), plus absolute average error from work reactions calculation method (see Table in Appendix II).

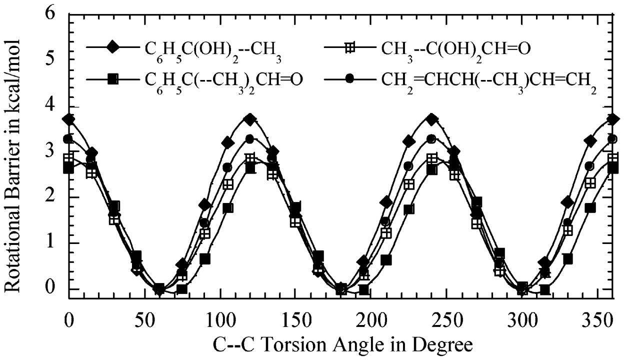


Figure 2. Potential barriers for internal rotations about C−C bonds in $C_6H_5C(OH_2)-CH_3$, $C_6H_5C(-CH_3)_2CH{=}O$, $CH_2{=}CHCH(-CH_3)$-$CH{=}CH_2$, and $CH_3-C(OH)_2CH{=}O$.

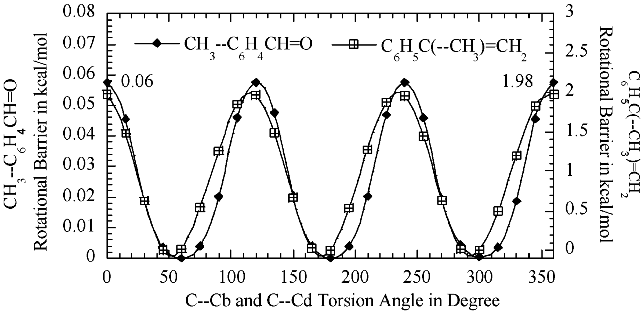


Figure 3. Potential barriers for internal rotations about $C-C_b$ and $C-C_d$ bonds in $CH_3-C_6H_4CH{=}O$ and $C_6H_5C(-CH_3){=}CH_2$.

represents the entropy of mixing of rotational conformations or optical conformations. Entropy contributions from conformers resulting from intramolecular rotations are included in the entropy contribution calculated by the Rotator code. The energy levels for the internal rotor are calculated and the partition function corresponding to the rotor is determined and used in the calculation of the rotation entropy.

The overall determined S°_{298} and $C_{pf298}(T)$ are used to determine the entropy and heat capacity of new groups for use in group additivity (GA).

4. Rotational Barriers. Potential barriers versus torsion angle for internal rotation in all species listed in Tables 2−4 are calculated at the B3LYP/6-31G(d,p) level. Entropy and heat capacity contributions from the internal rotors are estimated using these potentials and the calculated structure in Rotator code described in the computation section.

The potential energy as function of dihedral angle is determined by scanning individual torsion angles from 0° to 360° at 15° intervals and allowing the remaining molecular structural parameters to be optimized. The optimized structure of each species is described in Table SM2 of the Supporting Information. Data on the maxima rotational barriers in each of the internal rotors are summarized in Table 6.

Data on the rotation barriers and total energies for each internal rotor, both the stable molecules and radicals, are included in Tables SM5−26, of the Supporting Information. The lines in Figures 2−12 are the results of the Fourier expansion fit to the data. Values for the coefficients of the Fourier expansion, a_i and b_i in eq I, are obtained from the fitting program in Sigma Plot version 2.0, and then used in “Rotator”

TABLE 4: Calculated $\Delta_f H^\circ_{298}$ Radical Groups and Bond Energies in kcal mol^{-1} and Reference Reactions

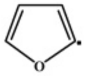
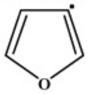
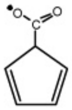
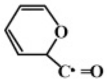
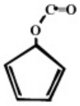
Bond Energy Name	Reactions Series	$\Delta_f H^0_{298}$	Error Limit[a]
	Furan	-8.29	
FURANJ1	***Furanj1*** + CH_3CH_3 → Furan + CH_3CH_2•	61.15	± 1.68
	***Furanj1*** + C_6H_6 → Furan + C_6H_5•	60.86	± 4.18
	Furanj1 + CH_2CH_2 → Furan + CH_2CH•	61.11	± 2.16
	Furanj1 + CH_3CH=O → Furan-CH=O + CH_3•	63.59	± 2.61
		Average **61.67 ± 1.28**	
FURANJ2	***Furanj2*** + CH_3CH_3 → Furan + CH_3CH_2•	61.27	± 1.68
	***Furanj2*** + C_6H_6 → Furan + C_6H_5•	60.99	± 4.18
	Furanj2 + CH_2CH_2 → Furan + CH_2CH•	61.24	± 3.16
	Furanj2 + CH_3CH=O → Furan-CH=O + CH_3•	63.72	± 2.61
		Average **61.80 ± 1.28**	
	Y(C_6H_6)=O + $2CH_4$ → CH_2=CHCH=O + CH_2=CH_2 + CH_3CH=CH_2	-4.80	± 2.35
	Y(C_6H_6)=O + CH_2CH_2 → C_6H_6 + CH_3CH=O	-4.79	± 1.45
Y(C6J)*O		Average **-4.80 ± 0.007**	
	***Y(C_6H_5•)=O*** + $2CH_4$ → CH_2=CHCH=O + CH_2CH_2 + CH_2=$CHCH_2$•	13.43	± 3.33
	Y(C_6H_5•)=O + CH_2CH_2 → Y(C_6H_6)=O + CH_2CH•	12.51	± 2.32
	Y(C_6H_5•)=O + CH_3CH_3 → Y(C_6H_6)=O + CH_3CH_2•	12.55	± 1.84
	Y(C_6H_5•)=O + CH_4 → C_6H_6 + CH_3O•	12.61	± 2.41
		Average **12.77 ± 0.44**	
Y(C5)COJ*O			
	***Y(C_5H_5)C(OH)=O*** + $2CH_4$ → Y(C_5H_6) + CH_3OH + CH_3CH=O	-53.54	± 2.67
	Y(C_5H_5)C(OH)=O + CH_3CH_3 → Y(C_5H_6) + CH_3CH_2C(=O)OH	-52.08	± 2.43
		Average **-52.81 ± 1.03**	
	Y(C_5H_5)C(O•)=O	**5.1**	Ref. 79
	C_6H_5CH=O	**-7.46 ± 0.27**	
	C_6H_5C•=O + CH_4 → C_6H_5CH=O + CH_3•	30.21	± 2.84
PhCJ*O	***C_6H_5C•=O*** + CH_4 → C_6H_6 + CH_3C•=O	28.46	± 3.09
	C_6H_5C•=O + CH_4 → C_6H_6 + CO + CH_3•	31.72	± 2.74
	C_6H_5C•=O + CH_3CH_3 → C_6H_5CH=O + CH_3CH_2•	31.11	± 3.09
		30.75 ± 1.42	
	Y(C_5H_5O)CH=O + CH_4 → Y(C_5H_6O) + CH_3CH=O	-26.34	± 3.93
	Y(C_5H_5O)CH=O → Y(C_5H_6O) + CO	-22.42	± 3.44
	Y(C_5H_5O)CH=O + CH_4 → Y(C_5H_5)OCH=O	-27.04	± 3.78
Y(C5O)CJ*O		Average **-25.27** ± **2.5**	
	***Y(C_5H_5O)C•=O*** + CH_4 → Y(C_5H_6O) + CH_3C•=O	10.10	± 2.95
	Y(C_5H_5O)C•=O + H_2 → Y(C_5H_6O) + CH•=O	9.12	± 2.07
	Y(C_5H_5O)C•=O + CH_3CH=O → Y(C_5H_5O)CH=O + CH_3C•=O	11.39	± 5.50
	Y(C_5H_5O)C•=O + CH_3CH_3 → Y(C_5H_5O)CH=O + CH_3CH_2•	11.63	± 6.07
		Average **10.56 ± 1.17**	
	Y(C_5H_5)OCH=O + CH_4 → C_5H_6 + CH_3OCH=O	-34.96	± 2.48
	Y(C_5H_5)OCH=O + CH_3CH_3 → C_5H_6 + CO + CH_3CH_2OH	-34.16	± 1.61
Y(C5)OCJ*O	***Y(C_5H_5)OCH=O*** + CH_4 → C_5H_6 + CO + CH_3OH	-34.88	± 1.49
		Average **-34.67 ± 0.44**	
	***Y(C_5H_5)OC•=O*** + CH_4 → Y(C_5H_5•) + Y(C5)OCH=O	8.19	± 2.46
	Y(C_5H_5)OC•=O + CH_4 → Y(C_5H_5•) + CH_3OH + CO	9.13	± 2.19
	Y(C_5H_5)OC•=O + CH_3CH_3 → Y(C_5H_5•) + CO + CH_3CH_2OH	9.84	± 2.34
	Y(C_5H_5)OC•=O + CH_2CH_2 → Y(C_5H_5•) + CO + CH_3CH=O	10.98	± 2.55
		Average **9.54 ± 1.17**	
	CH_3OCH=O + CH_3CH_3 → $CH_3OCH_2CH_3$ + CH_2=O	-83.63	± 2.23
	CH_3OCH=O + CH_4 → CH_3OCH_3 + CH_2=O	-84.45	± 2.14
	CH_3OCH=O → CH_3OH + CO	-82.09	± 1.95
COCJ*O		Average **-83.39 ± 1.19**	
	CH_3OC•=O + CH_3CH_3 → CH_3OCH=O + CH_3CH_2•	-41.31	± 3.28
	CH_3OC•=O + CH_4 → CH_3OH + CH_3C•=O	-42.59	± 2.23
	CH_3OC•=O + CH_4 → CH_3OCH=O + CH_3•	-42.20	-
		Average **-42.03 ± 0.65**	

TABLE 4 (Continued)

Bond Energy Name	Reactions Series	$\Delta_f H^0_{298}$	Error Limit[a]
	$CH_2{=}CHCH{=}O$	**-18.65 ± 0.95**	
C*CJC*O	**$CH_2{=}C\bullet CH{=}O$** + $CH_3CH_3 \rightarrow CH_2{=}CHCH{=}O + CH_3CH_2\bullet$	41.99	± 2.48
	$CH_2{=}C\bullet CH{=}O$ + $CH_2CH_2 \rightarrow CH_2{=}CHCH{=}O + CH_2CH\bullet$	41.96	± 2.96
	$CH_2{=}C\bullet CH{=}O$ + $CH_4 \rightarrow CH_2{=}CH\bullet + CH_3CH{=}O$	42.12	± 2.33
	$CH_2{=}C\bullet CH{=}O$ + $CH_3CH{=}O \rightarrow CH_2{=}CHCH{=}O + CH_3C\bullet{=}O$	41.76	± 2.91
	$CH_2{=}C\bullet CH{=}O$ + $CH_4 \rightarrow CH_2{=}CHCH_3 + CH\bullet{=}O$	42.03	± 1.14
	Average	**41.97 ± 0.13**	
C*CCJ*O	**$CH_2{=}CHC\cdot{=}O$** + $CH_4 \rightarrow CH_2CHCH{=}O + CH_3\bullet$	19.7	± 1.70
	$CH_2{=}CHC\cdot{=}O$ + $CH_3CH_3 \rightarrow CH_2CHCH{=}O + CH_3CH_2\bullet$	20.61	± 2.05
	$CH_2{=}CHC\cdot{=}O$ + $CH_3CH{=}O \rightarrow CH_2{=}CHCH{=}O + CH_3C\bullet{=}O$	20.37	± 3.25
	Average	**20.22 ± 0.47**	
	$CH_2{=}CHCH(CH{=}O)C\cdot CH$	**45.23 ± 0.22**	
VCJC*OC#C	**$CH_2{=}CHC\bullet(CH{=}O)C\cdot CH$** + $CH_3CH_3 \rightarrow CH_3CH_2\bullet + CH_2{=}CHCH(CH{=}O)C{\equiv}CH$	62.68	± 1.85
	$CH_2{=}CHC\bullet(CH{=}O)C\cdot CH$ + $CH_3CH_3 \rightarrow CH_2{=}O + CH{\equiv}C\bullet + CH_2{=}CHCH_2CH{=}CH_2$	62.80	± 3.46
	$CH_2{=}CHC\bullet(CH{=}O)C\cdot CH$ + $CH_4 \rightarrow CO + CH{\equiv}C\bullet + CH_2{=}CHCH_2CH_3$	62.94	± 3.32
	Average	**62.80 ± 0.13**	
	$CH(OH)_2CH{=}O$	**-119.08 ± 0.44**	
O*CCJ(OH)2	**$C\bullet(OH)_2CH{=}O$** + $CH_3CH_3 \rightarrow CH_3CH_2OH + CO + CH_2\bullet OH$	-96.15	± 3.13
	$C\bullet(OH)_2CH{=}O$ + $CH_4 \rightarrow CH_3OH + CO + CH_2\bullet OH$	-96.79	± 3.31
	$C\bullet(OH)_2CH{=}O$ + $CH_4 \rightarrow CH(OH)_2CH{=}O + CH_3\bullet$	-96.25	± 2.75
	$C\bullet(OH)_2CH{=}O$ + $CH_4 \rightarrow CH_3OH + CH_2{=}O + CH\bullet{=}O$	-93.93	± 2.27
	Average	**-95.78 ± 1.26**	
	$CH_2{=}CHCH(CH{=}O)CH{=}O$	**-39.56 ± 0.78**	
VCJ(C*O)2	**$CH_2{=}CHC\bullet(CH{=}O)CH{=}O$** + $CH_3CH_3 \rightarrow CH\bullet{=}O + CH_2{=}O + CH_2{=}CHCH_2CH{=}CH_2$	-19.25	± 2.10
	$CH_2{=}CHC\bullet(CH{=}O)CH{=}O$ + $CH_3CH_3 \rightarrow CH_3CH_2\bullet + CH_2{=}CHCH(CH{=}O)CH{=}O$	-19.62	± 2.96
	$CH_2{=}CHC\bullet(CH{=}O)CH{=}O$ + $CH_4 \rightarrow CH\bullet{=}O + CO + CH_2{=}CHCH_2CH_3$	-18.11	± 1.97
	$CH_2{=}CHC\bullet(CH{=}O)CH{=}O$ + $CH_2CH_2 \rightarrow CH\bullet{=}O + CO + CH_2{=}CHCH_2CH{=}CH_2$	-20.24	± 2.12
	Average	**-18.99 ± 0.78**	

[a] Sum of reported errors for each of the standard species (when available), plus absolute average error from work reactions calculation method (see Table in Appendix II).

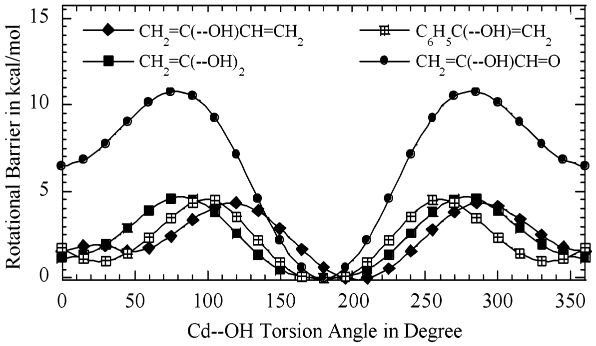


Figure 4. Potential barriers for internal rotations about C_d—OH bonds in $CH_2{=}C(—OH)CH{=}CH_2$, $CH_2{=}C(—OH)_2$, $C_6H_5C(—OH){=}CH_2$, and $CH_2{=}C(—OH)CH{=}O$.

to calculate the contribution of internal rotors to S°_{298} and $C_p{}^\circ(T)$ ($0.1 \leq T/K \leq 5000$). The Rotator program takes into account the entropy of mixing and the optical isomer corrections. The coefficients, a_i and b_i in eq I, are listed for each species in Table SM27−29 in the Supporting Information.

4.1. Rotational Barriers for Stable Species. Some representative potential energy curves for the above rotors are illustrated in Figures 2−12; all remaining potential energy curves are illustrated in the Supporting Information.

Methyl−Carbon Rotations. A potential energy diagram (ZPVE and thermal corrections included) for four methyl radical rotations, where the methyl is bonded to a substituted sp^3 carbon: $C_6H_5C(OH_2)—CH_3$, $C_6H_5C(—CH_3)_2CH{=}O$, $CH_2{=}CHCH(—CH_3)CH{=}CH_2$, and $CH_3—C(OH)_2CH{=}O$ is shown in Figure 2. These C—CH_3 rotor potentials are all similar, with 3-fold symmetry and barriers ranging between 2.6 and 3.7 kcal mol^{-1} (Table 6). The two molecules in this set containing a CH=O group bonded to the sp^3 carbon show slightly lower barriers, 2.8 and 2.6 kcal mol^{-1}, versus the OH or vinyl substituents.

Rotation barriers about $C_d—CH_3$ and $C_b—CH_3$ bonds show 3-fold symmetry with low barriers, $C_d—CH_3$ has a 1.98 kcal mol^{-1} barrier, in $C_6H_5C(—CH_3){=}CH_2$). The $C_b—CH_3$ is almost a free rotor, barrier of 0.06 kcal mol^{-1} in *p*-$CH_3—C_6H_4CH{=}O$ (Figure 3).

Hydroxyl Rotations. Rotation barriers about the RC—OH bond are shown in Figures SM1 and SM2. The RC—OH barriers in $CH(—OH)_2CH{=}O$, $CH_3C(—OH)_2CH{=}O$, $CH_2{=}CHC(—OH)_2$-$CH{=}CH_2$, and $C_6H_5C(—OH)_2CH_3$ species, all with two hydroxyl groups on the carbon (Figure 3), are about one to two kcal mol^{-1} higher than barriers in molecules that do not have a second hydroxyl group. $CH_2{=}CHCH(—OH)CH{=}CH_2$ and $C_6H_5CH_2—OH$ (Figure SM2) have barriers of 3.44 and 2.26 respectively.

Figure 4 illustrates rotation about C_d—OH bonds in $CH_2{=}C(—OH)CH{=}CH_2$, $CH_2{=}C(—OH)_2$, and C_6H_5-$C(—OH){=}CH_2$. The data show similar, 2-fold, symmetric potentials with barriers near 4.5 kcal mol^{-1}. The OH rotation barrier in 2-hydroxypropen-3-al, $CH_2{=}C(—OH)CH{=}O$ has

TABLE 5: Ideal Gas-Phase Thermodynamic Propertiesa,[a] $\Delta_fH^\circ_{298}$, S°_{298}, and C_p(300-1500 K)

species			$\Delta_fH^\circ_{298}$ (kcal mol^{-1})	S°_{298} (cal mol^{-1} K^{-1})	$C_p(T)$ [cal (mol^{-1} K^{-1})]						
					300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
$C_6H_5C(CH_3)_2CH=O$	TVR[d]			83.07	35.78	48.35	59.29	68.33	82.00	91.68	106.05
(1)[b]	IR[e]	C_b-C		7.57	2.3 3	2.03	1.81	1.64	1.43	1.30	1.15
(9)[c]		$C-C$		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
		$C-C$		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
		$C-CH=O$		5.64	3.23	2.77	2.35	2.03	1.64	1.42	01.19
	total		−21.96	105.32	45.52	57.27	67.31	75.56	88.17	97.18	110.77
$C_6H_5C(=CH_2)CH=O$	TVR[d]			85.24	31.41	41.74	50.48	57.54	67.95	75.15	85.62
(1)[b]	IR[e]	C_b-C_d		7.24	2.30	2.07	1.84	1.66	1.42	1.28	1.13
(1)[c]		$C_d-CH=O$		4.08	3.02	3.05	2.97	2.88	2.66	2.42	1.92
	total		11.98	96.56	36.73	46.86	55.29	62.08	72.03	78.85	88.67
$C_6H_5C(=CH_2)CH=CH_2$	TVR[d]			84.37	33.47	45.13	54.95	62.88	74.60	82.78	94.93
(1)[b]	IR[e]	C_b-C_d		6.68	3.11	2.77	2.37	2.05	1.64	1.42	1.18
(2)[c]		C_d-C_d		4.76	3.44	3.38	3.12	2.82	2.31	1.95	1.48
	total		52.84	95.81	40.02	51.28	60.44	67.75	78.55	86.15	97.59
$C_6H_5C(=CH_2)CH_3$	TVR[d]			77.99	30.48	41.33	50.58	58.14	69.43	77.40	89.30
(1)[b]	IR[e]	C_b-C_d		7.45	1.63	1.56	1.47	1.39	1.27	1.19	1.09
(6)[c]		C_d-C		4.86	2.07	1.88	1.68	1.53	1.33	1.22	1.10
	total		29.05	90.3	34.18	44.77	53.73	61.06	72.03	79.81	91.49
$C_6H_5C(=CH_2)OH$	TVR[d]			79.21	29.09	39.04	47.28	53.85	63.43	70.05	79.88
(1)[b]	IR[e]	C_b-C_d		6.72	2.23	2.11	1.96	1.81	1.58	1.42	1.21
(2)[c]		C_d-OH		2.64	2.68	2.45	2.25	2.08	1.81	1.61	1.33
	total		−8.14	88.57	34	43.6	51.49	57.74	66.82	73.08	82.42
$C_6H_5C(OH)_2CH_3$	TVR[d]			79.49	32.03	43.26	52.69	60.28	71.43	79.22	90.92
(1)[b]	IR[e]	C_b-C		6.57	2.29	2.34	2.29	2.18	1.94	1.72	1.40
(6)[c]		$C-OH$		2.06	3.11	3.19	2.92	2.59	2.06	1.73	1.34
		$C-OH$		2.06	3.11	3.19	2.92	2.59	2.06	1.73	1.34
		$C-C$		4.21	2.04	2.15	2.11	2.01	1.78	1.59	1.31
	total		−79.52	94.39	42.58	54.13	62.93	69.65	79.27	85.99	96.31
$C_6H_5CH=O$	TVR[d]			75.04	24.58	32.61	39.48	45.05	53.24	58.87	66.99
(1)[b] (2)[c]	IR[e]	$C_b-CH=O$		4.64	2.00	2.03	2.06	2.08	2.14	2.17	2.04
	total		−7.46	79.68	26.58	34.64	41.54	47.13	55.38	61.04	69.03
	NIST[f]		−8.90		26.84	35.01	41.92	47.47	55.50	60.95	68.67
C6H5OCH$=$O	TVR[d]			80.19	26.17	34.80	42.08	47.94	56.49	62.31	70.68
(1)[b]	IR[e]	C_b-O		7.43	1.48	1.46	1.42	1.37	1.27	1.20	1.11
(1)[c]		$O-CH=O$		5.02	2.47	2.27	2.12	2.05	2.02	1.99	1.82
	total		−51.49	92.64	30.12	38.53	45.62	51.36	59.78	65.5	73.61
$CH_3C_6H_4CH=O$	TVR[d]			80.25	28.75	38.03	46.10	52.77	62.79	69.79	80.03
(1)[b]	IR[e]	$C-C_b$		5.73	0.99	0.99	0.99	0.99	0.99	0.99	0.99
(3)[c]		$C_b-CH=O$		4.64	2.00	2.03	2.06	2.08	2.14	2.17	2.04
	total		−16.37	90.62	31.74	41.05	49.15	55.84	65.92	72.95	83.06
$C_6H_5CH=CH_2$	TVR[d]			77.43	26.90	36.21	44.11	50.50	59.94	66.54	76.30
(1)[b] (1)[c]	IR[e]	C_b-C_d		5.95	1.81	1.87	1.89	1.86	1.75	1.61	1.37
	total			83.38	28.71	38.08	46.00	52.36	61.69	68.15	77.67
	NIST[f]		35.11	82.48	28.90	38.19	46.03	52.34	61.66	68.16	77.72
$C_6H_5CH_2OH$	TVR[d]			75.64	25.72	34.70	42.45	48.76	58.10	64.62	74.28
(1)[b]	IR[e]	C_b-C		6.74	2.20	1.98	1.78	1.61	1.40	1.27	1.13
(2)[c]		$C-OH$		3.28	2.31	2.16	1.92	1.72	1.45	1.29	1.13
	total		−22.60[f]	85.66	30.23	38.84	46.15	52.09	60.95	67.18	76.54
$CH(OH)_2CH=O$	TVR[d]			67.50	15.31	19.16	22.52	25. 30	29.49	32.47	37.04
(1)[b]	IR[e]	$C-OH$		3.04	1.52	1.67	1.77	1.81	1.79	1.70	1.46
(1)[c]		$C-OH$		3.04	1.52	1.67	1.77	1.81	1.79	1.70	1.46
		$C-CH=O$		4.19	3.03	3.59	3.56	3.24	2.52	2.02	1.44
	total		119.08	77.77	21.38	26.09	29.62	32.16	35.59	37.89	41.4
$CH_3C(OH)_2CH=O$	TVR[d]			70.87	19.76	25.09	29.72	33.5	39.38	43.60	50.14
(2)[d]	IR[e]	$C-C$		4.10	2.39	2.61	2.64	2.56	2.25	1.96	1.51
(3)[c]		$C-OH$		2.48	1.98	2.03	2.07	2.06	1.95	1.79	1.49
		$C-OH$		2.48	1.98	2.03	2.07	2.06	1.95	1.79	1.49
		$C-CH=O$		3.88	1.96	1.99	1.88	1.75	1.53	1.38	1.19
	total		−130.57	83.81	28.07	33.75	38.38	41.98	47.06	50.52	55.82
$CH_2=C(OH)_2$	TVR[d]			64.55	14.62	18.19	21.11	23.43	26.86	29.35	33.38
(1)[b]	IR[e]	C_d-OH		2.36	2.54	2.56	2.46	2.32	2.02	1.78	1.42
(2)[c]		C_d-OH		2.36	2.54	2.56	2.46	2.32	2.02	1.78	1.42
	total		−73.95	69.27	19.7	23.31	26.03	28.07	30.9	32.91	36.22
$CH_2=C(OH)CH=CH_2$	TVR[d]			68.65	18.70	24.14	28.70	32.40	37.98	42.03	48.36
(1)[b]	IR[e]	C_d-OH		2.16	3.11	3.04	2.75	2.45	1.99	1.70	1.34
(1)[c]		C_d-C_d		4.28	2.36	2.86	3.09	3.08	2.74	2.34	1.70
	total		−18.0[f]	75.09	24.17	30.04	34.54	37.93	42.71	46.07	51.4
$CH_2=CHCH(OH)CH=CH_2$	TVR[d]			72.12	21.60	28.67	34.77	39.78	47.37	52.87	61.39
(1)[b]	IR[e]	C_d-C		6.00	2.94	2.45	2.10	1.85	1.54	1.36	1.17
(2)[c]	IR[e]	C_d-C		6.00	2.94	2.45	2.10	1.85	1.54	1.36	1.17
		$C-OH$		2.96	3.07	2.57	2.15	1.86	1.52	1.34	1.15
	total		−12.35	87.08	30.55	36.14	41.12	45.34	51.97	56.93	64.88

TABLE 5 (Continued)

species			$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	S°_{298} (cal mol^{-1} K^{-1})	$C_p(T)$ [cal (mol^{-1} K^{-1})]						
					300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
$CH_2=CHOCH=CH_2$	TVR[d]			66.86	18.07	23.50	28.15	31.97	37.77	41.99	48.49
(1)[b]	IR[e]	C_d-O		5.84	2.00	2.03	2.00	1.92	1.73	1.57	1.31
(2)[c]		C_d-O		5.84	2.00	2.03	2.00	1.92	1.73	1.57	1.31
	total		−6.15	78.54	22.07	27.56	32.15	35.81	41.23	45.13	51.11
$CH_2=CHCH_2CH=O$	TVR[d]			68.61	17.40	22.60	27.26	31.21	37.33	41.79	48.53
(1)[b]	IR[e]	C_d-C		5.47	2.11	1.76	1.54	1.40	1.24	1.15	1.07
(1)[c]		$C-CH=O$		5.73	1.91	1.63	1.46	1.35	1.22	1.15	1.07
	total		−20.62	79.81	21.42	25.99	30.26	33.96	39.79	44.09	50.67
$CH_2=CHCH(CH_3)CH=CH$	TVR[d]			73.27	23.25	31.14	38.20	44.17	53.45	60.27	70.82
(1)[b]	IR[e]	C_d-C		6.54	2.14	1.91	1.71	1.55	1.35	1.24	1.11
(3)[c]		C_d-C		6.54	2.14	1.91	1.71	1.55	1.35	1.24	1.11
		$C-C$		4.28	2.09	2.14	2.05	1.92	1.67	1.49	1.25
	total		17.98	90.63	29.62	37.1	43.67	49.19	57.82	64.24	74.29
$CH_2=CHCH(CH=O)CH=CH_2$	TVR[d]			76.77	24.23	31.68	38.22	43.66	52.01	58.03	67.13
(1)[b]	IR[e]	C_d-C		6.88	1.99	1.68	1.48	1.36	1.21	1.14	1.06
(2)[c]		C_d-C		6.88	1.99	1.68	1.48	1.36	1.21	1.14	1.06
		$C-CH=O$		6.49	2.09	1.84	1.64	1.50	1.32	1.22	1.10
	total		−0.83	97.02	30.3	36.88	42.82	47.88	55.75	61.53	70.35
$CH_2=CHCH(CH=O)CH=O$	TVR[d]			75.82	22.12	28.38	33.87	38.46	45.49	50.49	57.89
(1)[b]	IR[e]	C_d-C		6.56	2.39	1.99	1.74	1.56	1.35	1.24	1.11
(1)[c]		$C-CH=O$		6.29	1.90	1.88	1.78	1.67	1.47	1.34	1.17
		$C-CH=O$		6.29	1.90	1.88	1.78	1.67	1.47	1.34	1.17
	total		−39.56	94.96	28.31	34.13	39.17	43.36	49.78	54.41	61.34
$CH_2=C(CH=O)CH=CH_2$	TVR[d]			71.08	19.10	25.25	30.61	35.07	41.84	46.66	53.89
(1)[b]	IR[e]	C_d-C_d		5.82	2.41	2.20	2.05	1.92	1.70	1.53	1.29
(1)[c]		$C_d-CH=O$		3.72	2.80	3.15	3.25	3.20	2.92	2.60	1.99
	total		−2.56	80.62	24.31	30.6	35.91	40.19	46.46	50.79	57.17
$CH_2=CHC(OH)_2CH=CH_2$	TVR[d]			75.13	24.53	32.11	38.43	43.52	51.09	56.52	65.00
(1)[b]	IR[e]	C_d-C		5.57	2.82	2.60	2.38	2.18	1.86	1.64	1.34
(2)[c]		C_d-C		5.57	2.82	2.60	2.38	2.18	1.86	1.64	1.34
		$C-OH$		1.55	2.40	3.00	3.20	3.12	2.65	2.21	1.59
		$C-OH$		1.55	2.40	3.00	3.20	3.12	2.65	2.21	1.59
	total		−61.30	89.37	34.97	43.31	49.59	54.12	60.11	64.22	70.86
$CH_2=CHCH=O$	TVR[d]			62.70	14.14	17.69	20.88	23.59	27.80	30.85	35.48
(2)[d] (2)[c]	IR[e]	$C_d-CH=O$		3.79	2.83	3.07	3.08	2.97	2.62	2.28	1.72
	total		−18.65	66.49	16.97	20.76	23.96	26.56	30.42	33.13	37.2
	NIST[f]				17.11	20.97	24.21	26.87	30.81	33.51	37.38
$(YC_5H_5)C(OH)=O$	TVR[d]			76.87	24.22	32.49	39.27	44.60	52.26	57.47	65.12
(1)[b]	IR[e]	$C-C=O$		7.91	1.26	1.17	1.12	1.08	1.05	1.03	1.01
(1)[c]		$CO-OH$		0.57	1.30	1.86	2.29	2.62	2.99	3.11	2.87
	total		−52.81	85.35	26.78	35.52	42.68	48.3	56.3	61.61	69.00
$(YC_5H_5)OCH=O$	TVR[d]			78.38	24.06	32.05	38.79	44.19	52.05	57.44	65.27
(1)[b]	IR[e]	$C-O$		6.64	2.84	2.47	2.17	1.93	1.61	1.42	1.20
(1)[c]		$O-CH=O$		3.76	3.33	3.16	2.91	2.73	2.54	2.43	2.15
	total		−34.67	88.78	30.23	37.68	43.87	48.85	56.2	61.29	68.62
$(YC_5H_5O)CH=O$	TVR[d]			81.15	26.11	33.99	40.64	46.03	53.95	59.40	67.29
()[d] (1)[c]	IR[e]	$C-CH=O$		4.81	2.41	2.68	2.76	2.69	2.39	2.07	1.57
	total		−25.27	85.96	28.52	36.67	43.40	48.72	56.34	61.47	68.86
$Y(C_6H_6)=O$ (1)[b] (1)[c]	TVR[d]		−4.88	77.54	24.44	31.82	38.08	43.15	50.65	55.87	63.50
Furan (1)[b] (1)[c]	TVR[d]			66.46	15.75	21.19	25.71	29.26	34.32	37.76	42.81
	NIST[f]		−8.29		15.74	21.22	25.77	29.34	34.44	37.90	42.94
$CH_3OCH=O$	TVR[d]			61.26	12.42	15.51	18.54	21.23	25.52	28.68	33.43
(1)[b]	IR[e]	$C-O$		5.69	1.03	1.01	1.00	1.00	0.99	0.99	0.99
(3)[c]		$O-CH=O$		2.80	1.62	1.91	2.28	2.63	3.12	3.29	3.04
	total		−83.39	69.75	15.07	18.43	21.82	24.86	29.63	32.96	37.46
	NIST[f]		−84.97		15.44	18.54	21.58	24.27	28.56	31.71	36.44
$CH_2=CHCH(CH=O)C\equiv CH$ (1)[b] (1)[c]	TVR[d]		45.23	75.71	23.23	29.61	34.91	39.24	45.82	50.56	57.75
$CH_2=C(CH=O)C\equiv CH$ (1)[b] (1)[c]	TVR[d]		39.18	72.41	19.82	24.55	28.37	31.47	36.17	39.55	44.67
Furanj1 (1)[b] (1)[c]	TVR[d]		61.67	66.42	15.40	20.15	24.04	27.08	31.36	34.20	38.29
Furanj2 (1)[b] (1)[c]	TVR[d]		61.80	66.25	15.23	19.98	23.89	26.95	31.26	34.13	38.25
$CH_3OC^\bullet=O$	TVR[d]			62.43	12.09	14.59	17.01	19.15	22.54	25.03	28.77
(1)[b] (3)[c]	IR[e]	$C-O$		5.06	0.99	0.99	0.99	0.99	0.99	0.99	0.99
		$O-C^\bullet=O$		4.14	2.11	2.12	2.16	2.21	2.29	2.29	2.07
	total		−42.02	71.43	15.17	17.69	20.16	22.35	25.81	28.29	31.73
$CH_2=C^\bullet CH=O$	TVR[d]			68.62	16.38	19.21	21.70	23.82	27.12	29.51	33.08
(1)[b] (2)[c]	IR[e]	$C_d^\bullet-CH=O$		no rotor							
	total		41.97	68.62	16.38	19.21	21.70	23.82	27.12	29.51	33.08
$CH_2=CHC^\bullet=O$	TVR[d]			66.46	15.70	18.68	21.27	23.42	26.74	29.15	32.79
(1)[b] (2)[c]	IR[e]	$C_d-C^\bullet=O$		no rotor							
	total		20.22	66.46	15.70	18.68	21.27	23.42	26.74	29.15	32.79

TABLE 5 (Continued)

species			$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	S°_{298} (cal mol^{-1} K^{-1})	$C_p(T)$ [cal (mol^{-1} K^{-1})]						
					300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
$CH_2{=}CHC^{\bullet}(CH{=}O)CH{=}O$	TVR[d]			80.50	25.00	30.81	35.84	40.02	46.32	50.74	57.20
(1)[b] (1)[c]	IR[e]	$C_d{-}C^{\bullet}$		4.48	2.00	2.05	2.07	2.09	2.13	2.16	2.18
		$C^{\bullet}{-}CH{=}O$		no rotor							
	total		−18.99	84.98	27.00	32.86	37.91	42.11	48.45	52.90	59.38
$C^{\bullet}(OH)_2CH{=}O$	TVR[d]			67.80	14.19	17.59	20.50	22.85	26.33	28.75	32.42
(1)[b]	IR[e]	$C{-}OH$		1.69	2.50	2.82	2.88	2.81	2.53	2.23	1.70
(1)[c]		$C^{\bullet}{-}OH$		1.69	2.50	2.82	2.88	2.81	2.53	2.23	1.70
		$C^{\bullet}{-}CH{=}O$		2.08	1.96	2.09	2.18	2.28	2.52	2.77	3.11
	total		−95.78	73.26	21.15	25.32	28.44	30.75	33.91	35.98	38.93
$(YC_5H_5)C(O^{\bullet}){=}O$	TVR[d]			80.42	25.88	33.49	39.70	44.55	51.46	56.10	62.78
(1)[b](1)[c]	IR[e]	$C{-}C{=}O$		6.70	2.21	2.11	1.98	1.86	1.64	1.49	1.27
	total		5.10[g]	87.12	28.09	35.60	41.68	46.41	53.10	57.59	64.05
$(YC_5H_5)OC^{\bullet}{=}O$	TVR[d]			77.66	23.90	31.72	38.35	43.62	51.01	55.74	62.06
(1)[b]	IR[e]	$C{-}O$		7.66	1.88	1.57	1.39	1.28	1.16	1.10	1.04
(1)[c]		$O{-}C^{\bullet}{=}O$		4.27	2.37	2.29	2.27	2.29	2.34	2.34	2.11
	total		9.54	89.59	28.15	35.58	42.01	47.19	54.51	59.18	65.21
$(YC_5H_5O)C^{\bullet}{=}O$	TVR[d]			80.47	26.06	33.35	39.34	44.10	51.02	55.75	62.60
(1)[b] (1)[c]	IR[e]	$C{-}C^{\bullet}{=}O$		5.22	2.86	2.74	2.54	2.32	1.94	1.67	1.33
	total		10.56	85.69	28.92	36.09	41.88	46.42	52.96	57.42	63.93
$Y(C_6H_5^{\bullet}){=}O$ (1)[b] (1)[c]	TVR[d]		12.77	75.26	23.06	30.25	36.19	40.91	47.68	52.27	58.89
$C_6H_5C^{\bullet}{=}O$	TVR[d]			77.82	24.27	31.70	37.93	42.93	50.22	55.18	62.31
(1)[b] (2)[c]	IR[e]	$C_b{-}C^{\bullet}{=}O$		5.22	2.13	2.22	2.24	2.18	1.98	1.77	1.43
	total		30.75	83.04	26.4	33.92	40.17	45.11	52.20	56.95	63.74
$CH_2{=}CHC^{\bullet}(CH{=}O)C{\equiv}CH$ (1)[b] (1)[c]	TVR[d]		62.80	84.41	28.31	34.23	39.05	42.94	48.76	52.90	59.10

[a] Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm. [b] Optical isomers number. [c] Symmetry number. [d] The sum of contributions from translations, external rotations and vibrations. [e] Contribution from internal rotation about the corresponding bonds. [f] http://webbook.nist.gov/chemistry/. [g] Ref 79.

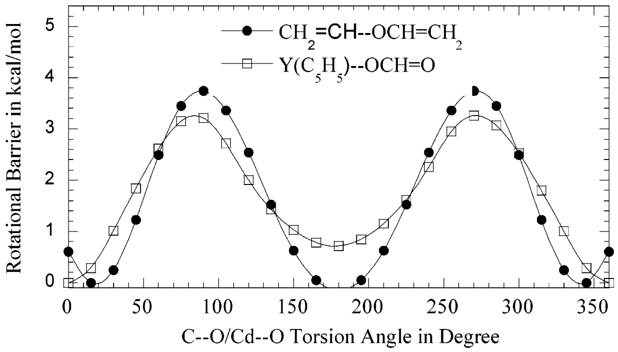


Figure 5. Potential barriers for internal rotations about $C_d{-}O$ bonds in $CH_2{=}CH{-}OCH{=}CH_2$ and $C{-}O$ bonds in $Y(C_5H_5){-}OCH{=}O$.

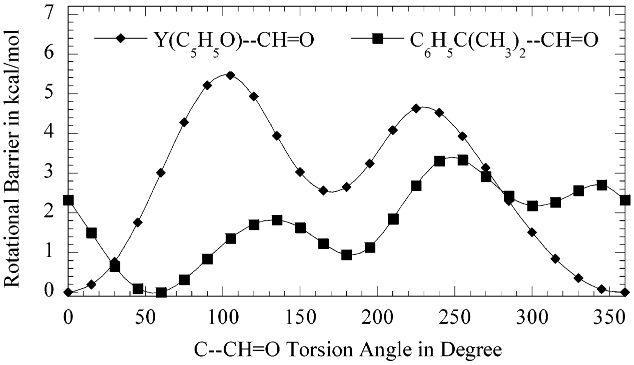


Figure 6. Potential barriers for internal rotations about $C{-}CH{=}O$ bonds in $Y(C_5H_5O)_2{-}CH{=}O$ and $C_6H_5C(CH_3)_2{-}CH{=}O$.

a similar potential shape, but with a high barrier, 10.7 kcal mol^{-1}.

Methyl−Ether−Oxygen Rotations. $CH_3{-}OCH{=}O$ has a typical "CH_3" symmetric 3-fold symmetry and almost no barrier, 0.24 kcal mol^{-1} (Figure SM3).

$C{-}OC$, $C_d{-}OC$, and $C_b{-}OC$ rotors show a 2-fold potential with barriers between 3.7 ($CH_2{=}CH{-}OCH{=}CH_2$) and 3.25 for ($Y(C_5H_5){-}OCH{=}O$) (Figure SM3 and Figure 5). ($C_6H_5{-}OCH{=}O$) rotation has a 2.72 kcal mol^{-1} barrier, as shown in Figure SM4.

Carbon (sp^3)−Carbonyl Rotations. Figures SM5 and SM6 and Figure 6 illustrate potential energy diagrams for $RC{-}CH{=}O$ barriers in seven carbonyl molecules. The rotation barriers for a substituted sp^3 carbon−carbonyl bond are similar at 2.53, 2.24, and 2.91 kcal mol^{-1} in $CH_2{=}CHCH_2{-}CH{=}O$, $CH_2{=}CHCH(CH{=}CH_2){-}CH{=}O$, and $CH_2{=}CHCH(CH{=}O){-}CH{=}O$, respectively (Figure SM5). Barriers about $C(OH)_2{-}CH{=}O$ increase slightly to 4.21 kcal mol^{-1} for $CH(OH)_2{-}CH{=}O$ and 5.05 kcal mol^{-1} for $CH_3C(OH)_2{-}CH{=}O$ (Figure SM6).

When the carbonyl is bonded to a cyclic moiety $Y(C_5H_5O){-}CH{=}O$ and $C_6H_5C(CH_3)_2{-}CH{=}O$ (Figure 6) the barriers are 5.46 and 3.35 kcal mol^{-1}, respectively. The $(C_5H_5){-}C(OH){=}O$ rotation has a significantly lower barrier at 1.12 kcal mol^{-1}, shown in Figure SM7, where OH replaces the H atom in the "$C{-}CH{=}O$" group.

Vinyl Carbon−Carbon (sp^3) Rotations. Rotation about vinyl $C_d{-}CCH{=}O$ bonds is illustrated in Figures SM8 and SM9 and Figure 7, where the barriers are moderately low and range from 1.96 to 2.6 kcal mol^{-1}. The molecules are: $CH_2{=}CH{-}CH_2{-}CH{=}O$, $CH_2{=}CH{-}CH(CH{=}O)CH{=}O$, $CH_2{=}CH{-}C(CH_3){-}CH{=}CH_2$, and $CH_2{=}CH{-}C(CH{=}O)CH{=}CH_2$ (also see Table 6). Figure 7 shows that the barrier about a vinyl $C_d{-}C(OH)_n$ increases with the substitution of OH group(s); 3.46 kcal mol^{-1} in $CH_2{=}CH{-}C(OH)CH{=}CH_2$ and it goes higher to 4.84 kcal mol^{-1} in $CH_2{=}CH{-}C(OH)_2CH{=}CH_2$.

C=C−C=C Rotations. The C=C−C=C rotation barriers in $CH_2{=}C{-}(CH{=}O)CH{=}CH_2$, $C_6H_5CH({=}CH_2){-}CH{=}CH_2$, and $CH_2{=}C{-}(OH)CH{=}CH_2$ are in the range 4.0−6.1 kcal mol^{-1}. The species with an OH group on one vinyl carbon has the higher rotation barrier (Figure SM10).

Carbon Double Bond−Carbonyl Rotations (C=C−CH=O). Potential barriers for internal rotations about $C{=}C{-}CH{=}O$ bonds (Figure 8) in $CH_2{=}CH{-}CH{=}O$, $CH_2{=}CHC({=}CH_2){-}$

TABLE 6: Maxima Rotational Barrier (298 K) (kcal mol^{-1})

	C_b−C	C_b−C_d	C_b−O	C_b−CH=O C_b−C$^•$=O	C−C	C−OH	C−CH=O	C_d−C	C_d−C_d	C_d−OH	C_d−CH=O	O−CH=O
$C_6H_5OCH{=}O$			2.72									9.59
$C_6H_5C(CO){=}CH_2$		2.55									8.29	
$C_6H_5C(OH)_2CH_3$	4.72				3.71	4.36						
$C_6H_5C({=}CH_2)CH{=}CH_2$		3.02							5.97			
$C_6H_5C(CH_3)_2CH{=}O$	2.99				2.66		3.35					
$C_6H_5CH{=}O$				4.52								
$C_6H_5C^•{=}O$				4.4								
$C_6H_5C({=}CH_2)OH$		3.30								4.49		
$C_6H_5C({=}CH_2)CH_3$		2.21						1.97				
$C_6H_5CH_2OH$	2.46					2.26						
$C_6H_5CH{=}CH_2$		4.42										
$CH_3C_6H_4CH{=}O$	0.06			10.31								

	C−C	C−OH C$^•$−OH	C−CH=O C$^•$−CH=O C−C$^•$=O	C−C(OH)=O C−C(O$^•$)=O	C_d−C C_d−C$^•$	C_d−C_d	C_d−OH	C_d−CH=O $C_d^•$−CH=O C_d−C$^•$=O	O−CH=O O−C$^•$=O	C_d−O	C−O
$(OH)_2CHCH{=}O$		5.44	4.21								
$(OH)_2C^•CH{=}O$		6.1	33.4								
$CH_2{=}CHCH(CH{=}O)CH{=}O$			2.91		2.57						
$CH_2{=}CHC^•(CH{=}O)CH{=}O$			no rotor		15.2						
$CH_3C(OH)_2CH{=}O$	2.8	5.68	5.05								
$CH_2{=}CHCH(CHO)CH{=}CH_2$			2.24		1.96						
$CH_2{=}CHC(OH)_2CH{=}CH_2$		5.17			4.84						
$CH_2{=}CHCH{=}O$								6.44			
$CH_2{=}C^•CH{=}O$								no rotor			
$CH_2{=}CHC^•{=}O$								no rotor			
$CH_2{=}C(OH)_2$							4.56				
$CH_2{=}CHCH(CH_3)CH{=}CH_2$	3.27				2.5						
$CH_2{=}C(CHO)CH{=}CH_2$						4.03		7.99			
$CH_2{=}CHOCH{=}CH_2$										3.7	
$CH_2{=}C(OH)CH{=}O$							10.7	16.5			
$CH_2{=}CHCH(OH)CH{=}CH_2$		3.44			3.46						
$CH_2{=}C(OH)CH{=}CH_2$						6.1	4.32				
$CH_2{=}CHCH_2CH{=}O$			2.53		2.19						
$Y(C_5H_5)C(OH){=}O$				1.12					13.53		
$Y(C_5H_5)C(O^•){=}O$				4.56							
$Y(C_5H_5)OCH{=}O$									10.58		3.25
$Y(C_5H_5)OC^•{=}O$									9.6		1.58
$Y(C_5H_5O)CH{=}O$			5.46								
$Y(C_5H_5O)C^•{=}O$			4								
$CH_3OCH{=}O$									14		0.24
$CH_3OC^•{=}O$									9.2		0.02

CH=O, $C_6H_5C({=}CH_2)$−CH=O, and $CH_2{=}C(OH)$−CH=O show relatively high barriers. The barrier in $CH_2{=}CH$−CH=O is 6.4 kcal mol^{-1}; barriers in $CH_2{=}CHC({=}CH_2)$−CH=O and $C_6H_5C({=}CH_2)$−CH=O are 8 and 8.3 kcal mol^{-1}, respectively. The barrier in $CH_2{=}C(OH)$−CH=O, which contains an OH group on the olefin, is 16.5; this is ca. 11 kcal mol^{-1} higher than the rotation about C=C−CH=O.

Phenyl−Carbon Rotations. Rotation barriers about carbon-(sp^3)−phenyl bonds, C_{Ph}−C (Figure SM11), vary from 2.4 for C_6H_5−CH_2OH, 3.0 for C_6H_5−$C(CH_3)_2CH{=}O$, to 4.7 kcal mol^{-1} for C_6H_5−$C(OH)_2CH_3$.

Styrene, Substituted Styrenes. The carbon−phenyl−carbon double bond, C_{Ph}−C_d, rotation barriers vary from 2.21 to 4.42 kcal mol^{-1}. The highest internal rotation about C_{Ph}−C_d is in styrene, C_6H_5−$CH{=}CH_2$, at 4.42 kcal mol^{-1}, followed by 3.3 in C_6H_5−$C({=}CH_2)OH$. The methyl-substituted styrene C_6H_5−$C({=}CH_2)CH_3$ has a 2.2 kcal mol^{-1} barrier. C_6H_5−$C({=}CH_2)$-CH=O and C_6H_5−$C({=}CH_2)CH{=}CH_2$ have barriers of 2.5 and 3 kcal mol^{-1}, respectively (Figure 9). The data suggest a stronger coupling of the styrene vinyl with the aromatic ring relative to the methyl or carbonyl substituted vinyl groups. The 4.42 barrier for styrene is in good agreement with the experimental results of Lewis and Zuo,[32] and other values referenced in their article.

Phenyl−Carbonyl Rotations. Figure SM12 shows potential barriers for internal rotation about C_{Ph}−CH=O in C_6H_5−CH=O, and p-$CH_3C_6H_4$−CH=O. Both show 2-fold symmetry, and both have barriers at ca. 10 kcal mol^{-1}.

Ether Oxygen−Carbonyl Rotations. Figure 10 illustrates internal rotation potentials for RO−CH=O bonds in CH_3O−CH=O, C_6H_5O−CH=O, $Y(C_5H_5)O$−CH=O, and $Y(C_5H_5)$−C(OH)=O. The barriers are high due to resonance with the carbonyl group or with sp^2 bonds in the ring. Barriers are 9.6 kcal mol^{-1} for C_6H_5O−CH=O, 10.6 kcal mol^{-1} for $Y(C_5H_5)O$−CH=O, and 13.5 and 14 kcal mol^{-1} for $Y(C_5H_5)$−C(OH)=O and CH_3O−CH=O, respectively.

4.2. Rotational Barriers Involving Radicals. Potential energy curves for internal rotation in the radicals are illustrated in Figures 11 and 12 and in Figures SM13, SM14, and SM15−SM18 of the Supporting Information. The maximum barrier for each system is also listed in Table 6.

RO−Carbonyl Radical. The internal rotation barriers about RO−C$^•$=O in CH_3O−C$^•$=O and $Y(C_5H_5)O$−C$^•$=O are shown in Figure 11. The potential diagram shows 2-fold symmetry over 360° rotation for each system, with barriers of 9.2 and 9.6 kcal mol$^{-1,}$ respectively. The barrier about RO−C$^•$=O bonds for these radicals is lower than the corresponding barrier of their respective parent molecules (14 and 10.58 kcal mol^{-1}).

These ether link rotors that involve a carbonyl carbon, C−OC$^•$=O for $Y(C_5H_5)$−OC$^•$=O and CH_3−OC$^•$=O, both have

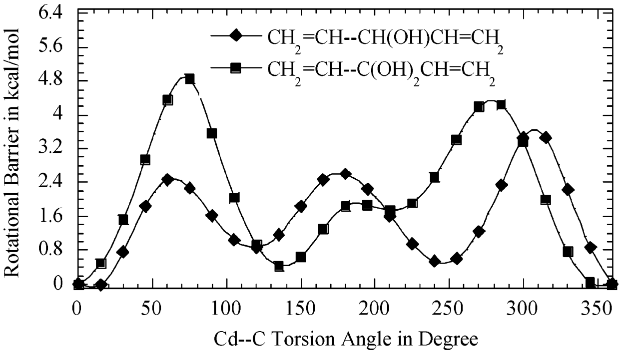


Figure 7. Potential barriers for internal rotations about C_d—C bonds in CH_2═CH—C(OH)CH═CH_2 and CH_2═CH—$C(OH)_2$CH═CH_2.

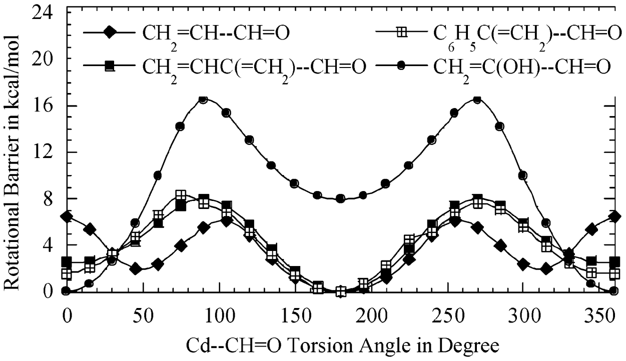


Figure 8. Potential barriers for internal rotations about C_d—CH═O bonds in CH_2═CH—CH═O, CH_2═CHC(═CH_2)-CH═O, C_6H_5C-(═CH_2)—CH═O, and CH_2═C(OH)—CH═O.

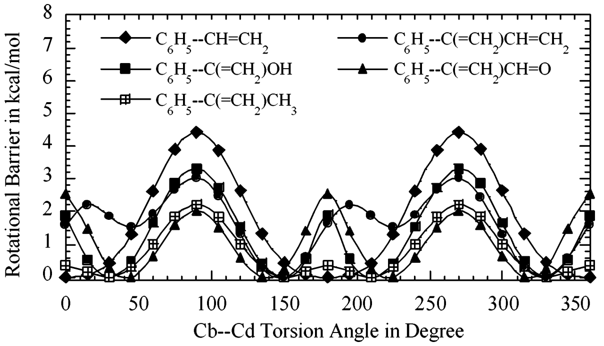


Figure 9. Potential barriers for internal rotations about C_b—C_d bonds in C_6H_5—CH═CH_2, C_6H_5—C(═CH_2)OH, C_6H_5—C(═CH_2)CH═CH_2, and C_6H_5—C(═CH_2)CH═O.

low barriers than the parent species, 1.58 and 0.02 kcal mol^{-1}, respectively (Figures SM13 and SM14).

The C_{Ph}—$C^{\bullet}$═O and C_{sp3}—$C^{\bullet}$═O rotation barriers are similar for C_6H_5—$C^{\bullet}$═O and $Y(C_5H_5O)$—$C^{\bullet}$═O, with higher barriers or 4.0 and 4.4 kcal mol^{-1}, respectively (Figure 12), about 1−1.5 kcal mol^{-1} lower than the barrier in the respective parent.

Carbonyl−Methyl Radicals. $C^{\bullet}(OH)_2$CH═O has three internal rotors, two hydroxy about the radical site and one carbonyl group rotor, $C^{\bullet}$—CH═O. The rotation barrier about $C^{\bullet}$—OH is 6.1 kcal mol^{-1} and differs by only 0.5 kcal mol^{-1} from the parent molecule. The rotation barrier about $C^{\bullet}$—CH═O has a surprisingly high value of 33.4 kcal mol^{-1}, whereas only 4.2 kcal mol^{-1} is needed to rotate about C—CH═O (Figures SM15 and SM16). This rotation results in reaction, which we discuss further in the bond energy section below.

Carbon−Carboxy Radicals. $Y(C_5H_5)C(O^{\bullet})$═O contains only one rotor, C—C($O^{\bullet}$)═O with 4.56 kcal mol^{-1} rotational barrier, some 3.5 kcal mol^{-1} higher than for the parent (Figure SM17).

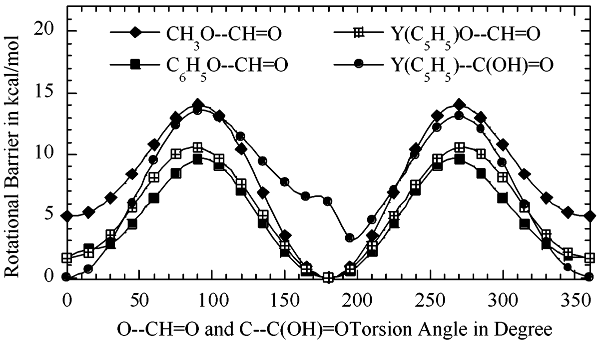


Figure 10. Potential barriers for internal rotations about O—CH═O bonds in CH_3O—CH═O, C_6H_5O—CH═O, $Y(C_5H_5)O$—CH═O, and $Y(C_5H_5)C(OH)$═O.

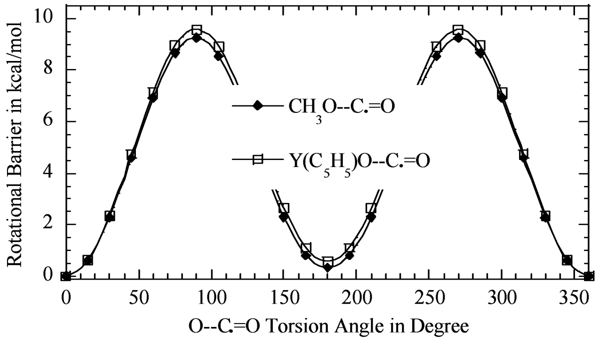


Figure 11. Potential barriers for internal rotations about O—$C^{\bullet}$═O bonds in CH_3O—$C^{\bullet}$═O and $Y(C_5H_5)O$—$C^{\bullet}$═O.

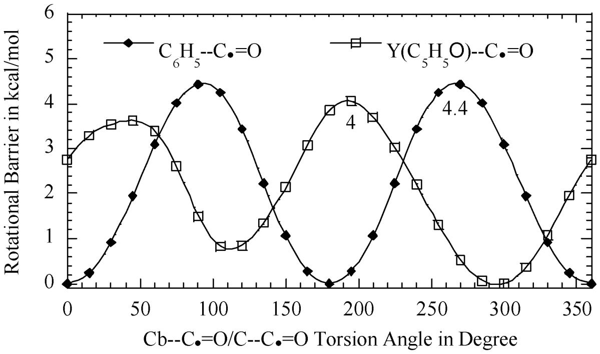


Figure 12. Potential barriers for internal rotations about C_b—$C^{\bullet}$═O/C—$C^{\bullet}$═O bonds in $Y(C_5H_5O)$—$C^{\bullet}$═O and C_6H_5—$C^{\bullet}$═O.

Carbon−Double Bond−Carbonyl Radicals. The radical CH_2═CH$C^{\bullet}$(CH═O)CH═O appears to have significant resonance through the molecule. The CH_2═C_dH—$C^{\bullet}(CH═O)_2$ internal rotation barrier for the radical is 15.2 kcal mol^{-1} (Figure SM18), which is some 12 kcal mol^{-1} more than with the parent. That is, while the two C—C═O rotors do not exist for the radical. While rotating, the radical dissociates via a β scission reaction, to form a stable molecule CH_2═CHC(CH═O)═C═O + H. The internal rotation barrier appears to be higher than the H atom elimination barrier.

5. Group Additivity Values. Group additivity[4] is an inexpensive and often an accurate calculation technique to estimate the thermodynamic properties for larger molecules; it is extensively employed for hydrocarbons and oxygenated hydrocarbons.[33] The GA method serves as a valuable estimation technique for many scientists and engineers whose work involves thermodynamic characterization of elementary and overall reaction processes. Group additivity calculations can be performed using the "THERM" code,[34,35] which is inexpensive in computation time and accurate for hydrocarbons.[33,36]

In this work, we calculate enthalpy, entropy, and heat capacity ($C_p(T)$) values for 26 groups in unsaturated oxygenated hydrocarbons; the groups are listed in Table 7. The target groups in this study were identified in our estimation of decomposition and oxidation paths for polynuclear aromatic hydrocarbons, dibenzo-dioxins and -furans; one oxidation sequence requiring groups from this study is illustrated in Figure 1. The target groups are those needed to estimate molecules in these oxidation and pyrolysis reaction paths. Appendix I references some recent work on group additivity.

We develop fifteen new groups, listed in the first column of Scheme 3, all based on unsaturated, oxygenated species with one exception: the C/CD2/C/H group, which has no oxygen. Eleven additional groups involve a phenyl ring carbon (CB for carbon benzene). The phenyl groups are listed in column 2 of Scheme 3. Enthalpy for species, where limited or no data were found in the literature, was calculated. Each group is estimated from only one molecule system.

SCHEME 3: Groups Developed

	phenyl containing groups
C/CD/CO/CO/H	C/CB/C/O2
C/CD/CO/CT/H	CD/CB/CD
C/CO/O2/H	C/CB/C2/CO
C/C/CO/O2	CB/CO
C/CD2/CO/H	CD/CB/CO
C/CD2/O2	O/CB/CO
CD/O2	CD/C/CB
CD/CD/CO	CD/CB/O
CD/CO/CT	CD/CB/H
C/CD2/H/O	CO/CB/H
C/CD/CO/H2	C/CB/H2/O
O/CD2	
CO/CD/H	
CD/CD/O	
C/CD2/C/H	

Green and Sumathi have reported values for the C/CD2/C/H group[7] as derived from G2 calculation on $(CH_2{=}CH)_2CHCH_2$-CH_3. The enthalpy estimated by Green and Sumathi for this group is found to be −1.10 kcal mol^{-1}, which is in good agreement with our value at −1.52 kcal mol^{-1}. The entropy and heat capacity (300 K) differences between the two studies are higher at 3.4 and 0.65 cal mol^{-1} K^{-1}, respectively. The thermodynamic values of Green and Sumathi are listed in Table 9 for comparison with our calculated values.

5.1. Enthalpies of Formation. A groups' enthalpy is determined using the calculated heat of formation of the stable molecule containing that group and use of the literature data on group additivity values for the remaining groups in the molecules.

An example of group additivity calculation for $\Delta_f H^\circ_{298}$ of the O/C$_b$/CO group is calculated on the following basis (eq 1):

$$\Delta_f H^\circ_{298}(C_6H_5OCH{=}O) = (\Delta_f H^\circ_{298}(C_b/H)) \times 5 + \Delta_f H^\circ_{298}(C_b/O) + \Delta_f H^\circ_{298}(CO/H/O) + \Delta_f H^\circ_{298}(O/CB/CO) \tag{1}$$

where the calculated heat of formation of $C_6H_5OCH{=}O$ is −51.49 kcal mol^{-1} (Table 3) and the reference group values are listed in Table 8.

$$\Delta_f H^\circ_{298}(O/CB/CO) = (-51.49) - (3.3 \times 5) - (-0.9) - (-32.1) = -34.99 \text{ kcal mol}^{-1}$$

All other groups enthalpies are estimated the same way and listed in Table 9.

5.2. Entropy. All values are intrinsic; that is the entropy group values exclude contributions to symmetry and optical isomer number in the parent molecule. The entropy, S°_{298} of each group, is derived from the calculated entropy of the stable molecules listed in Tables 2 and 3. As noted in the text, the entropy incorporates contributions from the species structure, vibration frequencies, internal rotors, symmetry, number of optical isomers, and number of conformers contributing. Our internal rotor treatment also includes contributions to entropy and heat capacity from rotational conformers.[19]

S°_{298} of O/C$_b$/CO calculation is determined from (eq 2):

$$S^\circ_{298}(C_6H_5OCH{=}O) = (S^\circ_{298}(C_b/H)) \times 5 + S^\circ_{298}(C_b/O) + S^\circ_{298}(CO/H/O) + S^\circ_{298}(O/CB/CO) + R\ln(OI) - R\ln(\sigma) \tag{2}$$

where $R = 1.987$ cal mol^{-1} K^{-1}, OI stands for number of optical isomer when greater than 1, and σ is the symmetry number. The calculated entropies for the 26 developed groups are summarized in Table 9.

Entropy for radical speciesinclude the above plus a $R\ln(2)$ term for the electronic degeneracy of the unpaired electron spin states.

Entropy values are listed in Table 5 along with the appropriate symmetry number of the parent molecules and the total number of optical isomers, when there is more than one.

5.3. Heat Capacity $C_{pf298}(T)$. Terms for use in group additivity to estimate heat capacity, $C_{pf298}(T)$ values, are determined similar to that described above for the enthalpy in reaction 1. The results are given is Table 9 for temperatures from 300 to 1500 K. In an example, the heat capacity $C_{pf298}(T)$ of O/CB/CO is determined as follows:

$$C_{pf298}(T)(C_6H_5OCH{=}O) = C_{pf298}(T)(C_b/H) \times 5 + C_{pf298}(T)(C_b/O) + C_{pf298}(T)(CO/H/O) + C_{pf298}(T)(O/CB/CO) \tag{3}$$

5.4. Carbon−Hydrogen Bond Energies and Hydrogen Bond Increment (HBI) Values. A method to estimate thermochemical properties for radicals from the corresponding properties of the parent using hydrogen bond increment (HBI) groups, is described by Lay et al.[33] and by Sun and Bozzelli.[37] The method uses the bond energy (298 K) corresponding to loss of a hydrogen on the radical site, central atom for the enthalpy term, the difference between the radical and the parent for the heat capacity ($C_p(T)$) term, and the intrinsic entropy difference between the radical and parent for the S_{298} term. HBI group values for entropy and $C_p(T)$ are added to the corresponding thermochemical properties (intrinsic) of the parent molecule to obtain the corresponding, intrinsic property of the radical. Thirteen new (HBI) increment groups for estimation of radical species thermochemistry and bond dissociation enthalpy (BDE) at 298 K are developed in this study.

The enthalpy ($\Delta_f H^\circ_{298}$), entropy (S°_{298}), and heat capacities ($C_{pf298}(T)$), values are derived as follows:

A hydrogen atom bond increment (HBI) group for $\Delta_f H^\circ_{298}$ reflects the enthalpy change due to loss of a H atom from a stable parent molecule in the form of the R−H bond energy (BDE), which is defined as the enthalpy of reaction for a simple carbon−hydrogen dissociation reaction. As an example for the

TABLE 7: Groups Identification in Calculated Species

species	to be calcd[a]	O/C/H	CO/CB/H	CD/H2	CB/H	CB/CO	CB/O	CB/C	CB/CD	CO/CD/H	CD/CD/H	CO/C/H	CO/H/O	C/CD/H3	O/CD/H	C/C/H3	C/CB/H3
$C_6H_5OCH{=}O$	O/CB/CO				*		*						*				
$C_6H_5C(CH{=}O){=}CH_2$	CD/CB/CO			*	*				*	*							
$C_6H_5C(OH)_2CH_3$	C/CB/C/O2	*			*			*								*	
$C_6H_5C({=}CH_2)CH{=}CH_2$	CD/CB/CD			*	*				*		*						
$C_6H_5C(CH_3)_2CH{=}O$	C/CB/C2/CO				*			*				*				*	
$C_6H_5CH{=}O$	CB/CO		*		*												
$CH_3C_6H_4CH{=}O$			*		*			*									*
$C_6H_5C({=}CH_2)OH$	CD/CB/O			*	*				*						*		
$C_6H_5C({=}CH_2)\ CH_3$	CD/C/CB			*	*				*					*			
$C_6H_5CH{=}CH_2$	CD/CB/H			*	*				*								
$C_6H_5CH{=}O$	CO/CB/H				*	*											
$C_6H_5CH_2OH$	C/CB/H2/O	*			*			*									

species	to be calcd[a]	O/C/H	CO/C/H	CD/H2	C/C/H3	CD/CO/H	O/CD/H	CD/CD/H	CO/CD/H	CD/H/O	CD/C/H	CT/C	CT/H	CT/CD
$CH(OH)_2CH{=}O$	C/CO/O2/H	*	*											
$CH_2{=}CHCH_2CH{=}O$	C/CD/CO/H2		*	*							*			
$CH_2{=}CHCH(CH{=}O)CH{=}O$	C/CD/CO/CO/H		*	*							*			
$CH_3C(OH)_2CH{=}O$	C/C/CO/O2	*	*		*									
$CH_2{=}CHCH(CH{=}O)CH{=}CH_2$	C/CD2/CO/H		*	*							*			
$CH_2{=}CHC(OH)_2CH{=}CH_2$	C/CD2/O2	*		*							*			
$CH_2{=}CHCH{=}O$	CO/CD/H			*		*								
$CH_2{=}C(OH)_2$	CD/O2			*			*							
$CH_2{=}CHCH(CH_3)CH{=}CH_2$	C/CD2/C/H			*	*						*			
$CH_2{=}C(CH{=}O)CH{=}CH_2$	CD/CD/CO			*				*	*					
$CH_2{=}CHOCH{=}CH_2$	O/CD2			*						*				
$CH_2{=}CHCH(OH)CH{=}CH_2$	C/CD2/H/O	*		*							*			
$CH_2{=}C(OH)CH{=}CH_2$	CD/CD/O			*			*	*						
$CH_2CHCH(CO)C^\circ CH$	C/CD/CO/CT/H		*	*							*	*	*	
$CH_2{=}C(CH{=}O)C^\circ\ CH$	CD/CO/CT			*					*				*	*

[a] Group which will be calculated in this work.

TABLE 8: Group Values

groups	ΔH°_{f298} (kcal mol^{-1})	S°_{f298} [cal (mol^{-1} K^{-1})]	$C_p(T)$ [cal (mol^{-1} K^{-1})]						
			300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
CD/H2[a]	6.26	27.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19
CD/C/H[b]	8.59	7.97	4.16	5.03	5.81	6.50	7.65	8.45	9.62
C/CD/H3[b]	−10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C/C/H3[b]	−10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
CD/CD/H	6.74	6.38	4.46	5.79	6.75	7.42	8.35	9.11	10.09
O/CD/H[c]	−46.30	25.34	4.68	6.02	7.02	7.72	8.22	8.38	8.59
O/C/H[b]	−37.90	29.07	4.30	4.50	4.82	5.23	6.02	6.61	7.44
CD/H/O[b]	8.60	6.20	4.75	6.46	7.64	8.35	9.10	9.56	10.46
CB/O[b]	−0.90	−10.20	3.90	5.30	6.20	6.60	6.90	6.90	7.07
CB/H[b]	3.30	11.53	3.24	4.40	5.46	6.30	7.54	8.41	9.73
CB/C	5.51	−7.69	2.67	3.14	3.68	4.15	4.96	5.44	5.98
CB/CD[d]	5.69	−7.80	3.59	3.97	4.38	4.72	5.28	5.61	5.75
CD/CO/H	4.32	6.38	4.46	5.79	6.75	7.42	8.35	9.11	10.09
CO/H/O[b]	−32.10	34.90	7.03	7.87	8.82	9.68	11.20	12.20	
CO/C/H[b]	−29.10	34.90	7.03	7.87	8.82	9.68	11.20	12.20	
CD/CO/O[e]	5.13	−14.60	4.40	5.37	5.93	6.18	6.50	6.62	6.72
CT/H[d]	26.93	24.70	5.28	5.99	6.49	6.87	7.47	7.96	8.85
CT/C	27.55	6.35	3.13	3.48	3.81	4.09	4.60	4.92	6.35
CT/CD[e]	28.20	6.43	2.57	3.54	3.50	4.92	5.34	5.50	5.80

[a] Chen and Bozzelli.[80] [b] Benson;[4] also used by Holmes,[71] Turecek,[69] and Cohen.[81] [c] Bozzelli et al.[82] [d] Stein and Fahr.[e] Stein and Fahr.[83] [e] Based on Bozzelli data.

TABLE 9: Thermodynamic Data Calculation for New Groups Using Group Additivity

groups	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	Diff[a]	S°_{f298} [cal (mol^{-1} K^{-1})]	$C_p(T)$ [cal (mol^{-1} K^{-1})]						
				300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
C/CO/O2/H	−14.18	−0.53	−14.14	6.04	9.48	11.37	12.16	12.38	12.39	26.19
C/CD/CO/CO/H	3.79	1.2	−9.95	5.55	8.06	9.63	10.76	11.93	12.85	41.56
C/C/CO/O2	−15.47	1.07	−38.54	6.01	8.88	10.43	10.98	10.77	10.31	23.35
C/CD2/H/O	−4.15	0.64	−12.57	2.35	4.8	5.92	6.28	6	5.67	5.88
C/CD/CO/H2	−6.37	−0.3	−1.79	9.08	11.65	13.87	15.74	18.5	20.61	37.47
C/CD2/CO/H	−1.43	−0.04	−8.81	4.74	6.23	7.36	8.17	9.01	9.63	23.91
C/CD2/O2	−15.20	−0.62	−39.25	7.83	11.51	13.29	13.62	12.55	11.34	9.74
C/CD/CO/CT/H	5.0	1.66	−25.82	−0.9	1.94	3.9	5.38	7.2	8.6	23.61
CD/O2	12.41	−0.04	−9.22	3.56	3.37	3.64	4.69	5.35	5.76	6.31
C/CB/H2/O	6.71		7.62	7.03	8.98	10.32	11.17	12.14	12.87	14.01
C/CB/C/O2	−15.53	0.46	−41.24	8.89	11.88	12.81	12.59	11.23	10.06	8.55
C/CB/C2/CO	5.53		−37.15	7.22	8.34	8.61	8.49	7.89	7.39	19.98
CD/CB/CO	12.76	1.37	−15.48	7.21	8.76	9.45	9.62	9.42	9.11	8.13
CD/CB/O	7.98	−0.79	−14.25	3.52	4.23	4.8	5.5	5.65	5.85	6.0
CD/CD/CO	7.37	−0.56	−13.16	5.03	6.57	7.55	8.12	8.56	8.57	8.06
CD/CD/O	9		−12.92	3.85	4.66	5.31	6.09	6.49	6.45	6.37
CD/CO/CT	7.02	0.17	−22.74	2.29	3.12	4.25	3.51	3.91	4.35	4.63
CB/CO	4.35	−0.17	−6.56	5.39	6.64	7.40	7.76	8.03	8.14	7.66
CO/CD/H	−29.23	−0.89	35.10	7.55	8.82	9.95	10.95	12.39	13.13	14.1
CO/CB/H[b]	−29.23		31.46	4.58	5.54	6.62	7.67	9.38	10.47	12.2
O/CB/CO	−34.99	1.05	7.64	3.84	5.25	5.88	6.16	6.11	6.97	19.07
O/CD2	−35.87	−0.92	11.18	2.91	3.24	3.61	3.97	4.39	4.33	4.35
CD/CB/H	6.66		5.47	4.01	5.66	6.84	7.62	8.61	9.23	10.13
C/CD2/C/H	−1.52 −1.10[c]	1.68	−9.60 −13.03[c]	4.89 5.28[c]	6.46 6.54[c]	7.61 7.67[c]	8.38 8.48[c]	9.3 9.45[c]	9.87 10.18[c]	10.59 11.24[c]
CD/C/CB	10.80	1.25	−14.28	3.15	4.41	5.14	5.51	5.82	5.86	5.87
CD/CB/CD	11.35	1.37	−15.78	5.52	6.56	6.95	7.04	6.9	6.51	6.06

[a] Diff is the difference between values from DFT calculations − values from G3MP2B3 calculations reported in ref 31 see text (discussion of the results, enthalpy). [b] $\Delta_f H^\circ_{298}$ and C_p are based on CO/CD/H. [c] From Green et al.[7]

reaction $CH_2{=}CHCH{=}O \rightarrow CH_2{=}CHC^{\bullet}{=}O + H$, we have

$$\Delta_f H^\circ_{298}(\text{radical}) + \Delta_f H^\circ_{298}(\text{H}) - \Delta_f H^\circ_{298}(\text{parent}) = \Delta H^\circ_{\text{rxn},298}(\text{BDE}) = \Sigma\Delta_f H(\text{products}) - \Sigma\Delta_f H(\text{reactants})$$

$$\text{BDE}(CH_2{=}CHC({=}O){-}H) = \Delta H^\circ_{\text{rxn},298} = 52.1 + (20.22) - (-18.65) = 90.97 \text{ kcal mol}^{-1}$$

Heat capacity, $C_{pf298}(T)$, is determined more directly; it is a simple difference in the corresponding $C_{pf298}(T)$ properties:

$$C_{pf298}(T)(\text{radical}) = C_{pf298}(T)(\text{parent}) - \text{HBI } C_{pf298}(T)(\text{radical})$$

The entropy (298 K) HBI group, S°_{298}, can be written as

$$[S^\circ_{298}(\text{radical})] = [S^\circ_{298}(\text{parent})S^\circ_{298} + R \ln \sigma_{\text{parent}}] + \text{HBI } S^\circ_{298}(\text{radical}) - R \ln \sigma_{\text{radical}} + R \ln(2)$$

σ is the symmetry. Electronic degeneracy (R ln(2)) of the radical

TABLE 10: Thermodynamic Properties for Bond Dissociation Energy

				$C_p(T)$ [cal (mol^{-1} K^{-1})]						
species	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	Diff[a]	S°_{f298} [cal (mol^{-1} K^{-1})]	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
C*CJC*O	112.72	0.79	1.76	2.58	3.55	4.25	4.74	5.29	5.6	6.01
O*CCJ(OH)$_2$	75.4	0.84	5.69	0.53	1.04	1.4	1.57	1.79	1.98	2.5
VCJC*OC#C	69.67	0.39	−0.88	0.62	1.19	1.72	2.19	2.98	3.6	4.6
VCJ(C*O)$_2$	72.67	−0.06	15.22	5.02	5.11	5.12	5.14	5.19	5.24	5.31
FURANJ1	122.06	−0.06	0.21	0.52	1.21	1.82	2.31	3.06	3.63	4.56
FURANJ2	122.19	−0.49	0.04	0.35	1.04	1.67	2.18	2.96	3.56	4.52
C*CCJ*O	90.97	−1.05	2.58	3.2	4.04	4.66	5.11	5.65	5.95	6.29
PhCJ*O	90.31	−0.44	0.9	−0.17	0.32	0.94	1.54	2.56	3.33	4.46
Y(C6J)*O	69.75	0.31	2.28	1.38	1.57	1.89	2.24	2.97	3.6	4.61
Y(C5)COJ*O	110.01	−1.49	1.34	0.64	1.88	2.98	3.87	5.19	6.01	6.96
Y(C5O)CJ*O	87.93	−0.58	0.27	−0.4	0.58	1.53	2.32	3.38	4.03	4.88
Y(C5)OCJ*O	96.31	−1.39	−0.94	1.73	1.94	1.83	1.72	1.79	2.21	3.44
COCJ*O	95.05	0.79	−2.28	0.23	1.03	1.91	2.72	4.06	4.76	5.65

[a] Diff is the difference between values from DFT calculations − values from G3MP2B3 calculations reported in ref 31 see text (discussion of the results, enthalpy).

electronic state is included in HBI group. The entropy value also includes correction for spin degeneracy of the electron and loss of the optical isomer, when appropriate (example: loss of H in ROOH, hydroperoxides).

The following notation is used to describe the structures and bond sites: * is for double bond, J is for radical site on a central atom, # for triple bond, Ph for phenyl (C_6H_5−), V for vinyl ($CH_2{=}CH$−) and Y designates start of a cyclic structure.

Thermochemical properties for the HBI groups are listed in Table 10. The descriptive string represents the radical structure with a J at the radical site. An example is loss of a hydrogen atom from the secondary vinylic carbon in $CH_2{=}CHCH{=}O$, represented by C*CJC*O ($CH_2{=}C^\bullet CH{=}O$). The calculated BE structures (Table 10) are represented in Table 4 with the corresponding parent and radical.

The unpaired electrons on several of the carbonyl radicals (CJ*O) in this study have the possibility for resonance overlap with adjacent unsaturated carbons. Two of these resonance systems are the C*CCJ*O group (dissociation of $CH_2{=}CHCH{=}O$ to $CH_2{=}CHC^\bullet{=}O$ + H) and the PhCJ*O group ($C_6H_5C({=}O){-}H$). One involves a vinyl and the second has a phenyl ring bonded to the CJ*O. The bond dissociation energies of these two groups are effectively identical at 90.97 and 90.31 kcal mol^{-1}. A third is the Y(C5O)CJ*O radical from Y(C_5H_5O)C(=O)−H has slightly lower bond energy, 87.81 kcal mol^{-1}, implying the ring oxygen in this structure involves more overlap and results in a more stabilized (resonant) structure with the carbonyl radical relative to the olefin or phenyl ring.

Comparison of these bond energies with those of formaldehyde and acetaldehyde shows that the bond energies are similar to more common carbonyl radicals. The bond energy in $H_2C{=}O$ to $HC^\bullet{=}O$ + H is 90.20 kcal mol^{-1} and CCJ*O (from $CH_3CH{=}O$ to $CH_3C^\bullet{=}O$ + H) determined by Gutman[38] of 89.0 kcal mol^{-1} and more recently by Lee and Bozzelli[27] 89.82 kcal mol^{-1}. The values determined from the density function calculations in this study suggest that there is little resonance overlap of the unpaired electrons on the carbonyl radicals with the adjacent unsaturated vinyl or phenyl groups. The slight increase in the bond energy, ca. 1 kcal mol^{-1}, may even indicate withdrawal of the electron from the stabilized carbonyl to the unsaturated sites being a de-stabilizing effect. Higher level calculations or calculations with a larger basis set may show more insight; with multiple configuration interaction calculations the most appropriate; but are beyond the scope of this study.

There are several other formyl radical groups in this study. Two groups have the CJ*O group attached to an ether oxygen link, where the other ether bond is to a sp^3 carbon. Our data show that the ether linked carbonyl radical, RO−CJ*O bond increases significantly, 5−7 kcal mol^{-1}, relative to normal aldehydes.[27] The COCJ*O bond energy is 95.05 in the $CH_3OCH{=}O$ to $CH_3OC^\bullet{=}O$, whereas Y(C5)OCJ*O) (Y(C=C-C=CCH−)OC$^\bullet$=O) from Y(C_5H_5)OC−H=O (Y(C=CC=CCH−)OCH=O) is even higher at 96.31 kcal mol^{-1}.

The secondary vinylic carbon−hydrogen bond in 2-propenal-2-yl radical, C*CJC*O, resulting from the dissociation of $CH_2{=}C{-}H(CH{=}O)$ has a bond of 112.72 kcal mol^{-1}. This BDE is similar to the primary vinyl bond energy of ethylene C=C−H,[39] 111.2 kcal mol^{-1}, and 7 kcal mol^{-1} stronger than the secondary vinyl C−H bond in propene,[40] 105.6 kcal mol^{-1}; the 2-propenyl radical is estimated in this study (see text above and Table 1). The carbonyl group appears to withdraw electrons from the adjacent vinyl carbons and therefore increase the dissociation energy of the C_d−H bond. Separate calculations by G3MP2B3 method support this value.[31]

The C−H bond strength in the acetaldehyde methyl group, $CH_3CH{=}O$ to $CH_2{}^\bullet CH{=}O$ + H of 96.4 kcal mol^{-1} [27] shows resonance stabilization of the methyl radical with the carbonyl of ca. 4.5 kcal mol^{-1} relative to the 101.1 value of ethane.

The C−H bond energy in the CH_3 group bonded to the carbonyl further decreases when replacing one hydrogen on the methyl by an OH, where the dissociation energy for $CH_2(OH)CH{=}O$ to $CH^\bullet(OH)CH{=}O$ + H[35] is reported as 91 kcal mol^{-1}.

We note a surprisingly large decrease of the dihydroxy carbon C−H bond energy in $CH(OH)_2CH{=}O$ to $C^\bullet(OH)_2CH{=}O$ + H. This decrease may be due to the electronegative OH groups and a resulting conjugation. The derived bond dissociation energy, (O*CCJ(OH)2) has a value of 75.4 kcal mol^{-1}, which appears abnormally low. We have looked at the structure of the corresponding radical, $C^\bullet(OH)_2CH{=}O$, as given by the density functional calculations shown in Figure 13. The geometry of the radical, which is fully optimized, shows a significant shortening of the C−C and the two C−O bond distances. That suggests resonance in the two C−O and C−C bonds. The similar bond length in the two C−O bond (1.33 Å) also suggests O−C−O resonance. The geometries of the molecule $CH(OH)_2CH{=}O$ and the radical $C^\bullet(OH)_2CH{=}O$ are given in the Supporting Information.

The Y(C5)COJ*O radical from dissociation of Y(C_5H_5)C(OH)=O [Y(C=CC=CCH−)C(=O)OH] to Y(C=CC=CCH−)C(=O)O$^\bullet$ + H), where the carboxyl group is attached to an a sp^3 carbon, has a BE of 110.01 kcal mol^{-1}. The bond dissociation energy value of benzoic acid reported by Blanksby[41] at 111 kcal mol^{-1} is slightly higher. A second comparison acid O−H bond occurs in the dissociation of prop-2-enoic acid, $CH_2{=}CHC(O{-}H){=}O$ to $CH_2{=}CHC(O^\bullet){=}O$, where we find 110.14 kcal mol^{-1}, in agreement with the three values above.

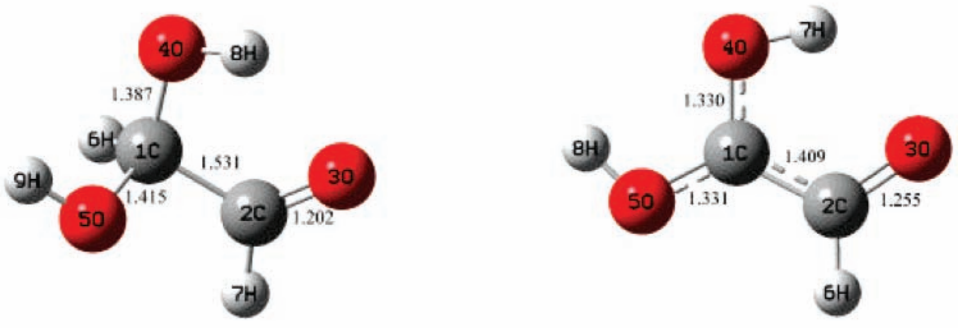


Figure 13. Dissociation of $CH(OH)_2CH{=}O$ to $C^{\bullet}(OH)_2CH{=}O$.

TABLE 11: Enthalpies of Formation (kcal mol^{-1})

species[a]	B3LYP/6-31G(d,p)	CBS-Q
$C(OO^{\bullet})H_2CHO$	−21.26 ± 0.47	−21.01 ± 0.24
$C(OOH)H_2C^{\bullet}O$	−20.33 ± 0.09	−19.64 ± 0.04
$C(OOH)H_2CHO$	−56.02	−56.19
$CH_3C({=}O)OOH$	−83.21	−84.80
$C^{\bullet}H_2C({=}O)OOH$	−32.67	−32.95
$CH_3C({=}O)OO^{\bullet}$	−37.52	−38.57

species[b]	B3LYP/6-31G(d)	B3LYP/6-311++G(3df,2p)	CBS-Q//B3LYP/6-31G(d,p)
$(CH_3)_3CCH_2OOH$	−57.28	−56.91	−58.60
$(CH_3)_3CCH_2OO^{\bullet}$	−26.54	−26.51	−27.61
$(CH_2^{\bullet})_2(CH_3)CCH_2OOH$	−8.60	−8.43	−9.43
$(CH_3)_3CCH{=}O$	−59.92	−59.28	−58.74
$CH_2{=}C(CH_3)CH_2OOH$	−20.04	−19.85	−22.35

[a] Reference 27 and 28. [b] Reference 47.

TABLE 12: Calculated Enthalpies of Formation ($\Delta_f H^{\circ}_{298}$ (kcal mol^{-1}), 298 K) for Ethers and the Corresponding Radicals[a]

	//B3LYP/6-31G(d,p)			//MP2/631G(d,p)		
	G3MP2	CBSQ	B3LYP/6-311+G(3df,2p)	G3MP2	CBSQ	MP2/6-311+G(2df,2p)
$CH_3CH_2OCH_3$	−52.28	−52.32	−52.04	−52.31	−52.35	−52.32
$(CH_3)_2CHOCH_3$	−60.04	−60.23	−59.54	−60.37	−60.26	−60.44
$(CH_3)_3COCH_3$	−67.93	−68.04	−66.51	−68.02	−68.10	−68.06
$C^{\bullet}H_2CH_2OCH_3$	−1.76	−1.77	−1.70	−1.71	−1.71	−1.64
$C^{\bullet}H_2CH(CH_3)OCH_3$	−10.03	−10.27	−9.70	−10.30	−10.27	−10.28
$C^{\bullet}H_2(CH_3)_2COCH_3$	−17.91	−18.05	−16.83	−17.94	−18.07	−17.83
$CH_3CH_2OC^{\bullet}H_2$	−8.02	−8.06	−7.89	−8.02	−8.06	−8.01
$(CH3)_2CHOC^{\bullet}H_2$	−16.71	−16.86	−16.37	−17.02	−16.89	−17.11
$(CH_3)_3COC^{\bullet}H_2$	−24.60	−24.87	−23.46	−24.68	−24.95	−24.70
$CH_3C^{\bullet}HOCH_3$	−9.17	−9.49	−9.86	−9.12	−9.42	−8.89
$(CH_3)_2C^{\bullet}OCH_3$	−16.87	−17.46	−18.09	−17.20	−17.51	−16.83

[a] Reference 29.

The cyclic group Y(C6J)*O, where the carbonyl group is adjacent to the sp^3 radical, is derived from the dissociation of $Y(C_6H_6){=}O$ to $Y(C_6H_5^{\bullet}){=}O$ ($Y(C{=}CC^{\bullet}C{=}CC{-}){=}O$) + H at 69.75 kcal mol^{-1}. VCJC*OC#C derived from $CH_2{=}CHCH(CH{=}O)C{\equiv}CH$ to $CH_2{=}CHC^{\bullet}(CH{=}O)C{\equiv}CH$ + H is 69.67 kcal mol^{-1}; both have the same bond energy about 69.7 kcal mol^{-1} due to the double allylic resonance and the resonance with the carbonyl group.

The VCJ(C*O)2 group resulting from $CH_2{=}CHCH(CH{=}O)_2$ to $CH_2{=}CHC^{\bullet}(CH{=}O)_2$ + H has resonance with two carbonyl groups C*O and results in a low C−H bond energy of 72.7 kcal mol^{-1}.

Furanj1 (the radical is on the first carbon after oxygen) and Furanj2 (the radical is on the second carbon after oxygen) have very high BDE's, 122.0 kcal mol^{-1}.

Summary

Thermodynamic properties ($\Delta_f H^{\circ}_{298}$, S°_{298} and $C_{pf298}(T)$), bond energies, barriers to internal rotations, and groups for group additivity of a series of oxygenated and non-oxygenated species are reported. Thermochemical properties, $\Delta_f H^{\circ}_{298}$, S°_{298} and $C_{pf298}(T)$ are determined for 28 species and 12 radicals. Group additivity parameters are determined for 26 groups and for 13 hydrogen bond increment groups. Energies are determined for 13 C−H or O−H bonds in unsaturated oxygenated hydrocarbons.

Appendix I: Justification for Use of B3LYP Calculations To Determine Enthalpy

B3LYP/6-311G(d,p) is commonly used for enthalpies, structure optimization, and force constant calculation.[42−44] The calculations in this study for energies are at this same level, but improved accuracy is achieved by combination of the B3LYP calculation with isodesmic work reactions chosen for error cancellation using similarity in bond environment on both sides of the reaction, whenever possible. We justify the combined use of B3LYP/6-311g(d,p) and working reactions for energy determination on the oxygenated species in this study, through comparisons between DFT values and higher level calculations in several previous publications.[30,45,46]

Sun and Bozzelli[47] report comparisons on enthalpy of formation data for a number of hydroperoxides and their

TABLE 13: Work Reaction Computations

work reactions	$\Delta H^{\circ}_{rxn,298(cal)} - \Delta H^{\circ}_{rxn,298(exp)} = X_{cal} - X_{exp}$
R1: $CH_3CH_2OH + CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2OH + CH_3CH_3$	−0.5
R2: $CH_3CH_2OH + CH_3CH{=}CH_2 \rightarrow CH_2{=}CH_2 + CH_3CH_2CH_2OH$	0.04
R3: $CH_3C({=}O)CH_3 + CH_3CH_2CH_3 \rightarrow CH_3CH_2C({=}O)CH_3 + CH_3CH_3$	0.39
R4: $CH_3CH_2CH{=}O + CH_3CH_2OH \rightarrow CH_3CH{=}O + CH_3CH_3CH_2OH$	−0.05
R5: $CH_3CH{=}O + CH_3CH_3 \rightarrow CH_3CH_2CH{=}O + CH_4$	−0.25
R6: $C_6H_5OH + CH_3OCH_3 \rightarrow CH_3OH + C_6H_5OCH_3$	1.38
R7: $CH_3CH_2^{\bullet} + CH_2{=}CH_2 \rightarrow CH_3CH_3 + CH_2{=}CH^{\bullet}$	0.03
R8: $C_6H_5^{\bullet} + CH_3CH_3 \rightarrow C_6H_6 + CH_3CH_2^{\bullet}$	−0.27
R9: $C_6H_5^{\bullet} + CH_2{=}CH_2 \rightarrow C_6H_6 + CH_2{=}CH^{\bullet}$	−0.24
R10: $C_5H_5^{\bullet} + CH_3CH_3 \rightarrow C_5H_6 + CH_3CH_2^{\bullet}$	0.25
R11: $CH_3C^{\bullet}{=}O + CH_3CH_3 \rightarrow CH_3CH{=}O + CH_3CH_2^{\bullet}$	−0.23
R12: $CH_3OOCH_3 + CH_3O^{\bullet} \rightarrow CH_3OO^{\bullet} + CH_3OCH_3$	1.15
R13: $CH_3OOCH_3 + CH_3CH_2O^{\bullet} \rightarrow CH_3OO^{\bullet} + CH_3CH_2OCH_3$	0.72
R14: $CH_3CH_2OO^{\bullet} + CH_3OH \rightarrow CH_3OO^{\bullet} + CH_3CH_2OH$	−0.71
R15: $CH^{\bullet}{=}O + CH_3OCH_3 \rightarrow CH_3CH{=}O + CH_3O^{\bullet}$	−0.78
R16: $CH_2^{\bullet}CH{=}O + CH_3OCH_3 \rightarrow CH_2^{\bullet}OCH_3 + CH_3CH{=}O$	1.0
R17: $CH_2{=}O + CH_3O^{\bullet} \rightarrow CH^{\bullet}{=}O + CH_3OH$	2.0
R18: $CH_2{=}CHOOH + CH_3CH_2O^{\bullet} \rightarrow CH_2{=}CHOO^{\bullet} + CH_3CH_2OH$	1.75
R19: $CH_2{=}CHO^{\bullet} + CH_2{=}CHOOH \rightarrow CH_2{=}CHOO^{\bullet} + CH_2{=}CHOH$	1.85
R20: $CH_2{=}CHCH_2OO^{\bullet} + CH_3OH \rightarrow CH_3OO^{\bullet} + CH_2{=}CHCH_2OH$	−0.99
R21: $C_6H_5^{\bullet} + CH_3OCH_3 \rightarrow C_6H_5OCH_3 + CH_3^{\bullet}$	−0.22
R22: $C_6H_5^{\bullet} + CH_3OH \rightarrow C_6H_5OH + CH_3^{\bullet}$	−1.60
R23: $C_6H_5O^{\bullet} + CH_3OCH_3 \rightarrow C_6H_5OCH_3 + CH_3O^{\bullet}$	−0.52
R24: $C_6H_5O^{\bullet} + CH_3CH_2OH \rightarrow C_6H_5OH + CH_3CH_2O^{\bullet}$	−1.56
R25: $C_6H_5O^{\bullet} + CH_2{=}CHOH \rightarrow C_6H_5OH + CH_2{=}CHO^{\bullet}$	−0.51
R26: $C_6H_5O^{\bullet} + CH_2{=}CHOCH_3 \rightarrow C_6H_5OCH_3 + CH_2{=}CHO^{\bullet}$	0.35
R27: $CH_2{=}CHO^{\bullet} + C_6H_5OOH \rightarrow C_6H_5OO^{\bullet} + CH_2{=}CHOH$	1.7
Average Absolute deviation = (|R1| + |R2| + ... + |R27|)/27	0.78
$S = [\Sigma(X_{cal} - X_{exp})^2/(N - 1)]^{1/2}$	1.01

corresponding radicals, whereas enthalpy values by B3 and CBS methods for hydroperoxide substituted aldehydes and radicals are reported by Lee et al.[27,28] Data are illustrated in Table 11 and Table 12. The data show good agreement between the B3LYP and the higher level calculations through a range of ether species with a number of high-level calculation methods.

A recent study by Chen et al. on oxygenated hydrocarbons, ethers, and radicals also shows very good agreement between B3 and several G3 and CBS composite methods.[29]

The use of working reactions with similar bonding environment near each atom on both sides of the equations leads to good cancellation of errors and further increases our accuracy.[22] Redfern et al. have compared the deviation of enthalpies of formation from experimental data for C_1 to C_{16} *n*-alkanes using the B3LYP method.[48] They show that use of a bond isodesmic working reaction or a homodesmic working reaction with B3LYP calculations significantly improves the absolute accuracy in the calculations.

Appendix II

Table 13 presents data on the determination of the error resulting from the computation methods using work reactions with all species having known $\Delta_f H^{\circ}_{298}$ values.

Supporting Information Available: SM1 gives the total energies at 298 K (in hartrees) based on optimized geometries. **SM2** gives the geometry parameters for unsaturated oxygenated hydrocarbons and radicals. **SM3** lists the vibration frequencies calculated for all stables and radical species at the B3LYP/6-311G(d,p) level of theory and based on optimized geometries at the same level of theory. **SM4** lists the moment of inertia for the studied unsaturated oxygenated hydrocarbons and radicals. **SM5**: Total Energy and Internal Rotation Barriers about C−C bonds in $C_6H_5C(OH)_2{-}CH_3$, $C_6H_5C({-}CH_3)_2{-}CH{=}O$, $CH_2{=}CHCH({-}CH_3)CH{=}CH_2$ and $CH_3{-}C(OH)_2{-}CH{=}O$. **SM6**: Total Energy and Internal Rotation Barriers about C−C_b and C−C_d bonds in $CH_3{-}C_6H_4CH{=}O$ and $C_6H_5{-}C({-}CH_3){=}CH_2$. **SM7**: Total Energy and Internal Rotation Barriers about C−OH bonds in $CH_2{=}CHC({-}OH)CH{=}CH_2$ and $C_6H_5CH_2{-}OH$ and C−O bonds in $CH_3{-}OCH{=}O$. **SM8**: Total Energy and Internal Rotation Barriers about C−OH bonds in $CH({-}OH)_2CH{=}O$, $CH_3C({-}OH)_2CH{=}O$, $CH_2{=}CHC({-}OH)_2{-}CH{=}CH_2$ and $C_6H_5C({-}OH)_2CH_3$. **SM9**: Total Energy and Internal Rotation Barriers about C_d−OH bonds in $CH_2{=}C({-}OH)CH{=}CH_2$, $CH_2{=}C({-}OH)_2$, $C_6H_5C({-}OH){=}CH_2$ and $CH_2{=}C({-}OH)CH{=}O$. **SM10**: Total Energy and Internal Rotation Barriers about C_d−O bonds in $CH_2{=}CH{-}OCH{=}CH_2$ and C−O bonds in $Y(C_5H_5){-}OCH{=}O$ and C_b−O bonds in $C_6H_5{-}OCH{=}O$. **SM11**: Total Energy and Internal Rotation Barriers about C−CH=O bonds in $CH_2{=}CHCH_2{-}CH{=}O$, $CH_2{=}CHCH(CH{=}CH_2){-}CH{=}O$ and $CH_2{=}CHCH(CH{=}O){-}CH{=}O$. **SM12**: Total Energy and Internal Rotation Barriers about C−CH=O bonds in $CH(OH)_2{-}CH{=}O$ and $CH_3C(OH)_2{-}CH{=}O$. **SM13**: Total Energy and Internal Rotation Barriers about C−CH=O bonds in $Y(C_5H_5O){-}CH{=}O$ and $C_6H_5{-}C(CH_3)_2{-}CH{=}O$ and about C−C(OH)O bonds in $Y(C_5H_5){-}C(OH){=}O$. **SM14**: Total Energy and Internal Rotation Barriers about C_d−C bonds in $CH_2{=}CH{-}CH_2CH{=}O$ and $CH_2{=}CH{-}CH(CH{=}O)CH{=}O$. **SM15**: Total Energy and Internal Rotation Barriers about C_d−C bonds in $CH_2{=}CH{-}C(CH_3)CH{=}CH_2$ and $CH_2{=}CH{-}C(CH{=}O)CH{=}CH_2$. **SM16**: Total Energy and Internal Rotation Barriers about C_d−C bonds in $CH_2{=}CH{-}CH(OH)CH{=}CH_2$ and $CH_2{=}CH{-}C(OH)_2CH{=}CH_2$. **SM17**: Total Energy and Internal Rotation Barriers about C_d−C_d bonds in $C_6H_5CH({=}CH_2){-}CH{=}CH_2$, $CH_2{=}C{-}(CH{=}O)CH{=}CH_2$ and $CH_2{=}C(OH){-}CH{=}CH_2$. **SM18**: Total Energy and Internal Rotation Barriers about C_d−CH=O bonds in $CH_2{=}CH{-}CH{=}O$, $CH_2{=}CHC({=}CH_2){-}CH{=}O$, $C_6H_5C({=}CH_2){-}CH{=}O$ and $CH_2{=}C(OH){-}CH{=}O$. **SM19**: Total Energy and Internal Rotation Barriers about C_b−C bonds in $C_6H_5{-}CH_2OH$, $C_6H_5{-}C(OH)_2CH_3$ and $C_6H_5{-}C(CH_3)_2CH{=}O$. **SM20**: Total Energy and Internal Rotation Barriers about C_b−CH=O bonds in $C_6H_5-CH=O$, and $CH_3C_6H_4-CH=O$. **SM21**: Total Energy and Internal Rotation Barriers about C_b-C_d bonds in $C_6H_5-CH=CH_2$, $C_6H_5-C(=CH_2)OH$, $C_6H_5-C(=CH_2)CH=CH_2$ and $C_6H_5-C(=CH_2)CH=O$. **SM22**: Total Energy and Internal Rotation Barriers about $O-CH=O$ bonds in $CH_3O-CH=O$, $C_6H_5O-CH=O$, $Y(C_5H_5)O-CH=O$ and $Y(C_5H_5)C(OH)=O$. **SM23**: Total Energy and Internal Rotation Barriers about $C-O$ and $O-C^\bullet=O$ bonds in $CH_3-OC^\bullet=O$. **SM24**: Total Energy and Internal Rotation Barriers about $C_d-C^\bullet$ bonds in $CH_2=CHC^\bullet(CH=O)CH=O$, $C^\bullet-OH$ bond in $C^\bullet(OH)_2CH=O$ and $C^\bullet-CH=O$ bond in $C^\bullet(OH)_2CH=O$. **SM25**: Total Energy and Internal Rotation Barriers about $C-C(O^\bullet)=O$ in $(YC_5H_5)-C(O^\bullet)=O$, $C-O$ and $O-C^\bullet=O$ bonds in $(YC_5H_5)O-C^\bullet=O$. **SM26**: Total Energy and Internal Rotation Barriers about $C-C^\bullet=O$ in $(YC_5H_5O)C^\bullet=O$, and $C_b-C^\bullet=O$ bonds in C_6H_5-$C^\bullet=O$. **SM27−29:** Coefficient of Truncated Fourier Series. Representation Expansions for Internal Rotation Potentials^a. **SM30:** Thermochemical Properties for species in this study. **Fig SM1−SM18**: Potential barriers for internal rotations in stable molecules and radicals. This material is available free of charge via the Internet at http://pubs.acs.org.

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