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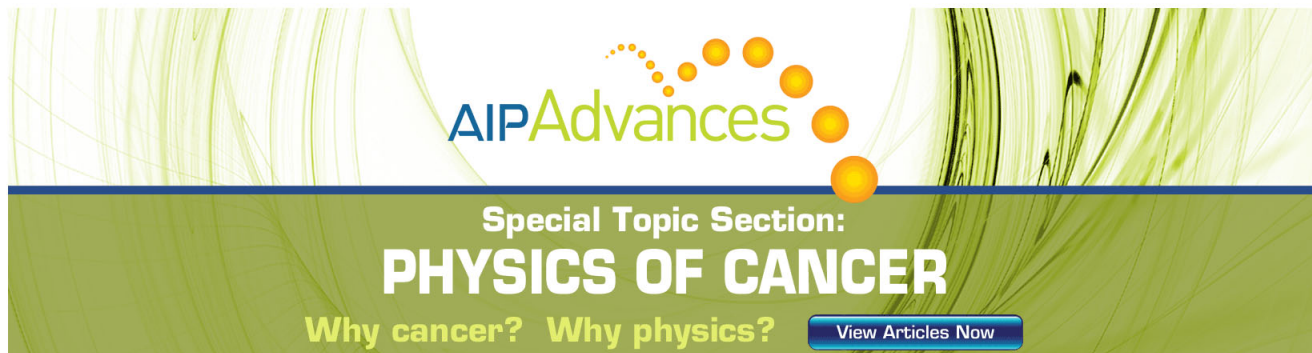
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Thermochemistry of radicals formed by hydrogen abstraction from 1-butanol, 2-methyl-1-propanol, and butanal

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We calculate the standard state entropy, heat capacity, enthalpy, and Gibbs free energy for 13 radicals important for the combustion chemistry of biofuels. These thermochemical quantities are calculated from recently proposed methods for calculating partition functions of complex molecules by taking into account their multiple conformational structures and torsional anharmonicity. The radicals considered in this study are those obtained by hydrogen abstraction from 1-butanol, 2-methyl-1-propanol, and butanal. Electronic structure calculations for all conformers of the radicals were carried out using both density functional theory and explicitly correlated coupled cluster theory with quasiperturbative inclusion of connected triple excitations. The heat capacity and entropy results are compared with sparsely available group additivity data, and trends in enthalpy and free energy as a function of radical center are discussed for the isomeric radicals. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4742968>]

I. INTRODUCTION

Small oxygen-containing radicals are present in the atmosphere and are regarded as responsible for health menaces and ozone depletion. Most reactions taking place in the troposphere involve or produce radicals. Radicals are also central to the investigation of fossil-fuel and alternative-fuel combustion, where they are important as intermediates. Therefore reliable prediction of the thermodynamic properties of radicals is required for understanding both atmospheric chemistry and energy production. Yet, thermodynamic data is much more plentiful for stable molecules than for radicals because radicals are difficult to investigate experimentally. Moreover, experimental techniques usually cover only small ranges of temperature, so when results are needed for broad temperature ranges, they usually can be obtained, if at all, only by interpolation or extrapolation, which can be unreliable. Modern theoretical methods based on the calculation of Born-Oppenheimer potential energy surfaces by electronic structure theory combined with a quantum statistical mechanical treatment of molecular partition functions do not have such limitations.

We recently developed a statistical mechanical method, called the multistructural method with torsional anharmonicity¹ (MS-T) that uses electronic structure theory to calculate thermodynamic properties of molecules and radicals having multiple conformations. We made initial applications to hydrocarbons (*n*-hexane,² 2-methylpentane,² *n*-heptane,³ and 2-methylhexane³), alcohols (ethanol,^{1,4} 1-butanol,^{1,5,6} and 2-methyl-1-propanol⁵), an aldehyde (butanal⁵), hydrocarbon radicals (1-pentyl,^{1,7} 2-pentyl,⁷ seven isomeric hexyls², 2-cyclohexyl ethyl,⁸ and 2-ethylcyclohexan-1-yl⁸), and oxygenated radicals (1-butoxyl,⁹

4-hydroxy-1-butyl,⁹ and 4-hydroxy-2-butyl⁶). In the present article, we consider the oxygenated radicals produced by hydrogen abstraction from 1-butanol, 2-methyl-1-propanol, and butanal:

- five radicals of 1-butanol: 1-butoxyl radical, 1-hydroxy-1-butyl radical, 1-hydroxy-2-butyl radical, 4-hydroxy-2-butyl radical, and 4-hydroxy-1-butyl radical;
- four radicals of 2-methyl-1-propanol: 2-methyl-1-propoxyl radical, 1-hydroxy-2-methyl-1-propyl radical, 3-hydroxy-2-methyl-2-propyl radical, and 3-hydroxy-2-methyl-1-propyl radical;
- four radicals of butanal: butanoyl radical, 1-oxo-2-butyl radical, 4-oxo-2-butyl radical, and 4-oxo-1-butyl radical.

We show the radicals and their names in Figure 1. Since most of them have a large number of conformational minima due to internal rotation (up to 19 pairs of mirror images yielding 38 distinguishable structures), we compute partition functions of all the radicals by employing the MS-T method incorporating all the conformers, which are also called structures.

The purpose of this study is to

- demonstrate the systematic application of the statistical mechanical method to families of radicals more complex than any treated previously;
- provide reliable thermodynamic data that can be used for atmospheric and combustion models;
- investigate enthalpy trends in the radicals that have the same chemical composition but different location of the radical center;
- compare the results of the multi-structural statistical mechanics method to thermodynamic properties calculated using Benson's group additivity rules for entropy, and heat capacity.

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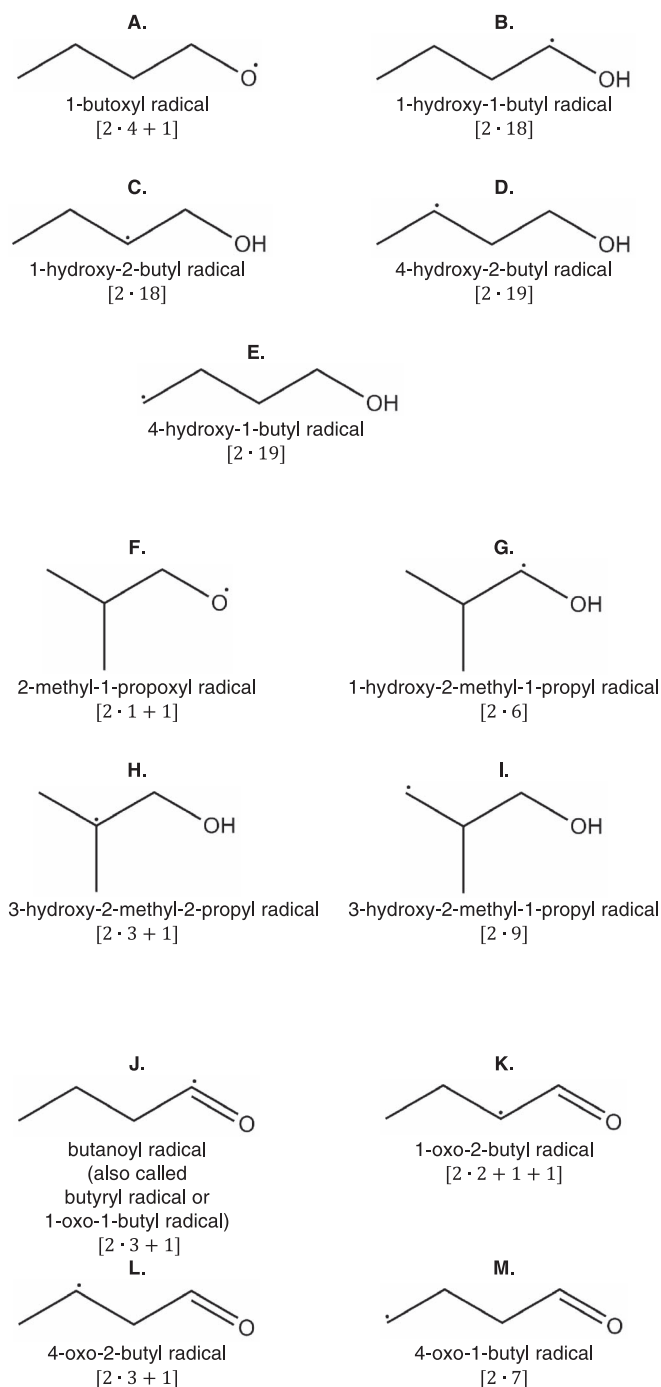


FIG. 1. Structures and names of radicals of 1-butanol, 2-methyl-1-propanol, and butanal studied in this work. The totals in the parentheses $[2 \cdot a + b + c]$ indicate the number of distinguishable conformational structures included in the calculations in our partition function calculations, where a is a number of pairs of mirror images, and $b \neq 1$ and $c \neq 1$ indicate existence of one (when $b = 1$ and $c = 0$) or two (when $b = 1$ and $c = 1$) conformers that are superimposable with their own mirror images.

Group additivity (GA) is widely used to compute thermodynamic properties of unknown molecules by using available data on similar compounds. In GA schemes, thermodynamic properties, such as entropy, enthalpy, and heat capacity, are estimated as additive sums of contributions from their component groups. The values for the contributions one uses to calculate a property of an unknown system are

empirically established and depend on the atomic numbers of the atoms and their bonded neighbors. Due to its empiricism and to the neglect of general intergroup interactions, group additivity is more reliable for molecules typical of those well represented in the training set than it is for radicals and less studied species. Numerous group additivity schemes have been developed;^{10–16} however, Benson's version¹⁷ is the most widely used. Large sets of parameters for stable molecules have been expanded and improved over the years by Benson and co-workers and other researchers.^{17–21} Literature on additivity rules for radicals is scarcer, but group additivity values are available for hydrocarbon radicals^{22–26} and for some oxygen-containing radicals.^{27–30} In this work, we compare our results to those calculated by Benson's group additivity using parameters from Refs. 17, 28, and 29.

II. COMPUTATIONAL DETAILS

Conformational geometry optimizations and frequency calculations for all the conformations of all the radicals were performed using the GAUSSIAN 09 (Ref. 31) program with the MN-GFM (Ref. 32) density functional extension. Stationary point searches were carried out with the M08-HX density functional³³ and the MG3S basis set³⁴ for 1-butanol and 2-methyl-1-propanol radicals and with M08-HX and the minimally augmented correlation consistent polarized valence-triple- ζ (maug-cc-pVTZ) basis set^{35–38} in the case of butanal radicals. Note that for the elements in this study (C, H, and O), the MG3S basis set is the same as the 6-311+G(2df,2p) basis set of Pople and co-workers.³⁹ After the initial conformational minima were found using an ultrafine grid for the density functional integrations, all the unique geometries were refined with an even finer grid having 99 radial points and 974 angular points and tight convergence criteria with a maximum force threshold of $0.000015 E_h/a_0$ or $0.000015 E_h/\text{rad}$ and a maximum displacement of $0.000060 a_0$ or 0.000060 rad (note: $1 E_h = 1$ hartree; $1 a_0 = 1$ bohr; $1 \text{ rad} = 1$ radian). Frequency calculations were performed for the refined structures. All frequencies were scaled by standard scale factors⁴⁰ of 0.973 and 0.976 for M08-HX/MG3S and M08-HX/maug-cc-pVTZ calculations, respectively. (This scale factor is the one that brings the zero point energy computed with harmonic oscillator formulas close to the experimental zero point energy, and it is used throughout this article except for the SS-HO results (Sec. III.D).)

In order to improve the accuracy of the conformational energy values from electronic structure calculations, single-point energy calculations were performed using explicitly correlated coupled cluster theory with single and double excitations and a quasiperturbative treatment of connected triple excitations. In particular, we used the CCSD(T)-F12a method⁴¹ with the jul-cc-pVTZ basis set³⁸ as the one-electron basis set for alcohol-derived radicals and the jun-cc-pVTZ basis set⁴² as the one-electron basis set for butanal-derived radicals. The “jun-” and “jul-” basis sets are less expensive alternatives to the original “aug-” scheme for adding diffuse basis functions. The jul-cc-pVTZ basis set is like the aug-cc-pVTZ except that the diffuse functions are omitted on the hydrogen atoms. The jun-cc-pVTZ basis set differs

from jul-cc-pVTZ in that the diffuse *f* functions are omitted on C and O. These “seasonal” basis sets have been tested and validated in Refs. 37, 38, 42, and 43. CCSD(T)-F12a calculations are coupled cluster calculations that employ a conventional expansion in Slater determinants formed from a one-electron Gaussian basis and augment this with excitation amplitudes corresponding to excitations into explicitly correlated functions^{44–55} containing short-range correlation. The basis set convergence with respect to the one-electron basis is much faster than for conventional CCSD(T) calculations such that the jul-cc-pVTZ and jun-cc-pVTZ basis sets should yield results close to the complete basis set limit.

The coupled cluster calculations were carried out using the MOLPRO 09 program suite.⁵⁶ These single-point energy calculations were used to upgrade the thermodynamics calculations, and in Sec. III we compare the upgraded calculations to the results obtained by using M08-HX/MG3S energies.

The partition function calculations were carried out using the MSTor computer program.^{57,58} In this program, the total partition function Q is calculated as a product of the translational (Q_{trans}), electronic (Q_{elec}), and conformational—rotational—vibrational ($Q_{\text{con-rovib}}$) partition functions.¹

$$Q = Q_{\text{trans}} Q_{\text{elec}} Q_{\text{con-rovib}}. \quad (1)$$

In the present article, we employ two multi-structural (MS) approximations to the $Q_{\text{con-rovib}}$ term that we described in Ref. 1. Both of them calculate the conformational—rotational—vibrational partition function as a sum over the contributions of all conformational structures for a given molecule, but they differ in how the individual contributions are put together.

In the first method, called the MS local quasiharmonic (MS-LQ) method, we calculate the contribution to the partition function for each structure as a product of the classical approximation to the rotational partition function and a local quasiharmonic oscillator approximation to the vibrational partition function. The quasiharmonic approximation uses the harmonic oscillator formulas, but with scaled frequencies, where the scaling corrects in an approximate way for anharmonicity as well as for the systematic overestimation in the higher frequencies by the electronic structure calculations. Therefore the MS-LQ (formerly called MS-LH for “local harmonic” because the formulas are based on the harmonic oscillator) results are partially anharmonic. In the second method, called MS-T, we improve upon the MS-LQ partition function by including factors for torsional potential anharmonicity. For a molecule with t torsions, there are $t + 1$ factors for each structure.¹ The first factor ensures that the partition function reaches the correct free-rotor limit in the high-temperature limit. The other factors adjust the harmonic result for the anharmonicity of each of the t internal-coordinate torsions.

Subsequently, based on the partition functions just described, which will be called Q_{elec} , $Q_{\text{con-rovib}}^{\text{MS-LQ}}$, and $Q_{\text{con-rovib}}^{\text{MS-T}}$, the standard state thermodynamic functions (enthalpy H_T° , heat capacity C_p° , entropy S_T° , and Gibbs free energy G_T°) are computed based on the total partition function by standard

formulas:

$$H_T^\circ = -\frac{\partial \ln Q}{\partial \beta} + k_B T, \quad (2)$$

$$C_p^\circ(T) = -\left(\frac{\partial H^\circ}{\partial T}\right)_p, \quad (3)$$

$$S_T^\circ = k_B + k_B \ln Q - \frac{1}{T} \left(\frac{\partial \ln Q}{\partial (1/(k_B T))}\right)_V, \quad (4)$$

and

$$G_T^\circ = H_T^\circ - T S_T^\circ, \quad (5)$$

where $^\circ$ denotes the standard state (1 bar pressure), k_B is Boltzmann’s constant, T is temperature, and Q is the partition function with the zero of energy at the vibrational zero point exclusive energy of the structure of the radical that has the lowest zero-point-inclusive energy. (This structure is called the global minimum (GM) and the choice of zero of energy is a special case of our general convention that partition functions without a tilde have their zero of energy at the local minimum of the Born-Oppenheimer potential energy surface.) The thermodynamic quantities above have been computed for a range of temperature and are given in Sec. III and in the supplementary material. In the case of enthalpy and Gibbs free energy, we list H_T° and G_T° values, where the subscript T refers to temperature. Note that, since our calculations are carried out for the gas phase, the thermodynamic data listed for the low temperatures (below the boiling or melting point) refer to the vapor phase above the liquid or solid.

III. RESULTS AND DISCUSSION

Figure 2 depicts the notation that we adopted for specific ranges of dihedral angles in order to label the conformational structures of the radicals. We follow the recommendations of International Union of Pure and Applied Chemistry (IUPAC) on nomenclature of the torsion angles.⁵⁹ Thus **T**, **T**⁺, and **T**[−] stand for “trans” and correspond to 180° exactly, (+150° to

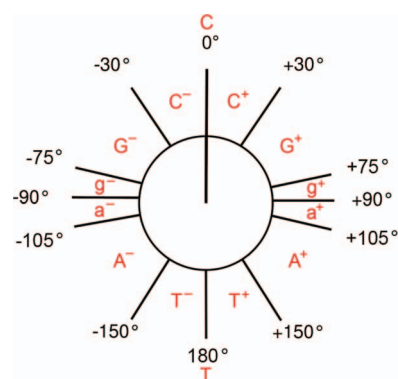


FIG. 2. Labeling scheme used in this article to define structures by their dihedral angles.

+180°), and (−150° to −180°), respectively. **C**, **C+**, and **C−** stand for “cis” and correspond to angles of exactly 0°, (0° to +30°), and (0° to −30°), respectively. Similarly, “gauche” and “anti” span the ranges of (±30°, ±90°) and (±90°, ±150°). In order to differentiate those gauche angles that are far from the typical ±60° and closer to ±90°, we chose to split the “gauche” range into two sub-ranges: **G±** (±30°, ±75°) and **g±** (±75°, ±90°). A similar division was made for the “anti” configuration by assigning **a±** to (±90°, ±105°) angle values and **A±** to those within (±105°, ±150°).

When labeling conformational structures we always start from the first torsion on the O-side of the chain and move by one bond along the chain. For example, structure **C+T−G+** of the 1-hydroxy-1-butyl radical corresponds to the conformer in which the first (H−O−C−C) torsional angle is +24.8°, the second (O−C−C−C) torsional angle is −173.0°, and the third (C−C−C−C) torsional angle is +65.0°. Rotation around the fourth bond, (C−C−C−H), does not produce distinguishable structures and is therefore omitted in labeling of the conformational structures.

All the alcohol-derived radicals considered in this article have the chemical formula C₄H₉O. Similarly, all the butanal-derived radicals have the same molecular composition (C₄H₇O). If the enthalpies and free energies of these radicals are computed with respect to a common zero of energy they may be considered a measure of relative stability of the isomeric radicals. That is why we defined the absolute zero of energy as the zero-point exclusive energy of the lowest energy structure of the GM. In the case of alcohol-derived radicals the GM is the **T+G−**, **T−G+** structure of 1-hydroxy-2-methyl-1-propyl radical, whereas for aldehyde-derived radicals, the **CT** structure of butanoyl radical is the GM. For other uses, some readers may wish to convert the zero of energy to either the equilibrium structure or the ground-state level of a particular radical of interest. That can easily be done with the data provided in our tables because we give the Born-Oppenheimer energy and zero-point inclusive energy of every structure of every radical in Tables I–VII.

In Tables I–VII we list the conformational structures for all the radicals, and Tables VIII–XIII provide their computed thermodynamics properties for three temperature values for H_T° and G_T° and three-to-six temperatures for S_T° and $C_p^\circ(T)$. Supplementary material includes data for a wider range of

TABLE I. Energy (kcal/mol, relative to the lowest energy structure of 1-hydroxy-2-methyl-1-propyl) of conformers of the 1-butoxyl radical.

Structure	Equilibrium ^a	0 K ^b
G+T−, G−T+	11.868	86.401
G+G+, G−G−	12.364	87.229
g+G−, g−G+	12.394	87.535
TT	12.198	86.464
T+G+, T−G−	12.676	87.591

^aCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy. The equilibrium energy is the Born-Oppenheimer energy at the local minimum of the potential energy surface.

^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy plus M08-HX/MG3S zero-point vibrational energy scaled by 0.973.

TABLE II. Energy (kcal/mol, relative to the lowest energy structure of 1-hydroxy-2-methyl-1-propyl) of conformers of the 1-hydroxy-1-butyl radical.

Structure	Equilibrium ^a	0 K ^b
T+G+G+, T−G−G−	1.493	76.997
T+G+T−, T−G−T+	1.318	76.749
T+G−G−, T−G+G+	1.500	76.941
C+G−G−, C−G+G+	1.883	77.361
T+G−T+, T−G+T−	1.220	76.656
T+T+G−, T−T−G+	1.818	77.128
T+T+T+, T−T−T−	1.496	76.733
C+G+G+, C−G−G−	1.854	77.240
C+T−G+, C−T+G−	1.963	77.294
C+g−T−, C−g+T+	1.697	77.117
C+g+G−, C−g−G+	2.103	77.511
T+g−G+, T−g+G−	1.956	77.392
C+T−T−, C−T+T+	1.680	76.916
C+g−G+, C−g+G−	2.387	77.874
C+G+T−, C−G−T+	1.667	77.025
T+T+G+, T−T−G−	2.073	77.400
T+g+G−, T−g−G+	2.314	77.730
C+T−G−, C−T+G+	2.202	77.548

^aCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy. The equilibrium energy is the Born-Oppenheimer energy at the local minimum of the potential energy surface.

^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy plus M08-HX/MG3S zero-point vibrational energy scaled by 0.973.

temperature.⁶⁰ Where GA parameters are available, we compare our results to values computed using these parameters.

III.A. 1-butanol radicals

We have identified nine distinguishable conformers (four pairs of mirror images plus one symmetrical structure **TT**)

TABLE III. Energy (kcal/mol, relative to the lowest energy structure of 1-hydroxy-2-methyl-1-propyl) of conformers of the 1-hydroxy-2-butyl radical.

Structure	Equilibrium ^a	0 K ^b
G+G+G+, G−G−G−	6.241	81.323
G+G+T−, G−G−T+	5.913	80.850
G+T−T+, G−T+T−	6.084	80.896
G+G+a−, G−G−a+	6.219	81.235
G+T−G−, G−T+G+	6.386	81.383
T−G+G+, T+G−G−	6.992	81.904
G+A−g+, G−A+g+	6.595	81.540
G+g+G−, G−g−G+	6.929	81.930
G−a+G−, G+a−G+	6.645	81.734
T−G+T−, T+G−T+	6.889	81.513
T−G+a−, T+G−a+	7.030	81.926
G+T−G+, G−T+G−	7.059	82.050
G+G−T−, G−G+T+	7.059	81.444
G+G−G−, G+G+G+	7.364	81.961
G+G−G−, G−G+G+	7.399	82.427
T−T−T+, T+T+T−	7.602	82.491
T+T+G+, T−T−G−	7.661	82.255
T+G+G−, T−G−G+	7.477	82.493

^aCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy. The equilibrium energy is the Born-Oppenheimer energy at the local minimum of the potential energy surface.

^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy plus M08-HX/MG3S zero-point vibrational energy scaled by 0.973.

TABLE IV. Energy (kcal/mol, relative to the lowest energy structure of 1-hydroxy-2-methyl-1-propyl) of conformers of the 4-hydroxy-2-butyl radical.

Structure	Equilibrium ^a	0 K ^b
G+G-T+, G-G+T-	4.778	79.604
G+G-G-, G-G+G+	5.327	80.263
G-G+G+, G+G-G-	5.055	79.919
G+G-A+, G-G+A-	5.276	80.067
G+G+T+, G-G-T-	5.645	80.222
T-G+T+, T+G-T-	5.641	80.313
G+G+G+, G-G-G-	6.189	80.936
T-G+g-, T+G-g+	5.746	80.551
T+T+T+, T-T-T-	5.703	80.183
G+G+g-, G-G-g+	5.863	80.716
G+T-T-, G-T+T+	5.755	80.199
G+T+T+, G-T-T-	5.765	80.232
T+G+G+, T-G-G-	6.336	80.980
G+T+G-, G-T-G+	5.798	80.527
G+T-G+, G-T+G-	5.844	80.552
T-T-G+, T+T+G-	5.979	80.597
T-G+G-, T+G-G+	6.808	81.641
G+G+G-, G-G-G+	6.833	81.616
G+g-C+, G-g+C-	6.959	81.984

^aCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy. The equilibrium energy is the Born-Oppenheimer energy at the local minimum of the potential energy surface.

^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy plus M08-HX/MG3S zero-point vibrational energy scaled by 0.973.

for the 1-butoxyl radical, 36 conformers (18 pairs of mirror images) each for the 1-hydroxy-1-butyl and 1-hydroxy-2-butyl radicals, and 38 conformers (19 pairs of mirror images) each for the 4-hydroxy-2-butyl and 4-hydroxy-1-butyl radicals. Tables I–V list all of the conformers along with their equilibrium energy (sometimes called the Born-Oppenheimer

TABLE V. Energy (kcal/mol, relative to the lowest energy structure of 1-hydroxy-2-methyl-1-propyl) of conformers of the 4-hydroxy-1-butyl radical.

Structure	Equilibrium ^a	0 K ^b
G-G+G-G-, G+G-G+G+	7.778	82.783
G+G-G-C-, G-G+G+C+	8.315	83.278
T-G+G+G+, T+G-G-G-	8.105	82.849
T+G-T+C-, T-G+T-C+	8.162	82.729
G+G+G+C+, G-G-G-C-	8.193	82.725
T-G+T+C-, T+G-T-C+	8.378	83.056
G-G-T+C-, G+G+T-C+	8.288	82.832
G+G+T-C-, G-G-T+C+	8.290	82.817
T+T+G+C+, T-T-G-C-	8.488	83.119
G+T+G-C-, G-T-G+C+	8.564	83.254
G+T+G+G+, G-T-G-G-	8.608	83.235
G+G-T-C-, G-G+T+C+	8.490	83.088
G-G+T+C-, G+G-T-C+	8.532	83.082
T-T-T+C-, T+T+T-C+	8.545	82.972
G+T+T-C-, G-T-T+C+	8.511	83.020
G+T+T+C-, G-T-T-C+	8.561	82.981
G-G-g+G+, G+G-g-G-	9.567	84.219
T-T+T+g-, T+T-T-g+	8.750	83.314
T-G+g-C+, T+G-g+C-	9.526	84.138

^aCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy. The equilibrium energy is the Born-Oppenheimer energy at the local minimum of the potential energy surface.

^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy plus M08-HX/MG3S zero-point vibrational energy scaled by 0.973.

TABLE VI. Energy (kcal/mol, relative to the lowest energy structure of 1-hydroxy-2-methyl-1-propyl) of conformers of the 2-methyl-1-propanol radicals.

Structure	Equilibrium ^a	0 K ^b
2-methyl-1-propoxyl		
G-, G+	10.210	84.607
T	10.391	84.753
1-hydroxy-2-methyl-1-propyl		
T+G-, T-G+	0.000	75.106
T+G+, T-G-	0.118	75.212
C-G-, C+G+	0.341	75.487
T+T+, T-T-	0.522	75.762
C-G+, C+G-	0.505	75.592
G+T-, G-T+	0.932	76.133
3-hydroxy-2-methyl-2-propyl		
G+C-, G-C+	2.092	76.728
T-G-, T+G+	3.095	77.553
TT	2.924	77.369
G+G+, G-G-	3.536	77.942
3-hydroxy-2-methyl-1-propyl		
G-T-G+, G+T+G-	6.554	81.132
G+G+G-, G-G-G+	6.518	81.101
G+G+g-, G-G-g+	6.536	80.933
T-G-G+, T+G+G-	6.900	81.293
T+G+G+, T-G-G-	7.000	81.392
G+G-G+, G-G+G-	6.949	81.319
G-G-G+, G+G+G-	6.980	81.382
G+T+C-, G-T-C+	7.534	82.040
T-T-C-, T+T+C+	7.618	82.112

^aCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy. The equilibrium energy is the Born-Oppenheimer energy at the local minimum of the potential energy surface.

^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy plus M08-HX/MG3S zero-point vibrational energy scaled by 0.973.

energy, the zero-point exclusive energy, the classical energy, the electronic energy, or the electronic energy including nuclear repulsion) and their zero-point-inclusive energy (which may also be called the 0 K energy or ground-vibrational-state energy). The equilibrium energies are presented as calculated by CCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S (where, as usual, A//B denotes a single-point energy calculation by method A at a geometry optimized by method B), and the zero-point-inclusive energies are presented only as calculated by CCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy plus M08-HX/MG3S zero-point vibrational energy with scaled frequencies.

The five lowest-energy structures of each radical are illustrated in Figure 3. The M08-HX/MG3S and CCSD(T)-F12a/jul-cc-pVTZ methods identify different structures as having the lowest equilibrium energy for the 1-hydroxy-1-butyl and 1-hydroxy-2-butyl radicals, whereas they identify the same lowest-equilibrium-energy structure for the other three radicals produced from 1-butanol. Another noteworthy difference in the predictions of the two methods is that in the cases of the 1-hydroxy-2-butyl and 4-hydroxy-1-butyl radicals the variation in the conformational energy is significantly lower in the coupled cluster calculations than in the density functional calculations.

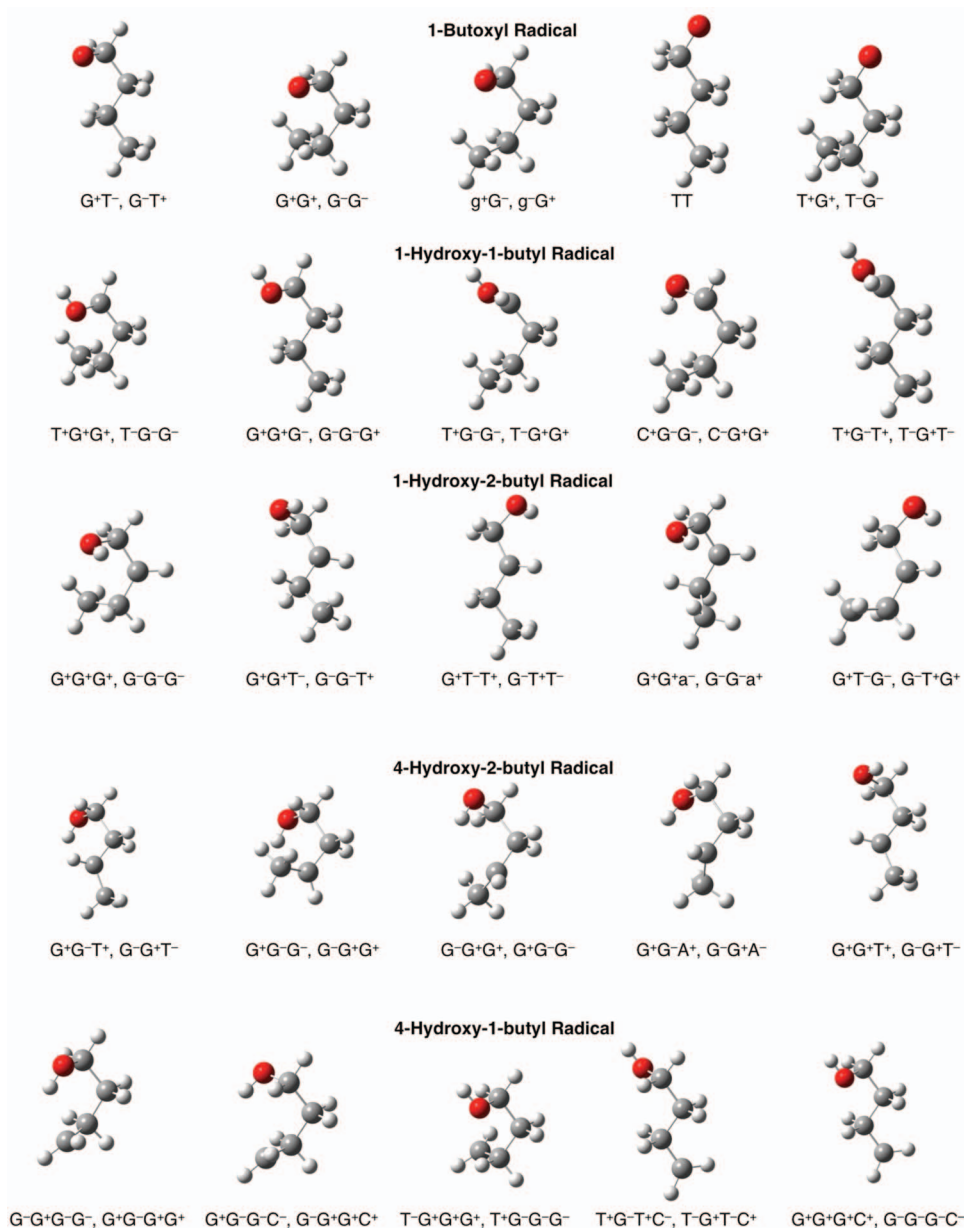


FIG. 3. Lowest energy conformers for 1-butanol radicals.

Table VIII provides the thermodynamics properties of the five 1-butanol radicals. Where group additivity coefficients are available, Table IX compares them to those obtained in this study. For 1-butoxyl radical, 4-hydroxy-2-butyl radical, and 4-hydroxy-1-butyl radical, there are two sets of parameters available for calculations of heat capacity and entropy by group additivity. The values in the column on the left were obtained using parameters taken from the second edition of Benson's book on thermochemical kinetics.¹⁷ The values on the right were obtained using a combination of parameters by Benson¹⁷ and more recently established parameters taken from Khan *et al.*²⁸ and Sabbe *et al.*²⁹ With one exception (M08-HX/MG3S results for 4-hydroxy-2-butyl) all of the heat capacity values computed by GA are lower than those computed in the present work. The coupled cluster results vary slightly more from the group additivity ones than do the DFT results. The heat capacities differ by as much as

1.8 cal mol⁻¹ K⁻¹ and 1.0 cal mol⁻¹ K⁻¹ in the case of the more recent parameters. In the case of entropy we find better agreement of DFT and CC results with group additivity for radicals than we found previously^{1,5} for 1-butanol, with mean error in the present case averaging 1.6 cal K⁻¹ mol⁻¹ and the highest error being 3.5 cal mol⁻¹ K⁻¹.

Comparing Gibbs free energy values for the radicals, all relative to the same zero of energy, one can also draw conclusions on their relative stability. Comparison of G_{298}° of the alcohol radicals leads to the conclusion that 1-hydroxy-1-butyl radical is the most stable product of the hydrogen abstraction from 1-butanol. It has a significantly lower G_T° than all the other radicals, by 2.7–10.8 kcal mol⁻¹ at 298 K, 2.1–12.7 kcal mol⁻¹ at 800 K, and 0.9–16.2 kcal mol⁻¹ at 2000 K. The Gibbs free energy increases in the following order: 1-hydroxy-1-butyl < 4-hydroxy-2-butyl < 1-hydroxy-2-butyl < 4-hydroxy-1-butyl < 1-butoxyl radical.

TABLE VII. Energy (kcal/mol, relative to the lowest energy structure of 1-hydroxy-2-methyl-1-propyl) of conformers of the butanal radicals.

Structure	Equilibrium ^a	0 K ^b
butanoyl		
C+G+, C-G-	0.053	61.910
CT	0.000	61.729
T-G+, T+G-	0.374	61.993
A-T-, A+T+	0.616	62.180
1-oxo-2-butyl		
C-A+, C+A-	2.241	63.625
CC	4.521	65.891
T+A+, T-A-	2.904	64.155
TC	3.890	65.286
4-oxo-2-butyl		
CT	11.457	71.269
C-G+, C+G-	11.598	71.820
a-g+, a+g-	11.281	71.558
A-T+, A+T-	12.217	72.102
4-oxo-1-butyl		
C+T-T-, C-T+T+	13.944	73.995
C+G+T-, C-G-T+	14.512	74.569
C+G+G-, C-G-G+	14.131	74.384
A-T-C+, A+T+C-	14.951	74.965
A-T-C-, A+T+C+	15.006	74.971
A-G+C+, A+G-C-	14.613	74.633
A-G-T+, A+G-T-	15.114	75.208

^aCCSD(T)-F12a/jun-cc-pVTZ//M08-HX/maug-cc-pVTZ electronic energy. The equilibrium energy is the Born-Oppenheimer energy at the local minimum of the potential energy surface.

^bCCSD(T)-F12a/jun-cc-pVTZ//M08-HX/maug-cc-pVTZ electronic energy plus M08-HX/maug-cc-pVTZ zero-point vibrational energy scaled by 0.976.

The impact of anharmonicity and multi-structural effects on the calculated relative stability is discussed in Sec. III.D.

III.B. 2-methyl-1-propanol radicals

We found three conformers (one pair of mirror images plus one symmetrical structure T) for the 2-methyl-1-propoxyl radical, 12 conformers (six pairs of mirror images) for the 1-hydroxy-2-methyl-1-propyl radical, seven conformers (three pairs of mirror image plus one image-superimposable structure) for the 3-hydroxy-2-methyl-2-propyl radical, and 18 conformers (nine pairs of mirror images) for the 3-hydroxy-2-methyl-1-propyl radical. Up to five lowest-energy structures of each radical are illustrated in Figure 4. Table VI lists all of the conformers and their classical CCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S energy values and CCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy plus M08-HX/MG3S zero-point-vibrational energy point conformational energy values. In the case of 2-methyl-1-propanol radicals prediction of the lowest energy structure based on M08-HX/MG3S and CCSD(T)-F12a/jul-cc-pVTZ energy values differs slightly (by 0.04 kcal/mol) only for one case: 3-hydroxy-2-methyl-1-propyl radical.

Table X summarizes the thermodynamics properties of the 2-methyl-1-propanol radicals. Variation in the Gibbs free energy values for these radicals is less than what we observed in the case of 1-butanol radicals. G values for the alkyl radicals increase as the radical center is located

TABLE VIII. Standard state thermodynamic properties, viz., enthalpy (H_T° in kcal mol⁻¹), heat capacities ($C_p^\circ(T)$ in cal K⁻¹ mol⁻¹), entropy (S_T° in cal K⁻¹ mol⁻¹), and Gibbs free energies (G_T° in kcal mol⁻¹) of 1-butanol-derived radicals. The zero of energy for this table is the zero-point-exclusive energy of the T+G- or T-G+ structures of 1-hydroxy-2-methyl-1-propyl.

T (K)	MS-T		MS-T	
	M08-HX ^a	CC ^b	M08-HX ^a	CC ^b
1-butoxyl radical				
		H_T°		$C_p^\circ(T)$
298	91.761	91.741	26.444	26.749
800	111.758	111.785	50.328	50.353
2000	186.201	186.240	68.888	68.891
		S_T°		G_T°
298	86.288	86.161	66.047	66.065
800	123.665	123.652	12.826	12.863
2000	179.199	179.197	-172.197	-172.154
1-hydroxy-1-butyl radical				
		H_T°		$C_p^\circ(T)$
298	82.127	82.203	26.630	26.709
800	101.831	101.922	49.282	49.304
2000	174.742	174.856	67.619	67.633
		S_T°		G_T°
298	90.368	90.306	55.198	55.292
800	127.260	127.232	0.022	0.136
2000	181.633	181.623	-188.525	-188.390
1-hydroxy-2-butyl radical				
		H_T°		$C_p^\circ(T)$
298	86.981	86.548	26.312	26.466
800	106.552	106.158	49.222	49.270
2000	179.493	179.137	67.643	67.663
		S_T°		G_T°
298	91.771	91.643	59.633	59.238
800	128.357	128.314	3.867	3.507
2000	182.725	182.713	-185.957	-186.289
4-hydroxy-2-butyl radical				
		H_T°		$C_p^\circ(T)$
298	85.649	85.373	26.061	25.822
800	105.131	104.827	49.180	49.196
2000	178.126	177.858	67.705	67.732
		S_T°		G_T°
298	91.906	91.933	58.261	57.977
800	128.287	128.240	2.501	2.235
2000	182.680	182.659	-187.233	-187.462
4-hydroxy-1-butyl radical				
		H_T°		$C_p^\circ(T)$
298	88.661	88.115	26.492	26.138
800	108.480	107.872	49.772	49.749
2000	182.086	181.498	68.236	68.262
		S_T°		G_T°
298	90.907	91.011	61.571	60.994
800	127.946	127.904	6.123	5.549
2000	182.815	182.784	-183.545	-184.070

^aThe basis set used for M08-HX is MG3S.

^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S.

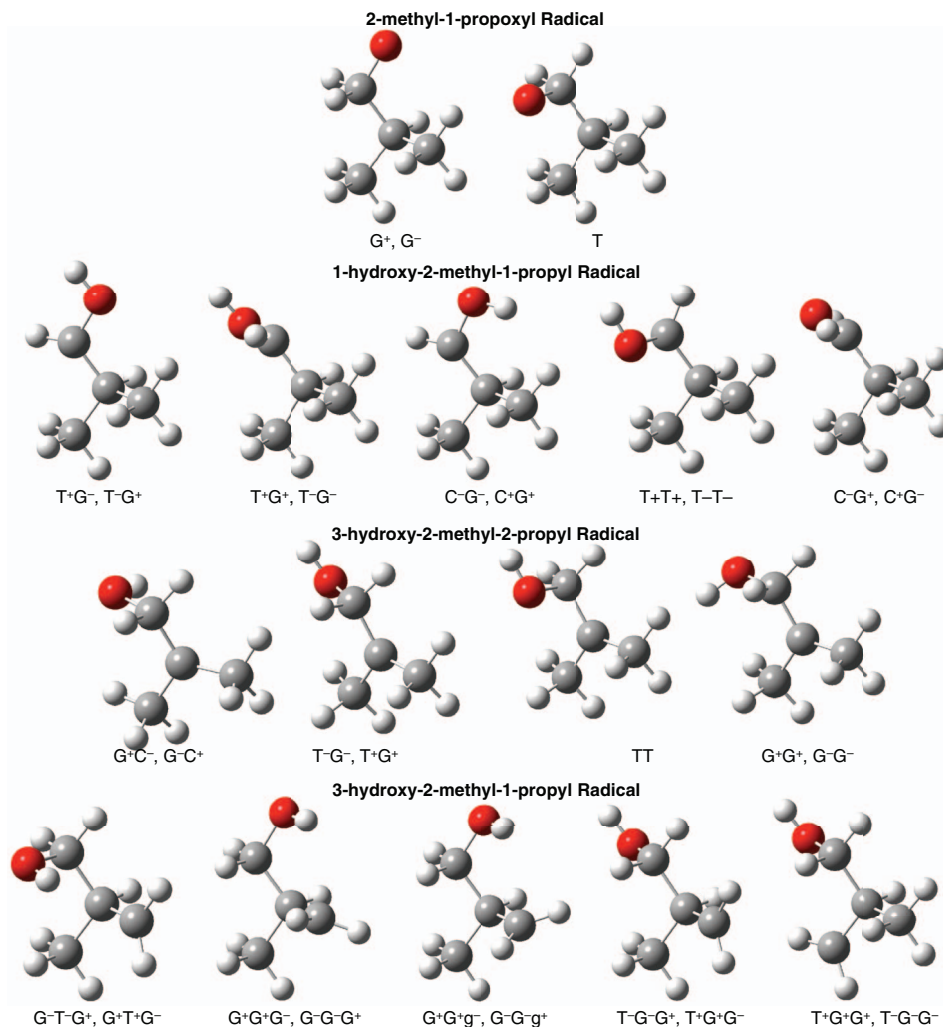


FIG. 4. Lowest energy conformers for 2-methyl-1-propanol radicals.

farther away from $-OH$ group along the heavy-atom chain. Figure 6 depicts comparison of G_T° at 298 K of the alcohol radicals. 1-hydroxy-2-methyl-1-propyl radical is the most stable product of the hydrogen abstraction from 2-methyl-1-propanol and the most stable among the alcohol derived radicals in this study. For the 2-methyl-1-propanol radicals the Gibbs free energy increases in the following order: 1-hydroxy-2-methyl-1-propyl < 3-hydroxy-2-methyl-2-propyl < 3-hydroxy-2-methyl-1-propyl < 2-methyl-1-propoxyl radical. The importance of anharmonicity and multi-structural effects in these calculations is discussed in Sec. III.D.

Table XI compares heat capacity and entropy values computed in this work to the group additivity values, considering large variation within the GA values computed with different parameters, it shows very good agreement.

III.C. Butanal radicals

We have optimized seven conformers (three pairs of mirror images plus one symmetrical CT structure) for the butanoyl radical, six conformers (two pairs of mirror images and two different structures superimposable with their own

images) for the 1-oxo-2-butyl radical, 7 conformers (three pairs of mirror images and one CT symmetrical structure) for the 4-oxo-2-butyl radical, and 14 conformers (seven pairs of mirror images) for the 4-oxo-1-butyl radical. Figure 5 illustrates up to five lowest-energy structures of each radical of butanal. Table VII lists all of the conformers and their classical CCSD(T)-F12a/jun-cc-pVTZ//M08-HX/maug-cc-pVTZ electronic energy plus M08/HX/maug-cc-pVTZ zero-point-vibrational energy. Similarly to 2-methyl-1-propanol radicals, prediction of the lowest energy structure for butanal based on M08-HX/maug-cc-pVTZ and CCSD(T)-F12a/jun-cc-pVTZ energy values agrees for all but one case: butanoyl radical with an 0.05 kcal/mol difference in conformational energy.

Table XII depicts the standard state thermodynamic properties, viz., enthalpy, heat capacity, entropy, and free energies for the butanal-derived radicals under consideration at temperatures 298, 800, and 2000 K. The lowest free energy belongs to butanoyl radical and the highest to the 4-oxo-1-butyl radical. The table reveals the fact that the values vary little with respect to the methods used. Table XIII compares

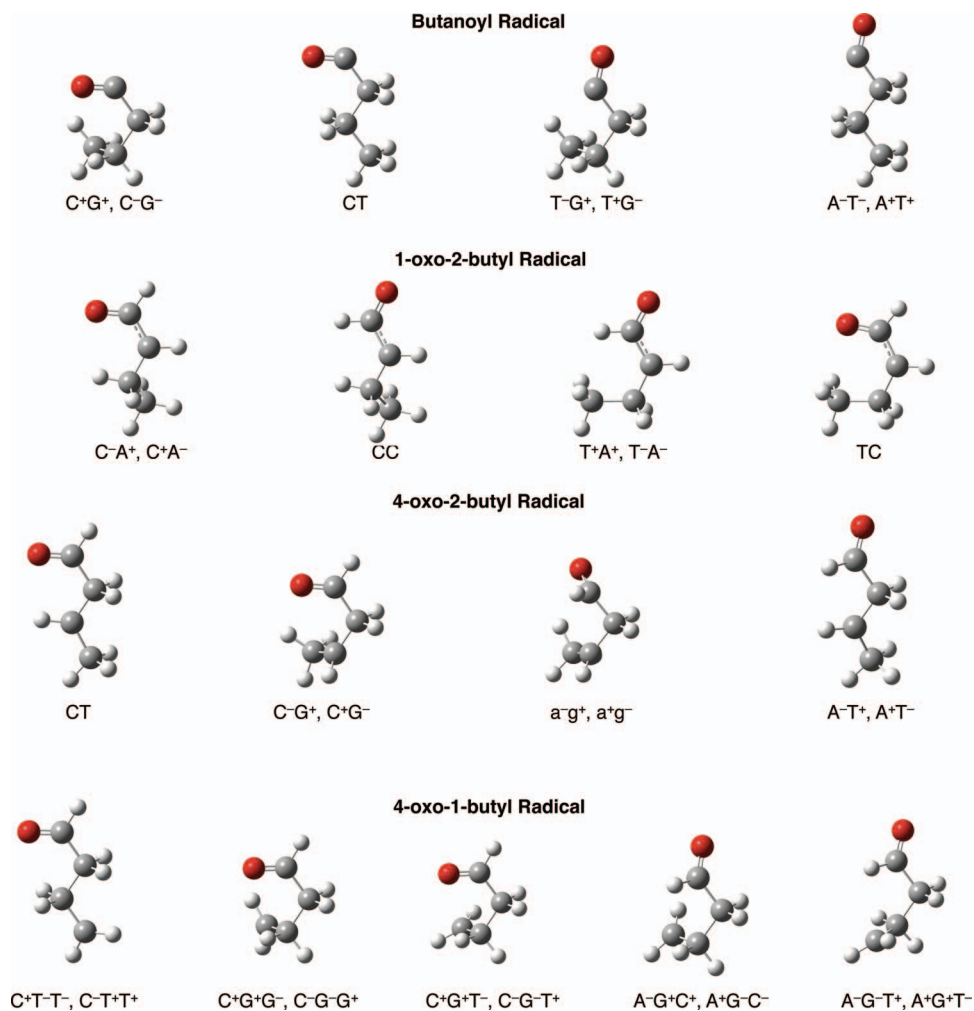


FIG. 5. Lowest energy conformers for butanal radicals.

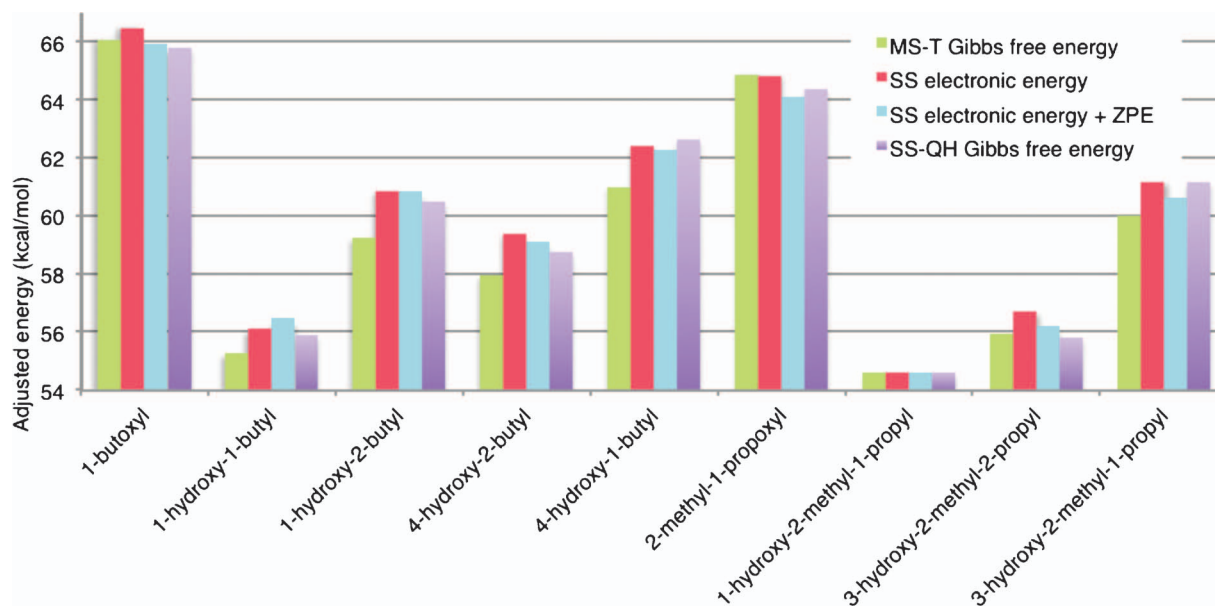


FIG. 6. Relative stability of 1-butanol and 2-methyl-1-propanol radicals. In green is the standard Gibbs free energy (G_{298}°) calculated using the MS-T method. Red columns illustrate the trends in CCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S electronic energy for the lowest energy conformational structures for every radical. Blue columns depict the same energy values as the red ones plus M08-HX/MG3S zero-point vibrational energy scaled by 0.973. In purple we show the single structure quasiharmonic approximation to the G_{298}° , where the frequencies are scaled by 0.984. In order to compare trends in values (rather than absolute electronic energy and Gibbs free energy values), all column heights were adjusted for the second, third, and fourth columns so that they match G_{298}° for 1-hydroxy-2-methyl-1-propyl radical. Thus the G_{298}° values are unadjusted, but the other three sets of values are adjusted.

TABLE IX. Comparison in the $C_p^\circ(T)$ and S_T° values between our computed results and group additivity data for 1-butoxyl radical, 4-hydroxy-2-butyl radical, and 4-hydroxy-1-butyl radical (in cal K⁻¹ mol⁻¹).

T (K)	$C_p^\circ(T)$			S_T°		
	CC (MS-T)	GA ^a	GA ^b	CC (MS-T)	GA ^{a,c}	GA ^{b,c}
1-butoxyl radical						
300	26.868	25.09	25.90	86.340	85.84	86.06
400	32.854	31.54	31.84	94.892	93.96	94.34
600	42.967	42.29	42.15	110.229	108.89	109.28
800	50.353	50.16	49.90	123.652	122.19	122.52
1000	55.883	55.85	55.54	135.508	134.03	134.30
4-hydroxy-2-butyl radical						
300	25.929	26.14	25.64	92.106	89.64	92.09
400	31.633	32.15	31.06	100.332	98.05	100.24
600	41.781	42.14	41.11	115.162	113.02	114.84
800	49.196	49.46	48.62	128.240	126.20	127.72
1000	54.702	54.88	54.31	139.826	137.85	139.21
1500	63.295		63.09	163.800		163.13
4-hydroxy-1-butyl radical						
300	26.257	26.28	26.49	91.186	88.61	90.92
400	32.266	32.39	32.01	99.558	97.03	99.32
600	42.421	42.46	41.83	114.655	112.17	114.26
800	49.749	49.69	49.06	127.904	125.42	127.31
1000	55.201	55.08	54.52	139.607	137.12	138.88
1500	63.775		63.02	163.778		162.78

^aGroup additivity parameters were taken from Ref. 17.^bGroup additivity parameters were taken from Refs. 17, 28, and 29.^cEntropy values obtained from group additivity were corrected by adding 0.026 cal mol⁻¹ K⁻¹ to convert from a standard pressure of 1 atm to a standard pressure of 1 bar.

heat capacity and entropy values computed in this work to the group additivity values showing very good agreement of our results with the GA using recent parameters.

The relative stability of the butanal radicals as estimated from MS-T Gibbs free energy decreases in the following order: butanoyl > 1-oxo-2-butyl > 4-oxo-2-butyl > 4-oxo-1-butyl radical.

III.D. Importance of anharmonicity and multi-structure effects on the relative stability of radicals

Comparison of the stability of various chemical species (reagents, intermediate products, transition states) is one of the most common applications of computational methods in mechanistic studies of chemical reactions. Stability of the transition states relative to the reactants controls branching ratios in the case of multiple possible reactive paths. Stability of the intermediate products of reactions involving many steps may affect which isomeric product will form or which mechanism of the reaction is favorable. Differences in the stability of the radicals has been shown to affect which reactive site is going to be substituted in chain reactions with radical-like transition states. Therefore, the estimation of relative stabilities of isomeric radicals and other species is ubiquitous and consequential in the chemistry literature. This relative stability is commonly estimated in the literature as the zero-point corrected and/or –uncorrected electronic energy of their low-

TABLE X. Standard state thermodynamic properties, viz., enthalpy (H_T° in kcal mol⁻¹), heat capacities ($C_p^\circ(T)$ in cal K⁻¹ mol⁻¹), entropy (S_T° in cal K⁻¹ mol⁻¹), and Gibbs free energies (G_T° in kcal mol⁻¹) of 2-methyl-1-propanol-derived radicals. The zero of energy for this table is the zero-point-exclusive energy of the $\mathbf{T}^+\mathbf{G}^-$ or $\mathbf{T}^-\mathbf{G}^+$ structures of 1-hydroxy-2-methyl-1-propyl.

T (K)	MS-T		MS-T	
	M08-HX ^a	CC ^b	M08-HX ^a	CC ^b
2-methyl-1-propoxy radical				
		H_T°	$C_p^\circ(T)$	
298	89.569	89.576	26.518	26.544
800	109.887	109.896	50.999	51.000
2000	184.804	184.816	69.127	69.129
		S_T°	G_T°	
298	82.905	82.894	64.864	64.874
800	120.875	120.871	13.187	13.200
2000	176.822	176.820	-168.840	-168.824
1-hydroxy-2-methyl-1-propyl radical				
		H_T°	$C_p^\circ(T)$	
298	80.612	80.554	27.640	27.492
800	100.672	100.579	49.660	49.627
2000	173.729	173.618	67.645	67.639
		S_T°	G_T°	
298	86.946	87.041	54.703	54.616
800	124.599	124.618	0.993	0.885
2000	179.116	179.119	-184.502	-184.620
3-hydroxy-2-methyl-2-propyl radical				
		H_T°	$C_p^\circ(T)$	
298	82.736	82.487	27.661	26.804
800	102.775	102.366	50.453	50.365
2000	178.066	177.641	69.964	69.979
		S_T°	G_T°	
298	88.752	89.111	56.288	55.933
800	126.255	126.243	1.771	1.371
2000	182.345	182.318	-186.624	-186.996
3-hydroxy-2-methyl-1-propyl radical				
		H_T°	$C_p^\circ(T)$	
298	87.083	86.312	26.745	26.831
800	107.086	106.337	49.920	49.943
2000	180.389	179.656	67.764	67.771
		S_T°	G_T°	
298	88.313	88.248	60.766	60.014
800	125.736	125.721	6.497	5.761
2000	180.428	180.424	-180.467	-181.192

^aThe basis set used for M08-HX is MG3S.^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/ MG3S.

est energy conformers. If frequency calculation is affordable for a system in question Gibbs free energy values (again, most often only for the lowest energy conformer) are used as a measure of the relative stability. Anharmonicity and torsional effects are assumed to have negligible effect on the stability of the species.

In order to evaluate the importance of including multiple conformational structures as well as the torsional

TABLE XI. Comparison in the $C_p^\circ(T)$ and S_T° values between our computed results and group additivity data for 2-methyl-1-propoxyl radical and 3-hydroxy-2-methyl-1-propyl radical (in $\text{cal K}^{-1} \text{mol}^{-1}$).

T (K)	$C_p^\circ(T)$			S_T°		
	CC (MS-T)	GA ^a	GA ^b	CC (MS-T)	GA ^{a,c}	GA ^{b,c}
2-methyl-1-propoxyl radical						
300	26.680	24.82	19.43	83.072	85.34	85.81
400	33.255	31.48	24.38	91.662	93.41	92.10
600	43.679	42.43	32.06	107.246	108.36	103.52
800	51.000	50.35	37.52	120.871	121.71	113.54
1000	56.413	55.99	41.33	132.861	133.59	122.34
3-hydroxy-2-methyl-1-propyl radical						
300	26.953	26.01	25.47	88.428	88.11	90.29
400	32.996	32.33	31.44	97.010	96.48	98.46
600	42.916	42.60	41.59	112.369	111.64	113.24
800	49.943	49.88	48.93	125.721	124.95	126.25
1000	55.163	55.22	54.35	137.443	136.69	137.79
1500	63.426		62.95	161.535		161.61

^aGroup additivity parameters were taken from Ref. 17.

^bGroup additivity parameters were taken from Refs. 17, 28, and 29.

^cEntropy values obtained from group additivity were corrected by adding $0.026 \text{ cal mol}^{-1} \text{ K}^{-1}$ to convert from a standard pressure of 1 atm to a standard pressure of 1 bar.

anharmonicity effects on the partition function, and consequently on the Gibbs free energy at 298 K, Figures 6 and 7 compare trends in the relative stability of the radicals. Gibbs free energy values computed by the MS-T method (shown in green) are the most computationally expensive because they take into account all the conformational minima and correct for anharmonicity. The other columns use quantities that are calculated for the single, lowest energy structure, which saves a certain amount of work and computational time. Red columns depict the trend in the Born-Oppenheimer electronic

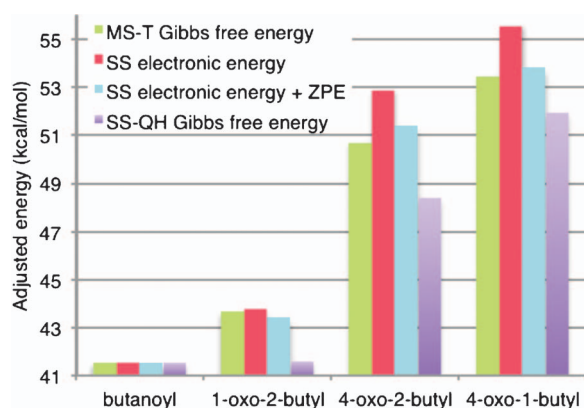


FIG. 7. Relative stability of butanal radicals. Red columns illustrate the trends in CCSD(T)-F12a/jun-cc-pVTZ/M08-HX/maug-cc-pVTZ electronic energy for the lowest energy conformational structures for every radical. Blue columns depict the same energy values as the red ones plus M08-HX/maug-cc-pVTZ zero-point vibrational energy scaled by 0.976. In purple we show the single structure quasiharmonic approximation to the G_{298}° , where the frequencies are scaled by 0.990. In order to compare trends in values (rather than absolute electronic energy and Gibbs free energy values), all column heights were adjusted for the second, third, and fourth columns so that they match G_{298}° for butanoyl radical. Thus the G_{298}° values are unadjusted, but the other three sets of values are adjusted.

TABLE XII. Standard state thermodynamic properties, viz., enthalpy (H_T° in kcal mol^{-1}), heat capacities ($C_p^\circ(T)$ in $\text{cal K}^{-1} \text{mol}^{-1}$), entropy (S_T° in $\text{cal K}^{-1} \text{mol}^{-1}$), and Gibbs free energies (G_T° in kcal mol^{-1}) of butanal-derived radicals. The zero of energy for this table is the zero-point-exclusive energy of the lowest energy structure of CT conformer of the butanoyl radical.

T (K)	MS-T		MS-T	
	M08-HX ^a	CC ^b	M08-HX ^a	CC ^b
butanoyl radical				
		H_T°	$C_p^\circ(T)$	
298	66.604	66.611	23.081	23.013
800	83.852	83.838	43.190	43.170
2000	147.320	147.305	58.508	58.513
		S_T°	G_T°	
298	84.050	84.094	41.557	41.551
800	116.320	116.318	-9.204	-9.217
2000	163.698	163.693	-180.077	-180.082
1-oxo-2-butyl radical				
		H_T°	$C_p^\circ(T)$	
298	67.078	68.338	23.405	23.288
800	84.701	85.948	44.240	44.264
2000	149.225	150.513	59.083	59.112
		S_T°	G_T°	
298	82.838	82.829	42.392	43.655
800	115.785	115.738	-7.926	-6.642
2000	164.004	163.987	-178.783	-177.462
4-oxo-2-butyl radical				
		H_T°	$C_p^\circ(T)$	
298	75.085	76.537	24.518	23.834
800	92.488	93.811	43.176	43.083
2000	155.885	157.155	58.429	58.406
		S_T°	G_T°	
298	86.457	86.821	49.322	50.665
800	119.135	119.196	-2.820	-1.546
2000	166.453	166.468	-177.022	-175.783
4-oxo-1-butyl radical				
		H_T°	$C_p^\circ(T)$	
298	78.051	79.276	24.743	24.120
800	95.591	96.674	43.316	43.222
2000	158.986	160.040	58.395	58.394
		S_T°	G_T°	
298	86.415	86.768	52.299	53.419
800	119.352	119.378	0.110	1.171
2000	166.652	166.649	-174.318	-173.259

^aThe basis set used for M08-HX is maug-cc-pVTZ.

^bCCSD(T)-F12a/jun-cc-pVTZ/M08-HX/maug-cc-pVTZ

energy of the radicals and constitute the least expensive, but also the crudest way of estimating relative stability of different species in this figure. In blue we show the same energy values, but corrected by the scaled vibrational zero-point energy. The scaling factors used here (unlike the rest of the paper) are those that correct the systematic errors partially inherent in a given electronic structure method (M08-HX/MG3S for alcohol-derived radicals and M08-HX/maug-cc-pVTZ for those derived from aldehyde) and partially due to the

TABLE XIII. Comparison of the $C_p^\circ(T)$ and S_T° values in this study to the group additivity results for 1-oxo-2-butyl radical and 4-oxo-1-butyl radical (in cal K⁻¹ mol⁻¹).

<i>T</i> (K)	$C_p^\circ(T)$			S_T°		
	CC (MS-T)	GA ^a	GA ^b	CC (MS-T)	GA ^{a,c}	GA ^{b,c}
1-oxo-2-butyl radical						
300	23.397	23.80		82.985	83.99	
400	28.796	29.05		90.459	91.58	
600	37.810	37.74		103.931	105.08	
800	44.264	44.06		115.737	116.85	
1000	48.924	48.71		126.137	127.21	
1500	55.800	55.87		147.438	148.45	
4-oxo-1-butyl radical						
300	24.208	24.69	24.15	86.930	84.81	87.32
400	28.847	29.69	29.10	94.516	92.61	94.96
600	37.112	37.68	37.08	107.836	106.23	108.35
800	43.222	43.81	43.25	119.378	117.95	119.90
1000	47.771	48.21	47.68	129.522	128.23	130.05
1500	54.810	55.04	55.04	150.359		150.90

^aGroup additivity parameters were taken from Ref. 17.

^bGroup additivity parameters were taken from Refs. 17, 28, and 29.

^cEntropy values obtained from group additivity were corrected by adding 0.026 cal mol⁻¹ K⁻¹ to convert from a standard pressure of 1 atm to a standard pressure of 1 bar.

harmonic approximation of the vibrational motion. The scaling factors used here are those that bring frequencies closest to the experimental results. The purple columns show trends in the single structure Gibbs free energies of radicals, where frequencies are scaled to match the best harmonic frequency. This method is called the single structure harmonic approximation (SS-QH) in our figures. The predictions of relative stability of radicals from different methods differ by up to about 1 kcal mol⁻¹ for alcohol-derived radicals and by up to about 2 kcal mol⁻¹ for the butanal-derived radicals. Furthermore, the predictions of the relative stability of the isomeric radicals from SS-QH and MS-T approximations differ significantly. For example, according to SS-QH butanoyl and 1-oxo-2-butyl radicals have nearly equal Gibbs free energy values as shown in Figure 7. However, MS-T predicts an over 2 kcal mol⁻¹ difference in free energy, which suggests abstraction from C1 produces a more favorable radical than abstraction from C2. In the case of alcohol-derived radicals in Figure 6 the conclusions on the relative stability of the radicals is actually reverse using MS-T and SS-QH for 1-hydroxy-1-butyl and 3-hydroxy-2-methyl-2-propyl radicals.

IV. CONCLUSIONS

In this study, we have computed thermodynamic data for five radicals of 1-butanol, four radicals of 2-methyl-1-propanol, and four radicals of butanal. We incorporated all conformational stationary points for each molecule by using the multiple-structure local quasiharmonic (MS-LQ) approximation and the multistructural method with torsional anharmonicity (MS-T). First-principles thermodynamics for such radicals has not been calculated before; for example, these molecules are much too large to be converged with

state-of-the-art path integral methods. Moreover, even empirical Benson-type group additivity parameters are not available for computing most of the results achieved here. Therefore our results constitute the first theoretical data for this kind of system. Where Benson's group additivity (GA) parameters are available, GA values for heat capacities and entropies (C_p° and S_T°) agree reasonably well with our results: to within ~ 2 cal mol⁻¹ K⁻¹ for S_T° and ~ 1 cal mol⁻¹ K⁻¹ for C_p° . In light of there being no experimental data with which to compare, we do not know which results (MS-T nor GA) are more accurate in these particular cases. It is promising that, as shown in this study, MS-T is a reliable non-empirical scheme for thermochemistry that does not rely on parameterization. This is especially important for combustion or atmospheric species, for which there is often no way to get reliable empirical numbers, because there is nothing to base them on. Enthalpies and free energies of the radicals studied here are examples of such quantities. Our enthalpies and free energies, to the best of our knowledge, are the first theoretical attempt to include multi-structural and anharmonicity effects for these systems. We show how important these improvements in the thermodynamic treatment are. There are countless examples in the literature of attempts to explain stability of chemical species solely in terms of electronic effects (e.g., inductive and steric effects), but we show here that the entropic effects (from many structures) play a significant role too.

Finally, we consider a statistical comparison of two methods of getting the input data for MS-T calculations. We find that (averaged over all the radicals and nine temperatures spanning the range from 200 K to 2400 K) the results obtained from DFT reproduce those from coupled cluster theory to within ~ 0.49 kcal mol⁻¹ for H° , ~ 0.15 cal mol⁻¹ K⁻¹ for C_p° , ~ 0.08 cal mol⁻¹ K⁻¹ for S_T° , and 0.48 kcal mol⁻¹ for G_T° . This agreement is even better for C_p° and S_T° at high combustion temperatures, with the average deviation at 2400 K dropping to ~ 0.01 cal mol⁻¹ K⁻¹, and below 0.005 cal mol⁻¹ K⁻¹, respectively. The uncertainties due to using DFT are found to be much smaller than the errors that would be incurred by neglecting multi-structural anharmonicity. As shown by the relative stability comparison for the isomeric radicals, the anharmonicity and multiple-structure effects have appreciable effects on the thermodynamic properties of radicals and are found to limit the accuracy of the results to a much higher degree than the choice of the electronic structure method.

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