PAPER

Multi-structural thermodynamics of C–H bond dissociation in hexane and isohexane yielding seven isomeric hexyl radicals†

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The C–H bond dissociation processes of *n*-hexane and isohexane involve 23 and 13 conformational structures, respectively in the parent molecules and 14–45 conformational structures in each of the seven isomeric products that we studied. Here we use the recently developed multi-structural (MS) thermodynamics method and CCSD(T)-F12a/jul-cc-pVTZ//M06-2X/6-311+G(2df,2p) potential energy surfaces to calculate the enthalpy, entropy, and heat capacity of *n*-hexane, isohexane, and seven of the possible radical products of dissociation of C–H bonds. We compare our calculations with the limited experimental data and with values obtained by group additivity fits used to extend the experimental data. This work shows that using the MS method involving a full set of structural isomers with density functional geometries, scaled density functional frequencies, and coupled cluster single-point energies can predict thermodynamic functions of complex molecules and bond dissociation reactions with chemical accuracy. The method should be useful to obtain thermodynamic data for complex molecules for which such data has not been measured and to obtain thermodynamic data at temperatures outside the temperature range where measurements are available.

1. Introduction

Accurate thermodynamic functions for hydrocarbon molecules and radicals over a wide range of temperatures are important in combustion chemistry. Due to the difficulty of generating and measuring the properties of free radicals directly, accurate experimental thermodynamic properties are unavailable for most hydrocarbons, radicals, and other organic molecules. Thermodynamic properties as a function of temperature are especially rare. For example, in the latest version of *CRC Handbook of Chemistry and Physics*,[1] thermodynamic properties as a function of temperature are listed for only 10 hydrocarbon molecules. Those experimental thermodynamic functions that are available in the literature sometimes have large uncertainties. Many of the "experimental" values are actually values calculated from spectral data or kinetics data by using statistical thermodynamic models. Therefore, the accuracy of these semi-experimental data is dependent on the approximations in the statistical thermodynamic models that were employed.

Benson' group additivity[2,3] (GA) method has been widely used to calculate thermodynamic functions when experimental data are not available. The GA method is an empirical method that is fitted to the limited number of available experimental data. For example, the GA method uses experimental data for a limited number of hydrocarbons to derive group additivity values (GAVs), and it assumes that these GAVs are applicable to all kinds of hydrocarbons. The validity of this kind of extrapolation needs to be examined. The group additivity values are also limited; for example Cohen and Benson[3] pointed out that, "Group additivity has provided only limited relief for such problems since GAV tables are incomplete".

Given the circumstance of largely absent experimental data and discrepancies among the available experimental data, the question arises as to whether high-level electronic structure methods together with statistical thermodynamics methods can provide a means to predict accurate thermodynamic properties for complex species with questionable or missing experimental data. About two decades ago, the situation was aptly described as follows:[3] "theoreticians have struggled to attain the stage where they can with pride calculate enthalpy quantities with 2–4 kcal mol^{-1} uncertainty, they are not solving the practical problems at hand"; since then the rapid development of theoretical methods and the growth of high-performance computing technology make it practical to achieve chemical accuracy (1 kcal mol^{-1}) for thermodynamics even on systems larger than 20 atoms. In this paper, we will use high-level electronic structure methods and our recently developed internal-coordinate multi-structural thermodynamics method[4] including torsional anharmonicity to calculate thermodynamic functions of isomers of hexane and hexyl radicals.

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2. Methods

2.1 Electronic structure methods

The M06-2X[5] density functional with the 6-311+G(2df,2p)[6,7] basis set is used to optimize all the structures. To ensure the convergence of vibrational frequency calculations, the grid used for density functional integration has 96 radial shells around each atom and a spherical product angular grid having 32 θ points and 64 φ points in each shell. Vibrational frequencies were scaled by a standard scaling factor[8] of $\lambda = 0.970$ to provide a better estimate of the zero-point energy.

The CCSD(T)-F12a method[9,10] was used to calculate single-point energies of all the optimized structures using the jul-cc-pVTZ[11] basis set. The resulting CCSD(T)-F12a/jul-cc-pVTZ energies should be close to the quality of the standard CCSD(T)[12] level with a higher-ζ basis set or even a complete basis set. All density functional calculations were performed using the *Gaussian 09*[13] program, and the *MOLPRO*[14] program was used for CCSD(T)-F12a calculations.

2.2 Thermodynamics methods

A recently proposed multi-structural statistical thermodynamic method including torsional anharmonicity[4] (the multi-structural method, MS) is used to calculate thermodynamics functions. We use the MS-AS-T version that takes account of the contributions of all the conformational structures (all structures, AS) in a molecule or a radical and adjusts the harmonic results by torsional (T) correction factors that are determined using internal coordinates. The MS-AS-T method was originally labeled MS-AS; in the present article we always use all structures and we shorten MS-AS-T to MS-T throughout the present paper.

The MS-T method makes it possible to include torsional anharmonicity in a practical way for complex molecules (e.g., hexane or larger molecules) even when the torsions are strongly coupled to one another and/or to other vibrational motions. To perform the MS-T calculations, one needs to determine the geometry, Hessian, and effective periodicity of each torsion for each conformational structure. The geometries and Hessians used in the MS-T calculations were obtained by the M06-2X/6-311+G(2df,2p) method, and single-point energies were calculated by the CCSD(T)-F12a/jul-cc-pVTZ method; for simplicity throughout this paper, we will use a short name, MS/F12, for the MS-T calculations using CCSD(T)-F12a/jul-cc-pVTZ//M06-2X/6-311+G(2df,2p) potential energy surfaces. When torsions are strongly coupled together, the effective periodicity of those torsions is approximated using a volume in torsional space calculated by Voronoi tessellation. All details of the MS-T method can be found in ref. 4 and will not be repeated here.

Note that the MS-T method involves, at various stages, both normal-coordinate frequencies and internal-coordinate frequencies. Rather than directly scaling the frequencies by the factor λ, we scale all Hessian elements by λ^2; this means that both kinds of frequencies are automatically scaled by λ.

In the first set of calculations with Benson's group additivity method, Benson's 1976 GAVs[2] are used for both stable molecules and radicals; such calculations are labeled as GA-B76 in

this paper, where B denotes Benson. A second set of calculations used the improved GAVs for alkane heat of formation at 298 K given by Cohen and Benson[3] in 1993, and are labeled as GA-B93. When GA-B76 and GA-B93 give identical results for a property, e.g. entropy, we use the label GA-B. An improved group additivity scheme for radicals by Lay *et al.*,[15] called the H atom bond increment (HBI) scheme, was also used for calculating thermodynamic functions of radicals; we distinguish it from GA-B76 and GA-B93 by the name GA-HBI. Values of $\Delta H_\mathrm{f}^\mathrm{o}$ and S^o at temperatures above 298 K are calculated by the following integrations:

$$\Delta H_T^\mathrm{o} = \Delta H_{T_0}^\mathrm{o} + \int_{T_0}^{T} \Delta C_\mathrm{p}^\mathrm{o} \mathrm{d}T \qquad (1)$$

$$S_T^\mathrm{o} = S_{T_0}^\mathrm{o} + \int_{T_0}^{T} \left(\frac{C_\mathrm{p}^\mathrm{o}}{T}\right) \mathrm{d}T \qquad (2)$$

For this purpose, the C_p^o and $\Delta C_\mathrm{p}^\mathrm{o}$ values obtained from GAV tables at all available temperatures are fitted to a cubic polynomial and then used in the integrations. However, these integrations are used only for interpolation (that is, for temperature up to the highest tabulated C_p^o), not for extrapolation.

2.3 Standard state

All standard-state quantities in this paper (both our own and those taken from the literature) are tabulated for a standard-state pressure of 1 bar. Using 1 atm would change some standard-state entropies by 0.01 cal mol^{-1} K^{-1}.

3. Results and discussion

3.1 Geometries

To find all the conformational structures, we searched the conformational space with grids of initial guesses that consist of 3–5 configurations for each torsion. For example, we generated 81 initial structures for 1-hexyl and optimization leads to 45 distinguishable structures, in particular, 22 pairs of mirror images plus one structure with C_s symmetry. Sometimes the search only finds one of a pair of mirror images, but it is not necessary to optimize the other one since they make identical contributions to the partition function. If there are some structures missed in our conformational search (which is always a possibility), they are probably high in energy and/or have a small volume in torsional space, and we expect that their contributions to the partition functions and thermodynamic functions are negligible.[4] Fig. 1 shows the isomers of hexane and hexyl radicals studied in this paper, their IUPAC nomenclature, the short name used in this paper, and the number of conformational structures that we found. The full sets of Cartesian coordinates are available in ESI.†

3.2 C–H bond dissociation enthalpy

Since there are no firm experimental data available for the C–H bond dissociation enthalpy (BDE, denoted ΔH_T^o, where T is the temperature) of either *n*-hexane or isohexane, we performed calculations for ethane to validate the MS/F12

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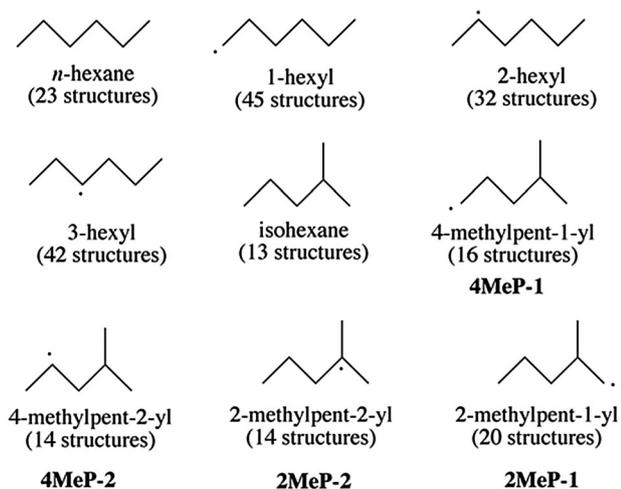
Fig. 1 Molecules and radicals studied in this work. The numbers in parentheses are the number of conformational structures found. The bold text gives the short names used for some of the radicals. The IUPAC name of isohexane is 2-methylpentane.

Fig. 2 Bond dissociation enthalpy of *n*-hexane or isohexane to primary radicals.

Fig. 3 Bond dissociation enthalpy of *n*-hexane or isohexane to secondary radicals.

method. The standard-state BDE of the C–H bond of ethane at 298 K is calculated to be 101.1 kcal mol^{-1} by the MS/F12 method. This is in good agreement with the experimental value[16] 100.5 ± 0.3 kcal mol^{-1} recommended by Luo.[17] The other experimental values of the ethane C–H BDE at 298 K are 100.8 ± 0.7[18] and 101.0 ± 0.4[19] kcal mol^{-1}. The GA-HBI scheme gives 101.1 kcal mol^{-1} for $\Delta H^{\mathrm{o}}_{298}$ and agrees with MS/F12 calculations up to 1000 K within 0.2 kcal mol^{-1}. The GA-B93 BDEs are about 3 kcal mol^{-1} lower than MS/F12 and GA-HBI values from 300–1000 K. The reason for the high accuracy of the GA-HBI value is that it is parametrized to the experimental BDEs (one of the goals of the present work is to learn how accurate the GA schemes are for molecules outside the parametrization set). The good agreement between MS/F12 and experimental values at 298 K and the agreement between MS/F12 and GA-HBI over the temperature range 300 K–1000 K indicate the high accuracy of the MS/F12 method. However, the GA-B93 method has an error of about 3 kcal mol^{-1} for reactions involving ethyl radicals.

Next we examine whether the MS/F12 and GA-HBI methods agree with each other for larger alkane C–H bond BDEs at various types of radical sites and at T = 300 K–1000 K. Fig. 2 shows the three C–H BDEs of *n*-hexane or isohexane on primary radical sites from 300 K to 2400 K. The GA-B93 values are still lower than all the others by about 3–4 kcal mol^{-1}. Because GA-HBI used a BDE of 101.1 kcal mol^{-1} at 298 K for all primary C–H bond dissociations, it gives this value for all three primary C–H bond dissociations of *n*-hexane and isohexane shown in Fig. 2. Both GA methods give a single curve (or very similar curves with differences less than 0.02 kcal mol^{-1}) that is the same (or almost same) for these three C–H bond dissociation processes. The MS/F12 method gives different curves for the three C–H bond dissociation processes although they all generate primary radicals.

Fig. 3 shows the three C–H BDEs of *n*-hexane or isohexane at secondary radical sites from 300 K to 2400 K. The GA methods give almost the same curves for the three processes
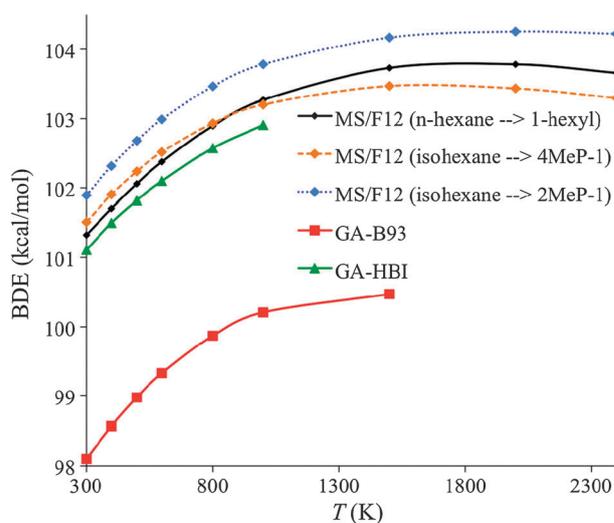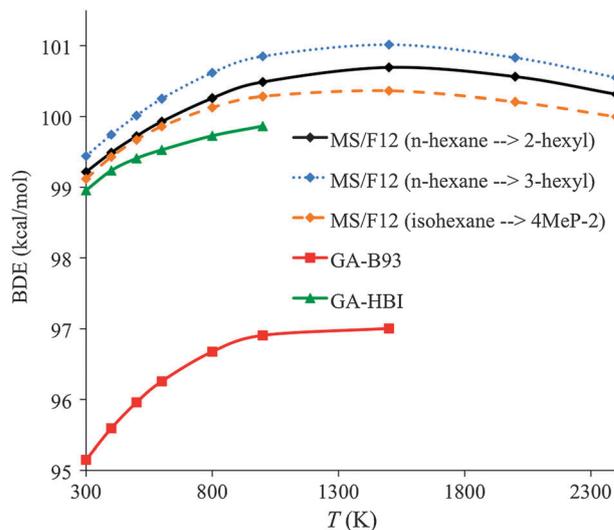
except that they differ for the processes of *n*-hexane dissociation to 2-hexyl and 3-hexyl radicals by 0.1–0.3 kcal mol^{-1}. The BDEs calculated by the GA-B93 method are lower than the others by about 4 kcal mol^{-1}. The MS/F12 method shows that the dissociation of *n*-hexane to a 3-hexyl radical has the largest BDE at all temperatures, and it differs from the GA-HBI method by 1.3 kcal mol^{-1} at 1000 K. These three C–H dissociation processes have slightly different temperature dependences when calculated by the MS-T statistical thermodynamics method.

Fig. 4 shows the BDEs for dissociation of isohexane to the 2MeP-2 radical. The GA-B93 values are 5 kcal mol^{-1} lower than the MS/F12 values and are 4 kcal mol^{-1} lower than the GA-HBI values.

The zero-point-energy-exclusive bond dissociation energy at the classical equilibrium geometry (D_{e}, also called the equilibrium dissociation energy), the zero-point-energy-inclusive
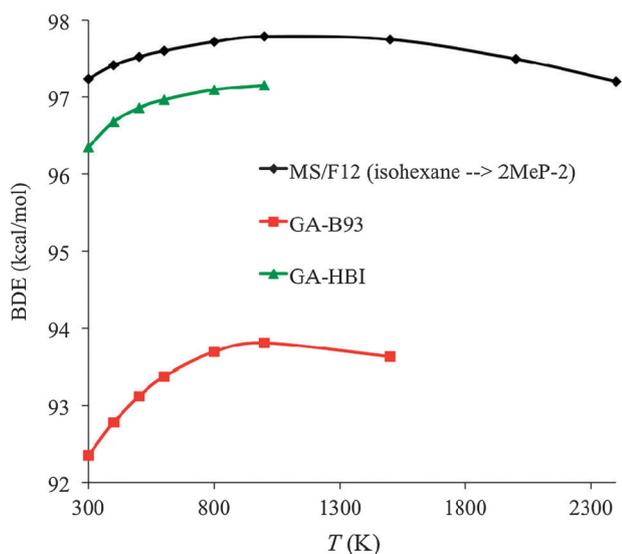
Fig. 4 Bond dissociation enthalpy of isohexane to tertiary 2MeP-2 radical.

bond dissociation energy (D_0, also called the ground-state dissociation energy) and the BDE at 298 K for various C–H bonds in *n*-hexane and isohexane are given in Table 1. Note that D_0 is the same as ΔH_0^o, and the BDE at 298 K is ΔH_{298}^o. This table also shows the best previously available estimates based on experiment. The BDEs for breaking the three primary C–H bonds differ by only 0.2 kcal mol^{-1} for D_e. These BDEs at 298 K deviate by 0.6 kcal mol^{-1}, and that deviation increases to 1.0 kcal mol^{-1} at 2400 K. It is quite reasonable that these three C–H bond dissociations are different at the finite temperatures because the three primary hexyl radicals have different vibrational frequencies and different torsional characters. The best estimate BDE, 99.017 kcal mol^{-1},[17] of *n*-hexane to form 1-hexyl is derived from the experimental heat of formation of *n*-hexane and 1-hexyl reported in ref. 20. This value is lower than the MS/F12 and GA-HBI values by 2 kcal mol^{-1}. Note that the BDEs by the GA-HBI scheme (101.1 kcal mol^{-1}) are average experimental BDEs of C2–C4 alkanes. This discrepancy indicates that the

experimental heat of formation given in ref. 20 may be inaccurate. When accurate experimental values are not available, high-level electronic structure calculations combined with a comprehensive statistical thermodynamics method may serve as a good resource to provide reliable data. We notice that our calculated BDE for the tertiary radical site is 1 kcal mol^{-1} or more higher than the GA values and reference values. But if we consider the 2 kcal mol^{-1} uncertainty of the 94.7 kcal mol^{-1} reported in ref. 21, all the 298 K data except the GA-B76 and GA-B93 schemes agree with the best previously available estimates.

Table 1 shows that dissociation of *n*-hexane to a 2-hexyl radical requires a smaller BDE than dissociation to a 3-hexyl radical, that is, the 2-hexyl radical is more stable than the 3-hexyl radical. However, this trend is not captured by the GA-B76 and GA-HBI group additivity parametrizations. At the CCSD(T) level, we see this trend not only in the equilibrium dissociation energies, but also at 0 K and at finite temperatures up to 2400 K (see Fig. 3). Table 2 provides another comparison of the BDEs for 2-hexyl and 3-hexyl; in particular it shows several ways to characterize the BDE. In particular, in addition to D_e, D_0, and the calculation by the MS-T method of the bond dissociation enthalpy, Table 3 shows results for the bond dissociation enthalpy calculated by the single-structure harmonic oscillator (SS-HO) approximation and by the multi-structural local harmonic approximation (MS-LH, which was originally[4] called the multi-structural harmonic approximation). All three types of calculations show that 2-hexyl is slightly more stable than 3-hexyl, which means that, at least in this case, the electronic and geometrical effects that determine the direction of the trend in D_e are not obscured by rotational–vibrational energy or multistructural effects. The relative stability of radicals is sometimes explained by the different electronegativities of the alkyl groups attached to the radical center (more electronegative substituents are more electron-withdrawing—a "negative inductive effect"—and electron withdrawal is assumed to stabilize the radical). Since there is less difference between propyl and butyl than between methyl and ethyl, the major difference between 2-hexyl and 3-hexyl is that a methyl group is attached to the radical site in 2-hexyl and an ethyl group is attached

Table 1 Zero-point energy exclusive C–H bond dissociation energy D_e, zero-point inclusive one D_0, and bond dissociation enthalpy ΔH_{298}^o (in kcal mol^{-1})

C–H bond	$D_e^{a,b}$	$D_0^{a,c}$	ΔH_{298}^o				
			GA-B76	GA-B93	GA-HBI	MS/F12^{a,d}	BPE^e
Primary hexyl radical							
H–CH$_2$(CH$_2$)$_4$CH$_3$	109.2	100.0	98.1	98.1	101.1	101.3	99.0^f
H–CH$_2$(CH$_2$)$_3$CH(CH$_3$)$_2$	109.2	100.0	98.1	98.0	101.1	101.5	
CH$_3$(CH$_2$)$_3$CH(H$_2$C–H)CH$_3$	109.4	100.3	98.1	98.4	101.1	101.9	
Secondary hexyl radical							
CH$_3$(HC–H)(CH$_2$)$_4$CH$_3$	106.6	97.3	94.6	94.6	98.5	98.7	98.0^f
CH$_3$CH$_2$(HC–H)(CH$_2$)$_2$CH$_3$	106.8	97.6	94.4	94.8	98.5	98.9	99.1^g
CH$_3$(HC–H)(CH$_2$)$_2$CH(CH$_3$)$_2$	106.1	96.9	94.6	94.5	98.5	98.6	
Tertiary hexyl radical							
CH$_3$(CH$_2$)$_3$C–H(CH$_3$)$_2$	104.2	95.3	92.2	92.3	96.3	97.2	94.7 $\pm$ 2^h, 95.4^g

^{a} Calculated by the CCSD(T)-F12a/jul-cc-pVTZ//M06-2X/6-311+G(2df,2p) method. ^{b} Based on a single structure with the lowest zero-point exclusive energy. ^{c} Calculations based on a single structure with the lowest zero-point inclusive energy and all structures lead to the same results. ^{d} Based on all structures. ^{e} Best previous estimate. ^{f} Recommended values in ref. 17. These values are derived from heat of formation reported in ref. 20 ^{g} From ref. 29. ^{h} From ref. 21.

Table 2 Bond dissociation energy and enthalpy at 0 K and 298 K for dissociation of *n*-hexane to 2-hexyl radical and 3-hexyl radical (in kcal mol^{-1})[a]

C–H bond	D_e	D_0	ΔH^o_{298}		
			SS-HO	MS-LH	MS-T
CH$_3$(HC–H)(CH$_2$)$_4$CH$_3$	106.6	97.3	99.1	98.9	98.7
CH$_3$CH$_2$(HC–H)(CH$_2$)$_2$CH$_3$	106.8	97.6	99.4	99.1	98.9

[a] Calculated by the CCSD(T)-F12a/jul-cc-pVTZ//M06-2X/6-311+G(2df,2p) method. The single structure calculations are based on the lowest energy structure. Note that zero-point inclusive energy and zero-point exclusive energy predict the same global minimum structure for *n*-hexane, 2-hexyl radical, and 3-hexyl radical, respectively.

Table 3 Standard enthalpies of formation at 298 K (in kcal mol^{-1})

	MS/F12	GA-B76	GA-B93	GA-HBI[a]	Expt.
Hexane	−39.4	−40.1	−40.0		−39.9[b]
Isohexane	−41.2	−42.4	−42.4		−41.7[b]
Primary hexyl radical					
1-Hexyl	9.7	5.9	5.9	8.9	
4MeP-1	8.2	3.6	3.5	6.6	
2MeP-1	8.6	3.7	3.9	6.6	
Secondary hexyl radical					
2-Hexyl	7.1	2.4	2.4	6.2	
3-Hexyl	7.4	2.2	2.6	6.2	
4MeP-2	5.3	0.1	0.0	4.0	
Tertiary hexyl radical					
2MeP-2	3.9	−2.2	−2.2	1.8	

[a] The GA-HBI method uses the GA-B93 GAV parameters for stable molecules. [b] From ref. 1.

to it in 3-hexyl. One usually assumes that ethyl is more electronegative than methyl,[22] but some considerations lead to the opposite conclusion.[23] Even if a unique and consistent prediction was made, this method suffers from a lack of explicit consideration of electron correlation energy. Probably the effect is too small to be explained reliably by this kind of consideration.

3.3 Standard enthalpy of formation

The standard enthalpy of formation at 298 K ($\Delta_f H^o$(298 K)) is an often used thermochemical property of a molecule or a radical. There is no unique way to calculate the standard enthalpy of formation. An often used approach[26] is to calculate the enthalpy of formation at 0 K, $\Delta_f H^o$(0 K), by subtracting calculated atomization energy from the known enthalpy of formation of the isolated atoms, and then to correct $\Delta_f H^o$(0 K) by enthalpy differences between 298 K and 0 K of the molecule and isolated atoms. However, it is difficult to obtain very accurate atomization energy (within 1 kcal mol^{-1}) from electronic structure calculation because of the open shell nature of atoms. For example, the CCSD(T)/aug-cc-pVTZ method has 2.6 kcal mol^{-1} error[27] for the atomization energies of SiH$_4$, SiO, S$_2$, propyne, glyoxal, and cyclobutane and the CCSD(T)/aug-cc-pVQZ method has a mean unsigned error of 2.3 kcal mol^{-1} for the atomization energies of a large number of molecules.[28] The work of Feller *et al.*[28] also shows that CCSD(T)-F12 has a mean unsigned error of 0.9 kcal mol^{-1} and a maximum error of 1.7 kcal mol^{-1} with a triple ζ basis

set for atomization energy. It is reasonable to expect that the errors could be even larger for larger molecules, e.g. hexane. Therefore, we adopt a different approach to calculate the standard enthalpy of formation, that is, to calculate the standard enthalpy of reaction ($\Delta_r H^o$) and use the experimental standard enthalpies of formation for the molecules involved in this reaction except the target molecule. The reactions we used are

$$C_6H_{14} + 2H_2 \rightarrow 3C_2H_6 \quad (R1)$$

$$C_6H_{13} + 2.5H_2 \rightarrow 3C_2H_6 \quad (R2)$$

where C$_6$H$_{14}$ stands for *n*-hexane or isohexane and C$_6$H$_{13}$ stands for one of the seven radicals that are studied in this paper. We use the experimental $\Delta_f H^o$(298 K) = −20.08 kcal mol^{-1} for ethane.[1] The standard heat of formation of C$_6$H$_{14}$ and C$_6$H$_{13}$ can be calculated by

$$\Delta_f H^o(M, 298\ K) = \Delta_r H^o(298\ K) + 3\Delta_f H^o(C_2H_6, 298\ K)$$

where M stands for either C$_6$H$_{14}$ or C$_6$H$_{13}$. The calculated standard enthalpies of formation by the MS/F12 method as well as group additivity methods are listed in Table 3 together with experimental values for *n*-hexane and isohexane. The standard enthalpies of formation for *n*-hexane and isohexane by the MS/F12 method have errors of 0.5 kcal mol^{-1}. The GA methods have errors less than 0.3 kcal mol^{-1} for standard enthalpies of formation for these stable molecules. For radicals, the MS/F12 method differs from the GA-B76 or GA-B93 method by 4–5 kcal mol^{-1}. The differences between the GA-HBI and the MS/F12 method are about 2 kcal mol^{-1} or less.

3.4 Entropy

Table 4 lists the entropy calculated by the GA schemes and that calculated by the MS/F12 method. For stable molecules, primary radicals, and secondary radicals, our calculations agree with those obtained by the GA-HBI within about 1 cal mol^{-1} K^{-1} at low temperature; for a few of the cases, e.g. 1-hexyl radical, the two methods also agree well from 300 K to 1000 K, but the difference between two methods becomes larger when the temperature increases. For example, 3-hexyl radicals have larger entropy at low temperature than 1-hexyl radicals; but the GA-HBI scheme predicts that 3-hexyl has a slightly lower entropy than 1-hexyl at 1000 K, and our method gives consistently higher entropy for 3-hexyl compared to 1-hexyl. For the tertiary radical, *i.e.* 2MeP-2, our methods give a larger entropy than the GA-HBI scheme by 2 cal mol^{-1} K^{-1} or more for T = 300–1000 K. Since there are no accurate experimental data available for entropies, it is difficult to judge the accuracy of these two methods. One major difference is that these two methods have different temperature dependences for both BDE and entropy. Therefore we will compare the constant-pressure heat capacity in the next section.

3.5 Constant pressure heat capacity

The constant pressure heat capacity (C_p^o for a species or ΔC_p^o for a reaction) represents the temperature dependence of the enthalpy, and it is also used to calculate the temperature dependence of the entropy. Waddington *et al.* measured C_p^o of *n*-hexane [24] and isohexane[25] over a narrow range of

Table 4 Standard state entropy S^{o} (cal mol^{-1} K^{-1})

T/K	GA-B[a]	GA-HBI	MS/F12	GA-B[a]	GA-HBI	MS/F12
n-Hexane				Isohexane		
300	93.0	93.0	94.2	91.6	91.6	92.0
400	104.2	104.2	105.6	102.8	102.8	103.4
500	114.8	114.8	116.3	113.4	113.4	114.3
600	124.9	124.9	126.4	123.5	123.5	124.6
800	143.5	143.5	145.0	142.2	142.2	143.5
1000	160.1	160.1	161.7	158.9	158.9	160.3
1500	194.9		196.5	193.7		195.3
1-Hexyl				2-Hexyl		
300	96.0	99.1	98.9	96.7	100.9	100.6
400	107.0	110.0	109.9	107.7	111.4	111.3
500	117.5	120.3	120.3	118.0	121.3	121.5
600	127.3	130.0	130.1	127.7	130.7	131.0
800	145.2	147.8	148.0	145.5	148.1	148.7
1000	161.2	163.7	164.0	161.3	163.8	164.5
1500	194.1		197.1	194.1		197.4
3-Hexyl				4MeP-1		
300	96.7	100.6	100.6	93.3	95.4	96.2
400	107.7	111.1	111.4	104.3	106.2	107.4
500	118.1	120.9	121.6	114.7	116.5	117.9
600	127.9	130.3	131.3	124.6	126.2	127.8
800	145.6	147.5	149.0	142.6	144.0	145.9
1000	161.4	163.2	164.8	158.5	159.9	161.9
1500	194.2		197.7	191.6		195.1
4MeP-2				2MeP-2		
300	94.0	96.8	97.9	94.5	96.9	99.0
400	105.0	107.3	108.8	105.4	107.5	109.6
500	115.3	117.2	119.1	115.7	117.5	119.6
600	125.0	126.6	128.9	125.4	126.9	129.1
800	142.9	144.1	146.7	143.0	144.2	146.7
1000	158.7	159.8	162.6	158.7	159.9	162.5
1500	191.6		195.7	191.4		195.5
2MeP-1						
300	93.3	95.4	96.3			
400	104.3	106.2	107.5			
500	114.7	116.5	118.2			
600	124.6	126.2	128.2			
800	142.6	144.0	146.4			
1000	158.5	159.9	162.5			
1500	191.6		195.9			

[a] GA-B76 and GA-B93 are identical for entropy.

Table 5 Constant pressure heat capacity C_{p}^{o} (cal mol^{-1} K^{-1})

T/K	Expt.	GA-B[a]	MS/F12
n-Hexane			
298.00		34.12	35.14
333.85	37.35	37.60	38.17
365.15	40.22	40.51	41.00
398.85	43.30	43.51	44.00
433.70	46.39	46.49	47.00
468.90	49.46	49.35	49.83
Isohexane			
298.00		33.85	35.10
325.10	36.77	36.56	37.83
362.15	40.30	40.10	41.17
402.25	44.08	43.75	44.83
436.20	47.14	46.68	47.83
471.15	50.16	49.56	50.83

[a] GA-B76 and GA-B93 are identical for constant pressure heat capacity.
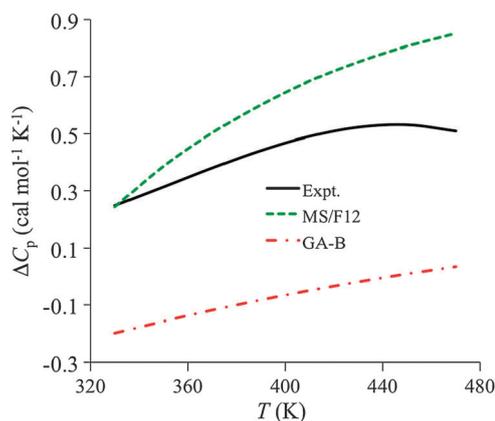
Fig. 5 Change of constant pressure heat of capacity for the isomerization *n*-hexane → isohexane.

temperatures (∼330 K–470 K). We will compare the calculated C_{p}^{o} only over this narrow range because extrapolation of the experimental data may be unreliable. The C_{p}^{o} of the MS/F12 calculations is calculated using finite numerical differences by varying T by ± 3 K:

$$C_{p}^{o} = \frac{\Delta H^{o}}{\Delta T} \qquad (3)$$

where $H^{o} = E^{o} + RT$ and E^{o} is the internal energy and is calculated by eqn (B2) and (B5) in ref. 4 from partition function (note that all thermodynamic functions except C_{p}^{o} in the MS-T method are calculated analytically and the corresponding formulae are described in ref. 4) The calculated C_{p}^{o} are listed in Table 5 along with experimental values. We fitted five scattered points given by Waddington *et al.*[24,25] for each molecule to a cubic polynomial and calculated the ΔC_{p}^{o} of the isomerization *n*-hexane → isohexane. The ΔC_{p}^{o} are plotted in Fig. 5.

The calculated C_{p}^{o} by both methods (Table 5) agree with experimental values within 1.3 cal mol^{-1} K^{-1}, and the GA-B method has smaller absolute errors than MS/F12. However, Fig. 5 shows that the MS/F12 results agree better with the

experimental ΔC_{p}^{o} of the isomerization *n*-hexane → isohexane than do the GA-B results. For example, the GA-B method predicts a negative ΔC_{p}^{o} below 430 K, while experiment has positive ΔC_{p}^{o}. This error occurs because the GA-B method overestimates the *n*-hexane C_{p}^{o} and underestimates the isohexane C_{p}^{o} while the MS/F12 method has consistent errors on both molecules. The empirical GA method usually can reproduce experimental values for a molecule or a radical very well since the parameters used in the GA method are obtained by fitting experimental data. However, when applying the GA method to a chemical reaction, the uncontrolled small fitting errors in different directions may lead to a qualitative error in the thermodynamic functions of chemical reactions. Furthermore, the GA methods are much less reliable for radicals than for *n*-hexane and isohexane since there is less experimental data for radicals.

4. Conclusions

In this work we calculated thermodynamic functions of *n*-hexane, isohexane, and seven hexyl radicals. This work shows that theoretical calculation can be a reliable and durable means for predicting thermodynamic functions with chemical accuracy for complex systems with many conformations when

using high-level electronic structure methods and our recently developed multi-structural statistical thermodynamic method. The GA method can usually predict accurate thermodynamic functions for stable molecules, especially hydrocarbons, but it has some limitations on general usage: (i) availability of group values, (ii) availability over a broad temperature range (below 300 K or higher than 1500 K) since extrapolation could be unreliable; and (iii) lack of group values for most transition states. Therefore it is valuable to have electronic-structure-based methods available for estimating thermodynamic properties of chemicals.

Acknowledgements

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