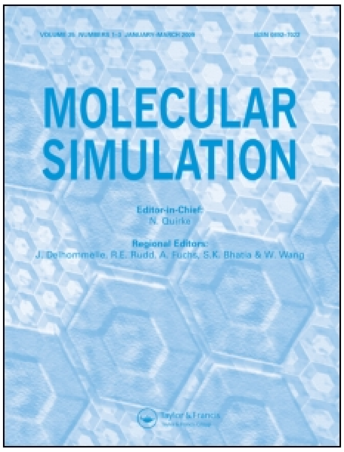

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The investigation of hydrocarbon cracking reaction energetics with composite energy methods

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The investigation of hydrocarbon cracking reaction energetics with composite energy methods

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Hydrocarbo cracking reactions are one of the most commonly encountered reactions in the petroleum industry, and the energetics of the reactions are crucial in understanding the reaction mechanisms and predicting reaction rates. In this work, a modified composite energy method (CBS-RAD(MP2)) is created as a version of the CBS-RAD method which gives accurate energetics for hydrocarbon free radical reactions. It replaces the time consuming QCISD(fc)/6-31g* method in the geometry optimization and frequency calculation steps with MP2(full)/6-31g* level calculations. The accuracy of the new CBS-RAD(MP2) method is compared with the widely used G2, G3 and CBS-QB3 composite methods for predicting heats of reaction and activation barriers of 14 hydrocarbon cracking reactions. We find that the new CBS-RAD(MP2) method has the second least RMS error of 1.22 kcal/mol for heats of reaction calculations. For activation energy calculations, the new CBS-RAD(MP2) method has the least RMS error of 1.37 kcal/mol. Moreover, the CBS-RAD(MP2) method was found to require only 81% of the computational time required compared to the CBS-QB3 method, 32% of G3 and 15% of the G2 method, making it an attractive alternative for predicting hydrocarbon cracking reaction energetics.

Keywords: Hydrocarbon cracking; Activation energy; CBS method; Computational time

1. Introduction

Hydrocarbon cracking is the process where higher-molecular-weight hydrocarbons are converted to lower-molecular-weight hydrocarbons through carbon–carbon bond scission processes [1]. Cracking reactions are key steps in many important petroleum refinery processes. Accurate energetics are required to predict kinetic and mechanistic pathways. However, because of the complexity of side reactions at high temperatures, it is very difficult to obtain specific thermodynamic hydrocarbon cracking reaction properties experimentally; experimental activation barriers and heats of reactions are known for relatively few reactions [2–8].

In the last few decades, it has become possible to use quantum mechanical methods to obtain reaction energetics for many systems successfully, ranging from semiempirical [9,10] to density functional theory [11–15] to Hartree-Fock methods [16–22]. *Ab initio* calculations have been used to find thermodynamic properties that have been difficult to measure experimentally. As computational power increases, so has the accuracy of the methods used to find relative energies, making them attractive alternatives to difficult experiments [23,24]. Composite energy methods accurately predict reaction energetics because they eliminate many of the difficulties of using a single method and basis set for calculating energies. For instance, the G2 method of Pople *et al.* has proven to be accurate in predicting heats of reactions, heats of formation and ionization potentials[25–29]. The mean absolute deviation in heats of formation for 125 experimental energies is 1.21 kcal/mol. However, the G2 method is limited by the expensive fourth-order Moller-Plesset (MP) calculation, MP4(SDTQ), using a 6- 311G(2df,p) basis set. This single point energy step makes the G2 method extremely time-consuming for larger molecules of interest.

Similarly, the more recent G3 method has shown great promise for predicting heats of reaction, ionization potentials and other phenomena [30–34] at a relatively low computational cost compared to the G2 method. This method is computationally much cheaper than the G2 method, yet still yields very accurate results for thermodynamic properties. However, the single point calculation using the G3Large basis set is again very expensive for larger species of interest.

More recently, another series of composite energy methods named the complete basis set methods have been

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developed [35–44]. These methods eliminate some of the empirical correlations that are included in the Gaussian-n series of methods while still giving very accurate predictions of heats of formation and enthalpies of reaction. There are several branches of the CBS methods which are CBS-APNO, CBS-4, CBS-q, CBS-Q and CBS-QB3. Among them, CBS-Q tends to have a good compromise between accuracy and computational cost. However, the unrestricted Hartree-Fock method used for geometry and frequency calculations in the CBS-Q method can be unreliable when spin contamination is large [40,45]. Also, the investigation of chemical reaction transition states encounters problems for the composite energy methods that use different geometry optimization methods than the zero point energy calculations, like G2 and CBS-Q [38]. As a modification of the CBS-Q method, the CBS-QB3 method proposed by Montgomery *et al.* uses density functional geometries and frequencies obtained at the B3LYP/6-311G(2d,p) level in the complete basis set model chemistry, fixing this difficulty [38]. This method accurately predicts bond dissociation energies, ionization potentials, electron affinities and proton affinities at a reduced cost. In 1998, Mayer, *et al.* proposed a new procedure called the CBS-RAD method for treatment of free radicals [40]. It modified the CBS-Q method and changed the geometry and zero-point energy method to QCISD/6-31g* while using the coupled-cluster theory in the single-point energy calculations. These modifications make the CBS-RAD method work especially well for free radicals, which have high spin contamination effects due to unpaired electrons on the species.

Blowers *et al.* [46] showed that, for 17 ligand transfer reactions, the CBS-RAD method decreased the root mean square (RMS) error by about 10% compared with the G2 method for activation energies. However, this increase in accuracy caused the CPU time to increase by 400%, which limits the application of the CBS-RAD method to systems with a small number of first and second row atoms. To reduce the computational cost while maintaining high accuracy, we propose replacing the time consuming QCISD(fc)/6-31g* geometry optimization and frequency calculation method in the CBS-RAD method with the MP2(full)/6-31g* method and basis set, and it is named the CBS-RAD(MP2) method.

The purpose of this work is to test the performance of the composite energy methods on hydrocarbon cracking reaction energetic estimations according to the reactions with reliable experimental data. Based on the results of this work, the specific method can be applied to the estimation of large hydrocarbon cracking reaction energetics where there is no experiment information.

2. Computational methods

All of the *ab initio* calculations were performed with the GAUSSIAN98 [47] software package. Geometries were optimized at the MP2(full)/6-31g* level of calculation instead of the larger QCISD(fc)/6-31g* method recommended in the CBS-RAD method to reduce computational costs. A comparison of calculations needed for the G2, G3, CBS-QB3 and CBS-RAD(MP2) composite energy methods is shown in table 1.

All products and reactants were verified to be stable structures with frequency calculations and all transition states were found to be first order saddle points with only one negative eigenvalue. Additionally, intrinsic reaction coordinate (IRC) calculations [48] showed that each reaction linked the correct products with reactants. For the CBS-RAD(MP2) method, zero point vibrational energies (ZPVEs) were obtained from harmonic vibrational frequencies calculated at the MP2(full)/6-31g* level with a scaling factor of 0.9661[49]. Frequencies were scaled with a factor of 0.9427 at the MP2(full)/6-31g* level and a factor of 0.9537 at the QCISD(fc)/6-31g* level [49]. For heats of reaction, an additional temperature correction was added to convert from internal energy to enthalpy with the change in number of moles. This term changes the energy by a factor of $+\Delta nRT$, where $\Delta n = 1$.

3. Results and discussions

Before considering the heats of reaction and activation energies, we compare geometries and frequencies obtained with the QCISD(fc)/6-31g* and MP2(full)/6-31g* methods in tables 2–4 for the propyl radical ($CH_2CH_2CH_3$), the neopentyl radical ($CH_2C(CH_3)_3$) and the transition state structure for the propyl radical beta-scission reaction ($CH_2CH_2CH_3 \rightarrow CH_2CH_2 + CH_3$). These comparisons are important, because changes in structures affect partition functions, which may affect reaction rates estimated through transition state theory.

From table 2, the geometries and frequencies obtained by the two different computational methods for the propyl radical show the largest bond length difference is 0.005 Å for carbon–carbon bonds while the carbon–hydrogen bond lengths are all identical. Meanwhile, the largest deviation in angle is 0.32° from A(9H–3C–2C). The scaled frequency results obtained by QCISD(fc)/6-31g* are lower than the MP2(full)/6-31g* results, but the largest difference is 10%.

For geometry results of the neopentyl radical in table 3, the largest bond length difference is 0.008 Å for carbon–carbon bonds while the carbon–hydrogen bond lengths are again all identical. The largest angle difference is for A(2H–1C–4C), which is 0.19°. However, the frequency calculations using the QCISD(fc)/6-31g* method were computationally demanding and were not complete after 64 h of CPU time using the IBM pSeries 655 supercomputer at Boston University. This highlights why the original CBS-RAD method using the QCISD geometry optimization is too expensive for larger species and shows our motivation for changing to a lower level for the geometry optimization and frequency calculation.

In table 4, the transition state structure of propyl radical beta-scission reaction is shown and the largest bond

Table 1. Brief description of the composite energy methods used in this work.

Method	*G2*	*G3*	*CBS-QB3*	*CBS-RAD(MP2)*
Geometry Optimization	MP2(full)/6-31G*	MP2(full)/6-31G*	B3LYP/6-311G(*2d,d,p*)	MP2(full)/6-31G*
Single Point Calculations	MP4SDTQ(fc)/6-311G**	MP4SDTQ(fc)/6-31G*	CCSD(T)/6-31 + G(*d(f),p*)	CCSD(T)(fc)/6-31 + G*
	MP4SDTQ(fc)/6-311 + G**	MPSDTQ(fc)/6-31 + G*	MP4SDQ/CBSB4	MP4SDQ(fc)/CBSB4
	MP4SDTQ(fc)/6-311 + G**(*2df,p*)	MP4SDTQ(fc)/6-31G(*2df,p*)	MP2/CBSB3	MP2(fc)/CBSB3
	QCISD(T)/6-311G**	QCISD(T)/6-31G*		
	MP2/6-311 + G(*3df,2p*)	MP2 = (full)/big basis		
Frequency	MP2(full)/6-31G*	MP2(full)/6-31G*	B3LYP/6-311G(*2d,d,p*)	MP2(full)/6-31G*
Empirical Corrections	ΔE(SO)	ΔE(SO)	Spin Contamination	Spin Contamination
	Higher Level Correction	Higher Level Correction	Empirical Correction	Empirical Correction
	Scaled ZPE	Scaled ZPE	Scaled ZPE	Scaled ZPE

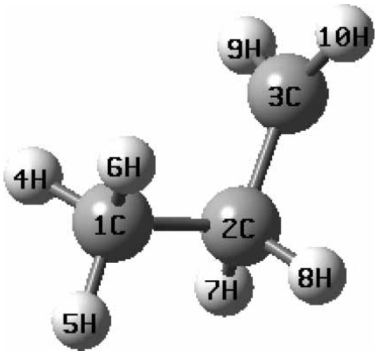
deviation is 0.02 Å for carbon–carbon bonds while the carbon–hydrogen bonds are still all identical. The largest deviation in angle is 0.15° for A(4H–1C–2C). From the frequency calculation results, all the differences are within 10% between the two methods.

With the results above, we see that geometries and frequencies obtained by QCISD(fc)/6-31g* and MP2(full)/6-31g* did not differ substantially from each other. This is the reason we propose replacing the QCISD(fc)/6-31g* method in the CBS-RAD method with the MP2(full)/6-31g* method in the new CBS-RAD(MP2) method. We next show the performance of the new CBS-RAD(MP2) composite energy method by comparing results for 13 hydro radical cracking reactions energetics with the G2 and G3 composite methods and experimental data in table 5. Both carbon–carbon bond cracking and carbon–hydrogen bond cracking reactions were investigated.

The experimental heats of reaction data were calculated with data from the National Institute of Standards and Technology (NIST) database [50]. The composite methods give similar results and the errors are within 4 kcal/mol compared to experimental values. The G2 energy has an root mean square (RMS) error of 1.88 kcal/mol and the maximum absolute deviation is 3.72 kcal/mol. The RMS error of G3 is 1.70 kcal/mol with a maximum absolute deviation of 2.52 kcal/mol. The CBS-QB3 method has an RMS error of 1.06 kcal/mol with a maximum absolute deviation of 1.96 kcal/mol. The CBS-RAD(MP2) method has an RMS error of 1.22 kcal/mol and the maximum absolute deviation is 2.06 kcal/mol. From the heats of reaction calculations of 13 hydrocarbon cracking reactions, the CBS-QB3 method has the lowest RMS error and the lowest maximum absolute deviation. The CBS-RAD(MP2) has slightly larger errors. However, the two CBS methods have much less errors compared with the G2 and G3 methods.

Table 6 is a comparison of the composite energy results of activation energies for the cracking reactions with the available experimental values [2–4] where the activation energies were obtained from the NIST Chemical Kinetics Database [51]. In general, experimental error estimates of the activation energy are ± 0.5 kcal/mol. From the results, the G2 energy has an RMS error of 1.73 kcal/mol and the maximum absolute deviation is 3.40 kcal/mol. The RMS error of the G3 energy is 1.78 kcal/mol with a maximum absolute deviation of 3.79 kcal/mol. The CBS-QB3 method has an RMS error of 2.17 kcal/mol with the maximum absolute deviation of 4.38 kcal/mol while the CBS-RAD(MP2) method shows the least RMS error of 1.37 kcal/mol with a maximum absolute deviation is of 2.88 kcal/mol. From the calculated results, the CBS-QB3 method performs most poorly for the activation energy calculations. The reason appears to be that the B3LYP density functional theory method tends to underestimate the transition state structure energies for chemical reactions and this may have some affect on the composite energies through incorrect structures. Moreover, there can be cases where the B3LYP method completely fails to find a transition state structure for a reaction [38].

Table 2. Geometry and frequency calculation results obtained by MP2(full)/6-31g* and QCISD(fc)/6-31g* methods for the propyl radical ($CH_2CH_2CH_3$).

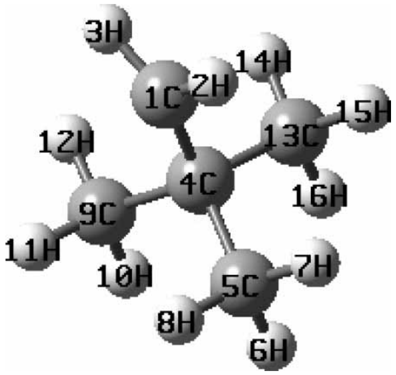


	R(1C–2C)	R(2C–3C)	R(4H–1C)	R(9H–3C)	A(1C–2C–3C)	A(9H–3C–2C)
mp2(full)/6-31g*	1.536	1.490	1.090	1.080	112.760	120.320
qcisd(fc)/6-31g*	1.541	1.490	1.090	1.080	112.950	120.640
	frequency (cm^{-1})					
mp2(full)/6-31g*	98, 253, 322, 499, 725, 872, 884, 1022, 1074, 1176, 1278, 1311					
	1378, 1446, 1465, 1474, 1481, 2925, 2928, 2973, 3012, 3020, 3047, 3149					
qcisd(fc)/6-31g*	88, 250, 320, 499, 725, 872, 883, 1024, 1073, 1179, 1282, 1313					
	1386, 1443, 1468, 1475, 1484, 2912, 2920, 2950, 2992, 2998, 3028, 3121					

Transition state structures of three carbon–carbon bond cracking reactions are compared with Saeys *et al.*'s work [24] and listed in table 7 so that the geometry optimization we have selected can be compared to high quality results from IRCmax calculations [52]. The geometries obtained by the MP2(full)/6-31g* method are closer to the IRCmax results than the B3LYP/6-311G(d,p) results. In fact, the bond difference between the two is less than 3 pm, suggesting that the MP2 level of theory is adequate for reactions involving hydrocarbon species. The B3LYP optimization has larger errors, explaining that the results from the CBS-QB3 composite energy method, which uses the B3LYP geometry optimization method, is less accurate for transition states.

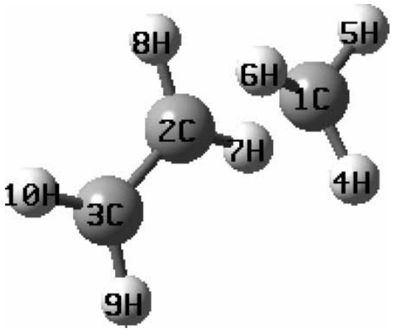
One can conclude from the calculated results in this work that for heats of reaction calculations, the CBS-RAD(MP2) method has a comparable performance with CBS-QB3 which has the least RMS error. For activation energy calculations, the CBS-RAD(MP2) method has the lowest RMS error, while the G2,G3 and CBS-QB3 methods have larger errors. However, the computational demands of the G2, G3, CBS-QB3 and CBS-RAD(MP2) methods are quite

Table 3. Geometry and frequency calculation results obtained by MP2(full)/6-31g* and QCISD(fc)/6-31g* methods for the neo-pentyl radical ($CH_2C(CH_3)_3$).



	R(1C-4C)	R(2H–1C)	R(6H–5C)	A(1C–4C–5C)	A(2H–1C–4C)	A(9C–4C–13C)
mp2(full)/6-31g*	1.497	1.080	1.090	109.770	120.180	109.110
qcisd(fc)/6-31g*	1.505	1.080	1.090	109.710	120.370	109.140
				frequency (cm^{-1})		
mp2(full)/6-31g*	153, 233, 281, 286, 301, 324, 376, 402, 405, 536, 726, 900, 913, 930, 935, 938					
	1012, 1049, 1196, 1253, 1267, 1393, 1370, 1391, 1436, 1455, 3007, 3008, 3028, 3130					
qcisd(fc)/6-31g*				not calcd		

Table 4. Geometry and frequency calculation results obtained by MP2(full)/6-31g* and QCISD(fc)/6-31g* methods for the transition state of the propyl radical beta-scission reaction ($CH_2CH_2CH_3 \rightarrow CH_2CH_2 + CH_3$).



	R(1C–2C)	*R(2C–3C)*	*R(4H–1C)*	*R(7H–2C)*	*A(1C–2C–3C)*	*A(4H–1C–2C)*
mp2(full)/6-31g*	2.260	1.340	1.080	1.080	109.520	101.660
qcisd(fc)/6-31g*	2.272	1.360	1.080	1.080	109.580	101.510
	frequency (cm^{-1})					
mp2(full)/6-31g*	591i, 108, 230, 368, 504, 532, 791, 805, 888, 964, 1047, 1211, 1277 1408, 1413, 1439, 1558, 3000, 3042, 3050, 3123, 3144, 3155, 3167					
qcisd(fc)/6-31g*	535i, 104, 220, 355, 502, 525, 766, 795, 827, 930, 979, 1205, 1252 1402, 1407, 1435, 1539, 2983, 3026, 3037, 3100, 3122, 3128, 3138					

Table 5. Comparison of computed composite heats of reaction (units in kcal/mol).

Reaction	*G2*	*G3*	*CBS-QB3*	*CBS-RAD(MP2)*	*Experiment*
$CH_2CH_3 \rightarrow CH_2CH_2 + H$	33.63	34.51	35.00	34.17	*36.24*
$CH_3CH_3 \rightarrow CH_2CH_3 + H$	101.34	99.65	100.20	100.49	*100.67*
$CH_3CH_2CH_2 \rightarrow CH_3CHCH_2 + H$	30.73	31.58	31.08	31.33	*33.05*
$CH_3CHCH_3 \rightarrow CH_2CHCH_3 + H$	33.67	34.25	34.56	34.31	*35.50*
$CH_3CH_2CH_3 \rightarrow CH_2CH_2CH_3 + H$	101.77	100.40	101.43	101.02	*101.12*
$CH_3CH_2CH_2CH_3 \rightarrow CH_2CH_2CH_2CH_3 + H$	103.63	99.99	100.94	100.69	*101.56*
$CH_3CH_2CH_2CH_3 \rightarrow CH_3CHCH_2CH_3 + H$	99.06	97.63	98.17	98.16	*98.71*
$CH_3C(CH_3)_2 \rightarrow CH_2C(CH_3)_2 + H$	33.77	34.20	34.51	34.43	*36.39*
$CH_2CH_3 \rightarrow CH_2 + CH_3$	98.69	97.49	100.79	98.53	*98.82*
$CH_2CH_2CH_3 \rightarrow CH_2CH_2 + CH_3$	24.21	20.96	22.77	21.76	*23.48*
$CH_2CH_2CH_2CH_3 \rightarrow CH_2CH_2 + CH_2CH_3$	21.25	21.10	21.85	22.16	*21.67*
$CH_2CH(CH_3)_2 \rightarrow CH_3 + CH_2CHCH_3$	19.27	20.19	22.21	21.20	*22.99*
$CH_3CHCH_2CH_3 \rightarrow CH_3 + CH_2CHCH_3$	21.30	21.05	23.43	22.32	*23.23*
Maximum absolute deviation	3.72	2.52	1.96	2.06	
Root mean square error	1.88	1.70	1.06	1.22	

Table 6. Comparison of computed composite activation energy (units in kcal/mol).

Reaction	*G2*	*G3*	*CBS-QB3*	*CBS-RAD(MP2)*	*Experiment*
$CH_2CH_3 \rightarrow CH_2CH_2 + H$	37.58	37.19	36.60	40.76	*40.98*
$CH_3CHCH_3 \rightarrow CH_2CHCH_3 + H$	36.78	36.16	35.19	35.74	*35.80*
$CH_3CH_2CH_2 \rightarrow CH_3CHCH_2 + H$	35.63	35.26	34.00	34.52	*37.40*
$CH_3C(CH_3)_2 \rightarrow CH_2C(CH_3)_2 + H$	35.76	35.16	34.55	34.92	*37.59*
$CH_2CH_2CH_3 \rightarrow CH_2CH_2 + CH_3$	30.90	30.40	28.93	29.55	*30.23*
$CH_2CH_2CH_2CH_3 \rightarrow CH_2CH_2 + CH_2CH_3$	29.87	29.43	28.10	28.62	*27.85*
$CH_3CHCH_2CH_3 \rightarrow CH_3 + CH_2CHCH_3$	30.64	30.07	29.34	29.49	*29.24*
$CH_2CH(CH_3)_2 \rightarrow CH_3 + CH_2CHCH_3$	31.04	30.54	29.53	29.66	*30.04*
$CH_2C(CH_3)_3 \rightarrow CH_2C(CH_3)_2 + CH_3$	30.51	30.08	29.53	29.35	*29.84*
Maximum absolute deviation	3.40	3.79	4.38	2.88	
Root mean square error	1.73	1.78	2.17	1.37	

Table 7. Carbon–carbon bond cracking reaction calculation results compared with Saeys, *et al.*'s work (distance in units of pm).

	*IRCMax**	*QCISD/6-31G(d)**	*MP2(full)/6-31G(d)*	*B3LYP/6-311G(d,p)*	*QCISD(fc)/6-31G(d)*
$CH_3^{\cdot} + CH_2{=}CH_2$	229.2	227.2	226.0	223.2	227.2
$CH_3CH_2^{\cdot} + CH_2{=}CH_2$	227	226.5	225.4	230.5	226.2
$CH_3^{\cdot} + CH_3\mathit{C}H{=}CH_2$	228.0	not calcd	225.1	233.2	not calcd

* Obtained from Saeys, *et al.*'s work [24].

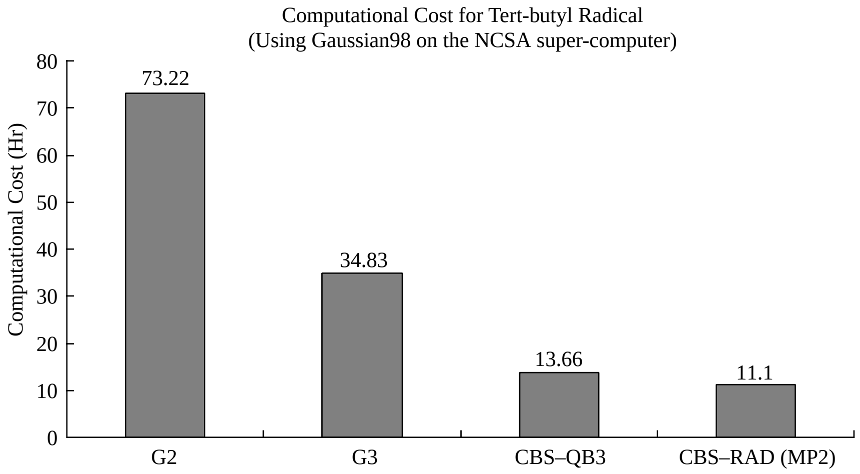


Figure 1. Computational cost of tert-butyl radical calculations using G2, G3, CBS-Q and CBS-RAD(MP2) methods.

different. A comparison of computational costs of the G2, G3, CBS-QB3 and CBS-RAD(MP2) methods for the single point and vibrational frequencies of t-butyl radical using the Gaussian98 program on the National Partnership for Advanced Computational Infrastructure supercomputer at Boston University is shown in figure 1.

This figure shows that, for tert-butyl energy calculations, the G2 method required 73.22 h of CPU time, while the G3 method required only 34.83 h, which is 48% of the G2 time. The computational cost for the CBS-RAD(MP2) method is 11.1 h, which is only 15% of the requirements for the G2 calculations. This is a large savings of 85% with an improvement in accuracy for predicting heats of reaction and activation energies for hydrocarbon reactions involving radicals. The CBS-QB3 method is composed of similar single point energy calculation steps. However, because of the large basis set used in the geometry optimization and frequency calculations, it takes 13.66 h, 23% more than CBS-RAD(MP2). These relative times are similar for the other species covered in this work. Because of the computational savings and the increased accuracy of the results, the CBS-RAD(MP2) method is recommended for the study of larger hydrocarbon cracking reactions where computational cost is a concern.

4. Conclusions

In this work, the G2, G3, CBS-QB3 and new CBS-RAD(MP2) composite energy methods are applied to calculations of the heats of reaction and activation energies of 14 hydrocarbon radical cracking reactions where reliable experimental data are available. The new CBS-RAD(MP2) method has the second least RMS error of 1.22 kcal/mol for heats of reaction calculations, very close to CBS-QB3 method which has the least RMS error of 1.06 kcal/mol. For the cracking reaction activation energy calculation results, the new CBS-RAD(MP2) method again has the least RMS error of 1.37 kcal/mol. In addition, the computational cost of the CBS-RAD(MP2) method is 81% of CBS-QB3, 32% of the G3 composite energy methods and only 15% of the G2 composite energy method. Because of the high accuracy and low computational cost, the CBS-RAD(MP2) composite energy method is useful for large hydrocarbon species.

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