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The application of composite energy methods to n-butyl radical β -scission reaction kinetic estimations

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Abstract Hydrocarbon cracking reactions are key steps in petroleum refinery processes and understanding reaction kinetics has very important applications in the petroleum industry. In this work, G3 and complete basis set (CBS) composite energy methods were applied to investigate butyl radical β -scission reaction kinetics and energetics. Experimental thermodynamic and kinetic data were employed to evaluate the accuracy of these calculations. The CBS compound model proved to have excellent agreement with the experimental data, indicating that it is a reliable method for studying other large hydrocarbon cracking reactions. Furthermore, a reaction kinetic model with pressure and temperature effects was proposed. For $P \leq P_0$, $k = 2.04 \times 10^9 \times P^{0.51} \times e^{(-9745.70/T)}$; for $P > P_0$, $k = 9.43 \times 10^{13} \times e^{(-15135.70/T)}$, where k is the reaction rate constant in units of s^{-1} ; P is pressure in units of kPa, T is temperature in units of Kelvin, and the switching pressure is $P_0 = 1.53 \times 10^9 \times e^{(-10610.24/T)}$. This model can be easily applied to different reaction conditions without performing additional expensive and complicated calculations.

Keywords Hydrocarbon cracking · Butyl radical · Rate constant · CBS method · G3 method

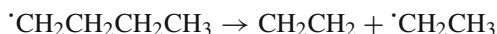
1 Introduction

Hydrocarbon cracking is the process by which higher-molecular-weight hydrocarbons are converted to lower-molecular-weight hydrocarbons through carbon–carbon bond scission [1]. There are three mechanisms for hydrocarbon cracking reactions including thermal cracking, catalytic cracking and hydrocracking. Among them, thermal crack-

ing is the dominant method for petroleum refinery processes [2] and the kinetic modelling of hydrocarbon thermal cracking has very important applications in modelling combustion and pyrolysis processes [3].

The mechanism for hydrocarbon thermal cracking is generally accepted to involve free-radical reactions. In general, hydrocarbon radical reactions are very difficult to study experimentally because of the various simultaneous reaction pathways and the very short lifetimes of radicals. As a result, the experimental kinetic information for hydrocarbon radical cracking reactions are only available for simple species, and the data are limited by the experimental conditions [4–10]. On the other hand, the dramatic increase of computer speed has greatly increased the ability to apply computational tools for investigating different chemical systems in the last decade, which makes quantum chemical approaches a good alternative [11, 12]. Particularly, the ab initio molecular orbital theory methods have been applied to investigate the structure, stability, reaction kinetics and mechanisms of different molecular systems [3, 13, 14, 16–21]. Ab initio calculations are based on the Schrödinger equation and have the advantage of depending on the fundamental laws of physics and universal constants only. Therefore, no empirical constants are required in the calculations. They are quite reliable and can reach an accuracy within a few kcal/mol for heats of formation calculations [22, 23].

In this work, ab initio methods were applied to investigate the butyl radical β -scission reaction:



Knyazev et al. studied the kinetics of this reaction using the master equation approach [4]. ΔE_{down} , the average energy transferred in deactivation collisions, was given with an uncertainty of $\pm 30\%$. The master equation approach with a large uncertainty range of ΔE_{down} constrains the ability of extending their results. In this work, a generalized kinetic model is proposed which can be applied to different reaction conditions to reduce the uncertainties in predictions.

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2 Computational method

2.1 Composite energy method

Traditionally, ab initio electronic structure energy calculations consist of a single computation. The calculation generally requires a very large basis set combined with high level method to reach high accuracy, which usually takes significantly long time to complete. Composite energy methods, also referred to as compound models, were proposed in order to reach a high level of accuracy at a relatively low computational cost. They are composed of a series of single point calculation steps whose results are then combined to obtain the final electronic energy.

For instance, the G3 method developed by Pople et al. has shown great promise for predicting heats of reaction, ionization potentials and other phenomena [24–28]. However, the single point calculation using the G3Large basis set is still very expensive for large species. Recently, another series of compound models named the complete basis set (CBS) methods have been developed [29–37]. 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. Blowers et al. [38] proposed the CBS-RAD(MP2) compound model as a modification to the computationally very expensive CBS-RAD model, which works especially well for free radicals with high spin contamination effects. The CBS-RAD(MP2) model replaces the time consuming QCISD(fc)/6–31 g* geometry optimization and frequency calculation method in the CBS-RAD with the MP2 (full)/6–31 g* calculation, which provides similar accuracy at a reduced computational cost, only 32% of the G3method. Hereafter, the CBS-RAD(MP2) method will be referred to as CBS.

In this work, the G3 and CBS compound models were used to study the reaction energetics and kinetics of the butyl radical β -scission reaction. All the ab initio calculations were performed with the GAUSSIAN98 [39] software package. Geometries were optimized at the MP2(full)/6–31 g* level of calculation. All products and reactants were verified with frequency calculations to be stable structures, and the transition state was found to be a first order saddle point with only one negative eigenvalue. Additionally, intrinsic reaction coordinate (IRC) calculations showed that the reaction linked the correct products with reactants. Zero point vibrational energies (ZPVE) were obtained from harmonic vibrational frequencies calculated at the MP2(full)/6–31 g* level with a scaling factor of 0.9661, and frequencies were scaled with a factor of 0.9427 [40]. These frequencies were used in the partition functions for the prediction of reaction rate constants. Thermal corrections were included in addition to the ZPVE at all temperatures where rate constants were calculated.

3 Rice–Ramsberg–Kassel–Marcus theory

Rice–Ramsberg–Kassel–Marcus (RRKM) theory is the most commonly used method for predicting reaction rate constants

for unimolecular reactions of polyatomic molecules [41,42]. The reaction rate constant for a unimolecular reaction can be modeled as:

$$k_{\text{uni}} = \frac{L Q_1^+ \exp(-E_0/kT)}{h Q_1 Q_2} \int_{E^+=0}^{\infty} \frac{W(E^+) \exp(-E^+/kT) dE^+}{1 + k_a(E^+)/\beta_c Z_{\text{LJ}}[M]}$$

$$k_a(E^*) = \frac{L Q_1^+ W(E^*)}{h Q_1 \rho(E^*)}$$

where L is the statistical factor; E^* the total vibrational and rotational energy; E^+ the total energy of a given state; E_0 the activation energy; Q_1^+ the partition function for the rotation of A^+ ; Q_1 the partition function for the rotation of A ; Q_2 the partition function for non-rotational modes; β_c the collision efficiency; Z_{LJ} the Lennard–Jones collision frequency; k Boltzmann's constant; h Planks constant; $[M]$ the concentration of the bath gas; $W(E^+)$ the sum of states and $\rho(E^*)$ the density of states.

The bath gas influences the rate constant through the Lennard–Jones collision frequency term Z_{LJ} , which can be obtained with:

$$Z_{\text{LJ}} = N_A \sigma_{A-M}^2 \sqrt{\frac{8RT}{\pi \mu_{A-M}}} \Omega_{A-M}$$

where N_A is the Avagadro's constant, A denotes the reactant, and M is the bath gas. σ_{A-M} the collision distance can be calculated by $\sigma_{A-M} = 1/2(\sigma_A + \sigma_M)$. μ_{A-M} the reduced mass can be calculated by $\mu_{A-M} = \frac{M W_A \times M W_M}{M W_A + M W_M}$. Ω_{A-M} the collisional integral, is only a function of reduced temperature $T^* = \frac{k_B T}{\epsilon_{A-M}}$ and can be calculated by $\Omega_{A-M} = (0.636 + 0.567 \log_{10} T^*)^{-1}$, where ϵ_{A-M} is the well depth. Physical constants which were not available in the literature were estimated from group additivity methods in Perry's handbook [43].

All the parameters listed can be obtained from quantum theory except for the collisional efficiency β_c , which is the ratio of the effective collisions that lead to products over total collisions. It is generally taken as an empirical parameter between zero and unity. We find that it is a good approximation to take its value to be 0.1 for hydrocarbon radical systems [44,45]. Actually, the rate constants increase less than a factor of 3 when increasing β_c from 0.1 to 1. In this work, it is taken as 0.1 and kept constant for all the calculations.

The difference between bath gases is described by the Lennard–Jones frequency Z_{LJ} , which is another parameter to describe the collision step. The sum of states $W(E^+)$ and the density of states $\rho(E^*)$ were calculated using the Beyer–Swinehart algorithm [46]. Hindered rotor effects were ignored because they changed the reaction rate by less than a few percent.

4 Canonical transition state theory

At high pressure limit conditions, the unimolecular rate constant does not depend on pressure and the RRKM expression simplifies to canonical transition state theory (CTST) [47,48]:

$$k_{\infty} = L \frac{kT}{h} \frac{Q^{\ddagger}}{Q} \exp(-E_0/RT)$$

where Q and Q^{\ddagger} are the complete vibrational–rotational partition functions for the reactant and the transition state.

Tunneling is a quantum effect where reactant molecules that do not have enough energy to cross the barrier can still sometimes react. Tunneling effects can be calculated with the following [49]:

$$\kappa(T) = 1 + \frac{1}{24} \left(\frac{h\nu c}{k_B T} \right)^2$$

where c is the speed of light; ν is the imaginary frequency that accounts for the vibrational motion along the reaction path and $\kappa(T)$ is the tunneling coefficient. Therefore, the reaction rate constants can be calculated as: $k = \kappa(T)k_r$.

5 Results and discussions

Table 1 shows the structures of butane, butyl radical and the transition state of butyl radical β -scission reaction optimized at the MP2/6–31G* level. For butane, the calculated C–C bond lengths are all identical at 1.525 Å. They are in excellent agreement with the experimental value, 1.526 Å [50]. For the butyl radical, because of the unsaturated C1 atom, the C1–C2 (α) bond length decreases to 1.49 Å, and the C2–C3 (β) bond length increases slightly to 1.529 Å. This information indicates that the β -bond is weaker than the α -bond and is prone to break. As the reaction takes place, the β -bond length increases and reaches 2.534 Å at the transition state, revealing the bond rupture mode. The α -bond length decreases and reaches 1.342 Å, which is close to the equilibrium C–C double bond length of ethylene, 1.331 Å. Meanwhile, the C1–C2 structure becomes mostly planar, suggesting the formation of ethylene products. Less geometric experimental information is available for radicals because of their short residence times. Therefore, the calculated results are impossible to compare directly with the experimental measurements for many radicals. However, the calculated methyl product C–H bond length is 1.080 Å, compared with the experimental value of 1.079 Å [51].

Table 2 lists the calculated energies of the reactant, transition state and products as well as heats of reaction and activation energy of the reaction. G3 and CBS compound models were chosen because of their proven compromise between accuracy and computational cost for hydrocarbon cracking reactions [38]. The calculated activation energy of the butyl β -scission reaction is 29.43 kcal/mol using the G3 method and 28.63 kcal/mol using the CBS method. Compared with the experimental activation energy from Knyazev

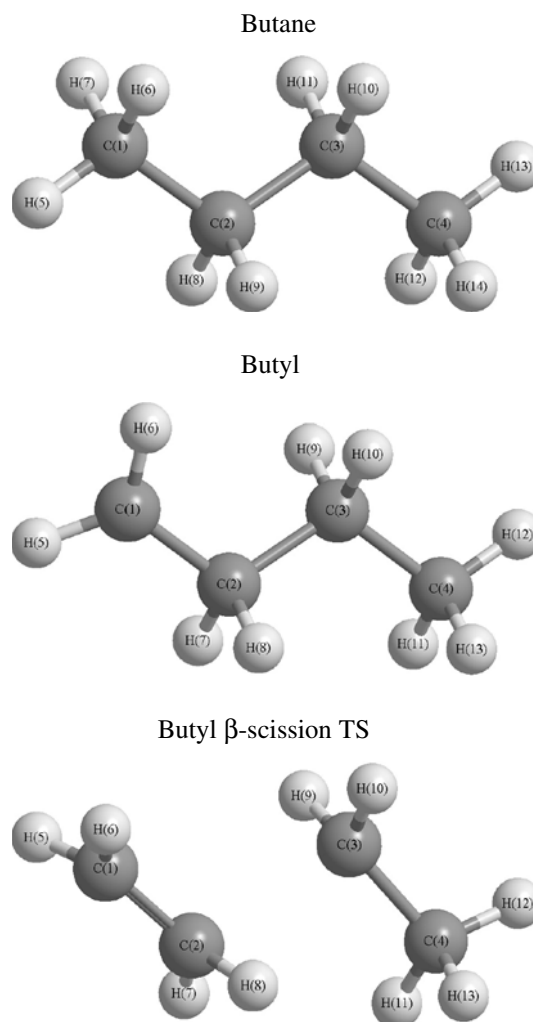


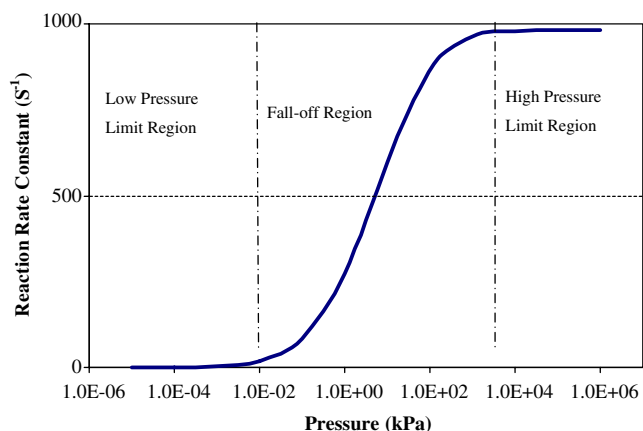
Table 1 Comparison of calculated geometry of butane, butyl and butyl β -scission transition state structure (Structures are optimized at MP2/6–31G* level. Units are in Å for bond length and degree for angles)

	Butane	Butyl	TS
R(C2C1)	1.525	1.490	1.342
R(C3C2)	1.525	1.529	2.534
R(C4C3)	1.525	1.524	1.497
R(H5C1)	1.094	1.083	1.084
R(H8C2)	1.097	1.103	1.084
R(H10C3)	1.097	1.083	1.085
A(C3C2C1)	112.871	113.213	110.988
A(C4C3C2)	112.861	112.623	104.521
A(H5C1H6)	107.868	117.353	116.482

et al, 27.82 kcal/mol [4], the CBS method has the best agreement with a relative error less than 3%, while the G3 method overestimates the activation energy by 1.61 kcal/mol. The calculated heat of reaction is 20.51 kcal/mol using the G3 method and 21.57 kcal/mol using the CBS method. Compared with heats of reaction from NIST [52], 21.67 kcal/mol, the CBS method again has an excellent agreement with a relative error less than 1% and the G3 method slightly under-

Table 2 Calculated energies of the butyl β -scission reaction (units are in Hartrees for reactant, TS and products; Units are in kcal/mol for heats of reaction and activation energy)

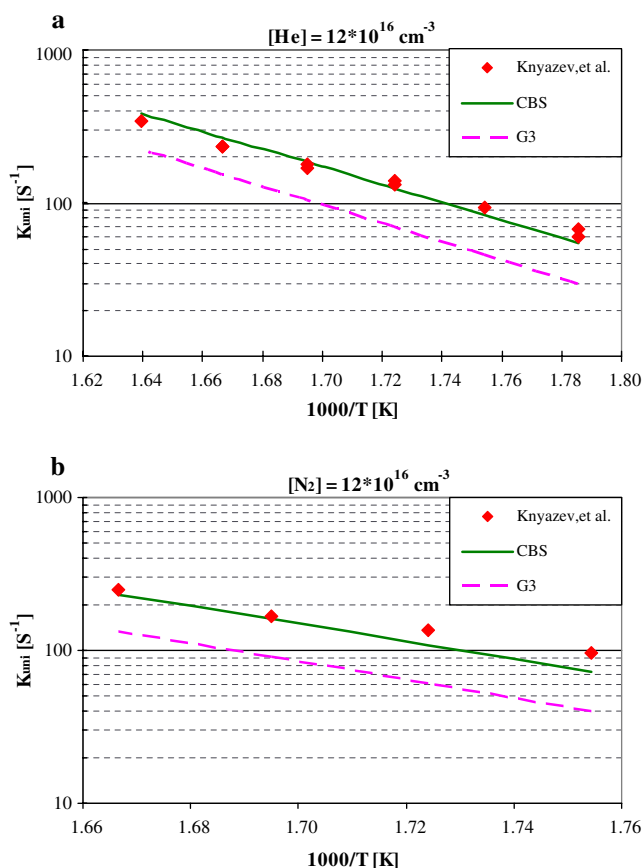
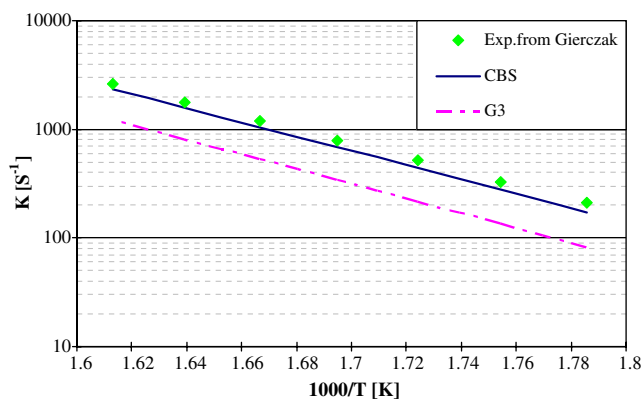
	Butyl	TS	Ethene	Ethyl	Heats of reaction	Activation energy
G3	-157.5999126	-157.553005	-78.506089	-79.061142	20.51	29.43
CBS	-157.4188053	-157.373193	-78.41548449	-78.96895229	21.57	28.62
Experiment	N/A	N/A	N/A	N/A	21.67 [52]	27.82 [4]

**Fig. 1** Butyl radical β -scission reaction rate constant calculations as a function of pressure at $T = 600$ K

estimates heats of reaction by 1.16 kcal/mol. These comparisons clearly show that the CBS and G3 compound models successfully predict the butyl β -scission reaction energies.

The pressure effect of the reaction rate constant is illustrated in Fig. 1, which is usually referred to as an S-curve. The calculations were performed at a temperature of 600 K using the CBS compound model. According to the rate dependence of pressure, the curve can be divided into three different regions. The middle region is called the fall-off region where the reaction rate is a strong function of pressure. In this region, RRKM theory is implemented to obtain the theoretical rate constants. The right-hand region is called the high pressure region where the reaction rate constant does not depend on pressure. In this region, canonical transition state theory is used to obtain the theoretical rate constants. The left-hand region is called the low pressure region. The reaction rate is so slow that it does not have any practical applications. Therefore, this region is not the object of this work.

In the fall-off region, RRKM theory is applied to calculate the reaction rate using both G3 and CBS methods. The results, together with the available experimental data, [4] are shown in Fig. 2. Two bath gases, He and N_2 , with different concentrations are considered in this work. The bath gas influences the rate constant through the Lennard-Jones collision frequency term, Z_{LJ} , in the RRKM expression. It can be seen from Fig. 2 that the CBS method successfully predicts the reaction rate constants and the errors are almost negligible compared with the experimental results. The G3 method estimates a slightly lower rate constant compared with CBS method because the activation energy obtained by G3 is 0.81 kcal/mol higher than the CBS one.

**Fig. 2** RRKM theory rate constants for the butyl β -scission reaction under different bath gases compared with experimental data from Knyazev, et al. [4]**Fig. 3** High pressure canonical transition state theory rate constant calculation results for the butyl β -scission reaction compared with experimental data from Gierczak, et al. [53]

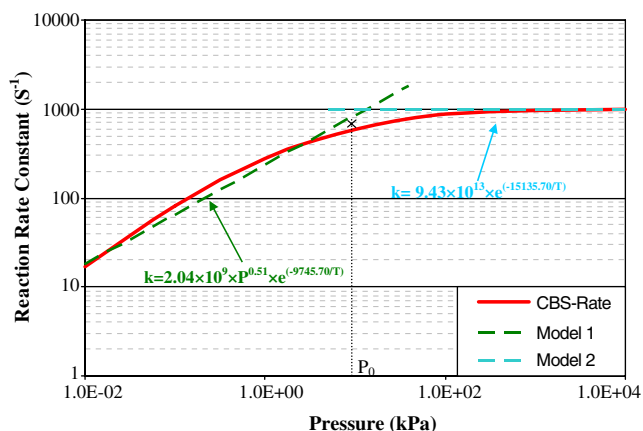


Fig. 4 Butyl radical β -scission reaction kinetic model at $T = 600$ K

In the high pressure region, the reaction rate is estimated using CTST compared with the experimental data from Gierczak et al. [53]. As shown in Fig. 3, the CBS method shows excellent agreement with the experiment, while the calculated results using the G3 method are somewhat lower.

Rate constants were then calculated in the pressure range of 0.1–10,000 kPa and the temperature range of 500–1,000 K using N_2 as the bath gas to extend the predictions to a wide range of conditions. The data in the fall-off region were modeled using the SAS software program package [54] and the models are shown below.

$$k[s^{-1}] = 2.04 \times 10^9 \times P^{0.51} \times e^{(-9745.70/T)} \quad \text{when } P \leq P_0 \quad (1)$$

$$k[s^{-1}] = 9.43 \times 10^{13} \times e^{(-15135.70/T)} \quad \text{when } P > P_0 \quad (2)$$

where P is pressure in the units of kPa and T is temperature in the units of Kelvin. Model (1) describes the reaction rate constants in the fall-off region, while model (2) is in the high pressure region and derived from the high pressure limit CTST. Then, P_0 , the switching pressure, is obtained by equalizing model (1) and (2) where $P_0 = 1.53 \times 10^9 \times e^{(-10610.24/T)}$ is acquired. The model, together with the calculated results at 600 K, is shown in Fig. 4. The calculation results indicate this model to be a very good description of the complicated quantum chemical-based chemical kinetics simulation data.

6 Conclusions

In this work, the butyl radical β -scission reaction energetics and rate constants were calculated using G3 and CBS compound models. The calculated results were then compared with the experimental data. The CBS compound model proved to be an accurate method for modeling the reaction energetics and kinetics. Furthermore, a kinetic model of the reaction with pressure and temperature effects, which can be easily applied to different reaction engineering conditions, is proposed.

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