Kinetic Modeling of *tert*-butyl Radical Decomposition Reaction

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Quantum chemical Gaussian-3 (G3), and complete basis set (CBS) composite energy methods are applied to investigate tert-butyl radical decomposition reaction kinetics and energetics. The available experimental thermodynamic and kinetic data are employed to assess the accuracy of these calculations. The CBS method proves to have good agreement with the experimental data, indicating it is a good method for studying other hydrocarbon cracking reactions involving large species. A kinetic model of the reaction with pressure and temperature effects is also proposed. For $P \leq P_0$, $k\,[s^{-1}] = (3.93 \times 10^{12}) \times P^{0.35} \times e^{(-17878.5/T)}$; *for* $P > P_0$, $k\,[s^{-1}] = (2.0 \times 10^{13}) \times e^{(-18096.0/T)}$, *where P is in units of kPa, T in units of Kelvin, and* $P_0 = (1.04 \times 10^2) \times e^{(-621.43/T)}$. *The advantage of this simple kinetic model is that it can be easily applied to different reaction conditions without performing additional costly calculations.* © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3216–3221, 2006

Keywords: hydrocarbon cracking, tert-butyl radical, rate constant, CBS method, G3 method

Introduction

Hydrocarbon thermal cracking is the process where high temperatures (typically in the range of 450°C to 750°C) are used to break large hydrocarbons into smaller ones.[1,2] Since it is the dominant method for petroleum refining processes, understanding the kinetics of hydrocarbon thermal cracking reactions has very important applications in the petroleum industry. The mechanism for hydrocarbon thermal cracking is generally accepted to be a free-radical chain reaction. The most important elementary steps are: chain initiation reactions where a hydrocarbon molecule is decomposed into two radicals, hydrogen transfer reactions, and radical decomposition reactions where a hydrocarbon radical decomposes into an olefin and a smaller radical.[3]

In general, radicals are highly reactive species and have very short lifetimes, which makes experimental study of their reaction kinetics very difficult. The experimental kinetic information for hydrocarbon radical thermal cracking is only available for several simple species.[4–10] Because under high temperatures, the product radicals are difficult to isolate before reacting further, even these experimental data are limited to moderate temperatures. Additionally, in the petroleum industry, the cracking reactions always take place at high-temperatures where the measured data may not be applicable.

Previous research from this group has shown that composite energy methods can be used to successfully predict propyl, *neo*-pentyl, and 1-chloroethyl radical cracking reaction thermodynamics and kinetics.[11–13] In this work, the focus will be on the *tert*-butyl radical decomposition reaction: $CH_3^*C(CH_3)_2 \rightarrow CH_2C(CH_3)_2 + {}^*H$, where * denotes an unpaired electron. This is a reaction where limited experimental information is available.[9,14] Therefore, this reaction can be applied as a benchmark to evaluate our choice of computation methods. With the accuracy of methods proven by this reaction, similar methods can be implemented for other hydrocarbon species where experimental data are currently unavailable.

Knyazev et al. have studied the kinetics of the decomposition reaction using the master equation approach. The average

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energy transferred in deactivations, $\langle \Delta E \rangle_{down}$, was derived with a significantly large uncertainty of $\pm 200\%$. $\langle \Delta E \rangle_{down}$ greatly depends on experimental conditions, and constrains the ability of extending their results to other conditions outside the scope of their work. In this work, a generalized kinetic model is proposed which can be applied to different reaction conditions while reducing the uncertainties in the predictions.

Computational Method

Composite energy methods

Ab initio quantum chemistry has long been applied as a major tool for investigating the structure, stability, reaction kinetics and mechanisms of different molecular systems.[3,15–23] *Ab initio* calculations, which are based on the Schrödinger equation and depend only on the fundamental laws of physics and universal constants, have the advantage of providing highly accurate predictions for a broad range of systems,[24] and require no empirical constants.

Electronic structure energy calculations traditionally consist of a single computation. However, the calculation generally requires a very large basis set and high-level method, which takes a significantly long time to reach high accuracy compared to experimental molecular structures or energetics. Composite energy methods, also referred to as compound models, were proposed in order to reach a high level of energetic accuracy at a reduced computational cost. They consist of a series of single point calculation steps where the results are combined to obtain the final electronic energy value. For instance, the Gaussian-3 (G3) method developed by Pople and coworkers has shown great promise for predicting heats of reaction, ionization potentials, and other phenomena[25–29] at a relatively low computational cost compared to its G2 ancestor. However, the single-point calculation using the G3-large basis set is very expensive for larger species of interest. More recently, another series of compound models named the complete basis set (CBS) methods have been developed.[30–38] 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.[39,40] proposed the CBS-RAD(MP2) composite energy method, which provides similar accuracy as the G3 method at a reduced computational cost, only 32% of G3.[40] Hereafter, the CBS-RAD(MP2) method will be referred to as CBS.

The G3 and CBS composite energy methods were used to study the reaction energetics and kinetics of the *tert*-butyl decomposition reaction. All of the *ab initio* calculations in this work were performed with the GAUSSIAN 98[41] software package. Geometries were fully optimized at the MP2(full)/6-31g* level. All products and reactants were verified with frequency calculations to be stable structures, and all transition states were found to be first-order saddle points with only one negative eigenvalue. Additionally, intrinsic reaction coordinate (IRC)[42] calculations proved that the transition state structure linked the correct products with reactants. Zero point vibrational energies (ZPVE) were obtained from harmonic vibrational frequencies calculated at the MP2(full)/6-31g* level with a scaling factor of 0.9661 and frequencies were scaled with a factor of 0.9427 at the MP2(full)/6-31g* level.[43]

Rice-Ramsperger-Kassel-Marcus (RRKM) theory

Rice-Ramsperger-Kassel-Marcus (RRKM) theory is the most commonly used method for predicting reaction rate constants for unimolecular reactions of polyatomic molecules.[44] The reaction rate constant for a unimolecular reaction can be modeled as

$$k_{uni} = \frac{LQ_1^+ \exp(-E_0/kT)}{hQ_1Q_2} \int_{E^+=0}^{\infty} \frac{W(E^+)\exp(-E^+/kT)dE^+}{1 + k_a(E^*)/\beta_c Z_{LJ}[M]}$$

$$k_a(E^*) = \frac{LQ_1^+ W(E^+)}{hQ_1\rho(E^*)}$$

where L is the statistical factor; E^*, the total vibrational and rotational energy; E^+, the total energy of a given transition state; E_0, the activation energy; Q_1^+, the partition function for the rotation of transition state A^+; Q_1, the partition function for the rotation of reactant A; Q_2, the partition function for non-rotational modes of reactant A; β_c, the collision efficiency; Z_{LJ} the Lennard-Jones collision frequency; k, Boltzmann's constant; h, Planks constant; $[M]$, the concentration of bath gas; $W(E^+)$, the sum of states; and $\rho(E^*)$, the density of states.[45]

All the parameters listed can be obtained from quantum theory except for the collisional efficiency β_c, which is usually taken as an empirical parameter with a value between zero and unity. We find that it is a good approximation to set its value to be 0.1 for hydrocarbon radical systems.[11–13] Actually, the rate constants increase less than a factor of 3 when increasing β_c from 0.1 to 1. In this work, β_c was taken as 0.1 and kept constant for all the calculations. 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 rate constant by less than a few percent.

Canonical transition state theory (CTST)

At high-pressure limit conditions, the unimolecular rate constant does not depend on pressure and the expression simplifies to canonical transition state theory (CTST)

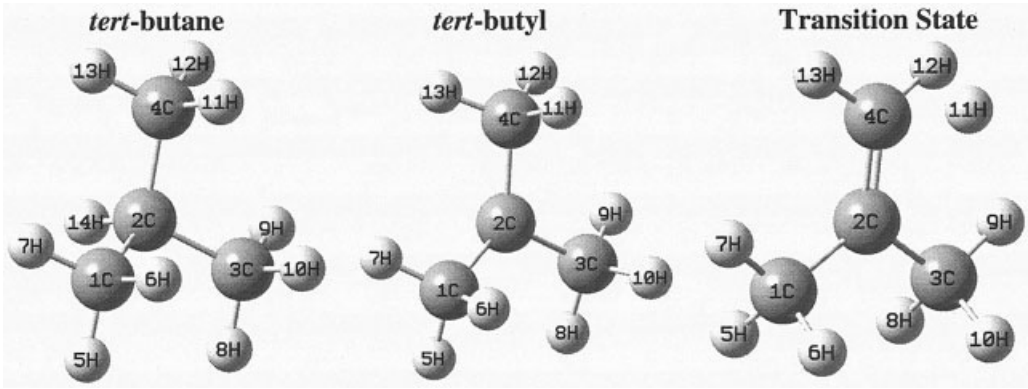
$$k_\infty = L\frac{kT}{h}\frac{Q^+}{Q}\exp(-E_0/RT)$$

where Q and Q^+ are the complete vibrational-rotational partition functions for the reactant and the transition state.

Results and Discussions

Table 1 shows the structures of the *tert*-butane, *tert*-butyl radical, and the transition state of the *tert*-butyl radical decomposition reaction calculated at the MP2/6-31G* level. For *tert*-butane, all three C-C bond lengths are identical, 1.526 Å, because of its C_{3v} symmetry. For the *tert*-butyl radical, carbon C2 has one unpaired electron, which is the reason for the high-activity of this radical. The radical keeps the symmetry, and the three C-C bond lengths are still identical, 1.493 Å, slightly shorter than that of *tert*-butane, which indicates stronger C-C bonds. As the decomposition reaction takes place, the

Table 1. Comparison of the Calculated Geometries of *tert*-butane, *tert*-butyl, and the *tert*-butyl Decomposition Reaction Transition State Structures



	tert-butane	*tert*-butyl	Transition State
R(C2C4)	1.526	1.493	1.341
R(C1C2)	1.526	1.493	1.498
R(H11C4)	1.095	1.102	1.824
A(C4C2C1)	110.84	118.01	121.89
A(C1C2C3)	110.82	118.01	115.97
A(H13C4H12)	108.03	108.29	116.07
D(C4C2C1C3)	−123.50	−152.45	−174.52

(Structures are optimized at the MP2/6-31G* level. Units are in Å for bond lengths and degrees for angles)

H11–C4 bond-length increases from 1.102 Å for *tert*-butyl reactant and reaches 1.824 Å at the transition state, showing this C-H bond rupture mode. Meanwhile, the C2-C4 bond length decreases from 1.493 Å for the *tert*-butyl reactant and reaches 1.341 Å at the transition state, close to the equilibrium bond length of *tert*-butene, 1.339 Å. The C1-C2-C3-C4 structure becomes mostly planar, indicating the formation of the *tert*-butene product. The imaginary frequency corresponding to the bond rupture mode is 1210 cm^{-1}, a typical value for C-H bond scission reaction.[3]

Table 2 lists the calculated energies of the reactant, transition state, and products, as well as the heat of reaction and the activation energy for the *tert*-butyl decomposition reaction. The G3 and CBS composite energy methods were chosen because of their proven compromise between accuracy and computational cost for hydrocarbon cracking reactions.[40] The calculated reaction pathway is shown in Figure 1. The heat of reaction is 33.60 kcal/mol using the G3 method and 33.83 kcal/mol using the CBS method. Compared to the experimental data from NIST, 36.33 kcal/mol,[14] our calculated numbers are slightly lower by 3 kcal/mol. The activation energy of the *tert*-butyl decomposition reaction is 35.16 kcal/mol using the G3 method, and 34.92 kcal/mol using the CBS method. Compared with the experimental activation energy obtained by Knyazev, 35.97 kcal/mol,[9] both methods have excellent agreement. For this reaction, the heats of reaction and activation energies obtained using G3 and CBS methods are very close to each other. Also, the comparison with the experiment data proves that both composite energy methods can accurately predict reaction energetics. Considering the computational cost of CBS method is only 32% of G3 method,[40] the CBS method is recommended especially when the reactions of interest involve large species.

The pressure effect of the reaction rate is illustrated in Figure 2, and is usually referred to as an S-curve. The calculations were performed at a temperature of 750 K using the CBS composite energy method. In this figure, three different regions can be seen according to the rate dependence of pressure. The region in the middle is the fall-off region where the reaction rate strongly depends on pressure. RRKM theory is implemented in this region to obtain the theoretical reaction rate. The region on the right is the high-pressure limit region where the reaction rate constant does not depend on pressure. CTST is implemented in this region to obtain the theoretical reaction rate. The region on the left is the low pressure limit region, where the reaction rate is so slow that it does not have any practical applications. Therefore, this region is not the subject of this research.

In the fall-off region, the reaction rate constant is calculated applying RRKM theory and using G3 and CBS composite energy methods. The calculated results, together with the available experimental data,[9] are shown in Figures 3a–b. In this work, β_c, the collisional efficiency in the RRKM expression is taken as 0.1 and kept constant for all calculations. Helium bath

Table 2. Calculated Energies of the *tert*-butyl Decomposition Reaction

	tert-butyl	TS	*tert*-butene	H	Heat of Reaction	Activation Energy
G3	−157.6095464	−157.5535231	−157.0549963	−0.501	33.60	35.16
CBS	−157.4285471	−157.3729011	−156.8746801	−0.49995	33.83	34.82
Experiment	—	—	—	—	36.33[14]	35.97[9]

(Units are in Hartrees for the reactant, TS and products; Units are in kcal/mol for heat of reaction and activation energy).

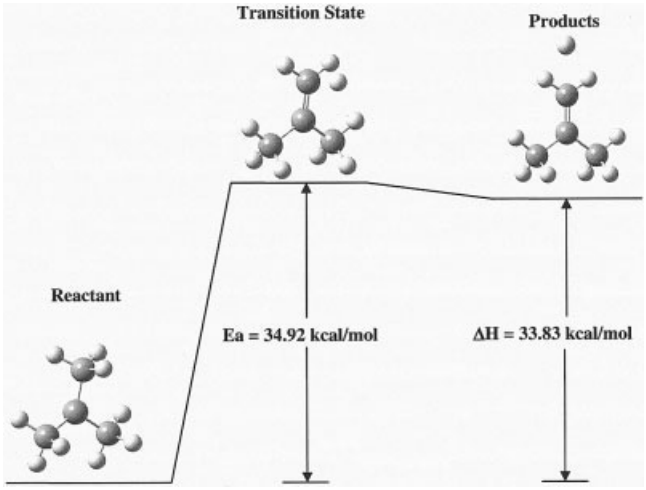


Figure 1. Calculated reaction coordinate of the *tert*-butyl radical decomposition reaction (structures are optimized at the MP2(full)/6-31G* level, and energies listed are calculated using the CBS method).

gas with different concentrations is considered, because it is the only bath gas studied in the experiments. It can be seen from Figure 3 that the G3 and CBS composite energy methods successfully predict the reaction rate under different He concentrations compared to the experimental results. The G3 method estimates a slightly lower reaction rate than the CBS method because the activation energy obtained by the G3 method is 0.24 kcal/mol higher than CBS.

In the high-pressure region, the reaction rate is estimated using CTST and compared to the experimental data from Tsang.[47] As shown in Figure 4, the G3 and CBS composite energy method results show very good agreement with the experiments, while the calculated results using the CBS method are relatively higher.

The reaction rate constants were then calculated in the pressure range of 0.1 kPa to 1,000 kPa, and the temperature range of 600 K to 1,000 K using N_2 as the bath gas to extend the predictions to a wide range of pressure and temperature conditions. Different bath gases influence the rate constant through the Lennard-Jones collision frequency term, Z_{LJ}, in the RRKM expression. The calculated kinetic data were then regressed using the SAS software program package.[48] A linear relation-

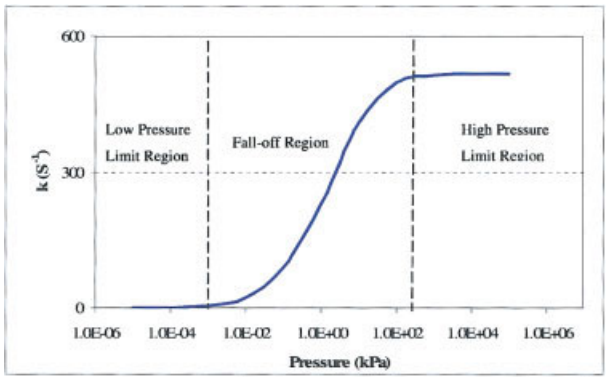


Figure 2. *Tert*-butyl radical decomposition reaction rate results as a function of pressure at T = 750 K.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

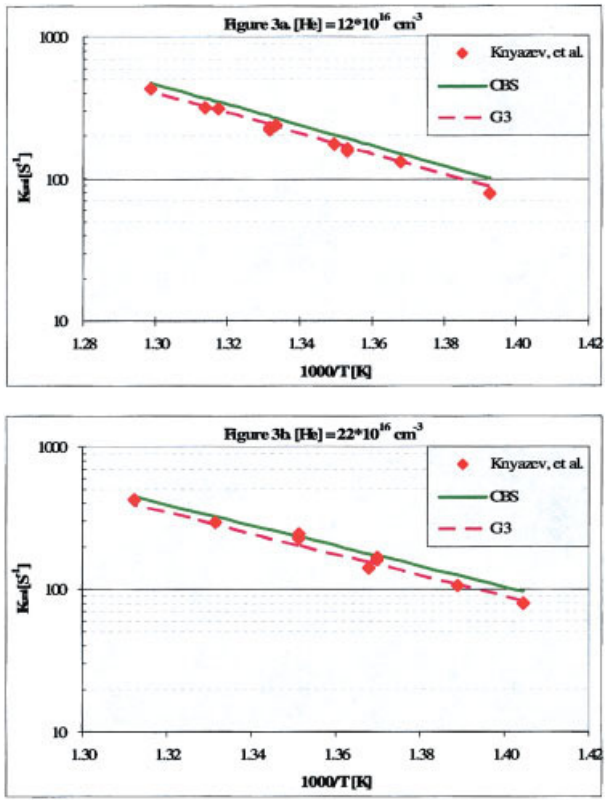


Figure 3. RRKM theory reaction rates for the *tert*-butyl radical decomposition reaction using different bath gases compared with experimental data from Knyazev et al.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

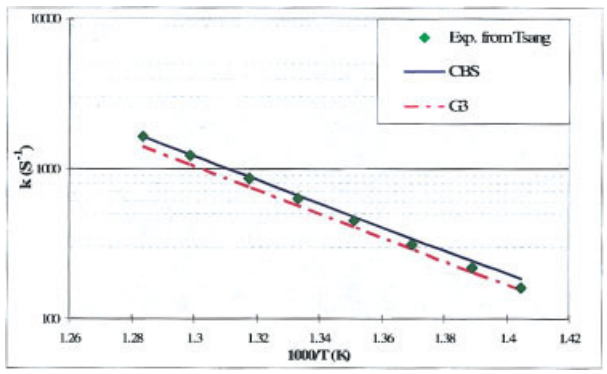


Figure 4. High-pressure canonical transition state theory rate constant results for the *tert*-butyl decomposition reaction compared with experimental data from Tsang.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

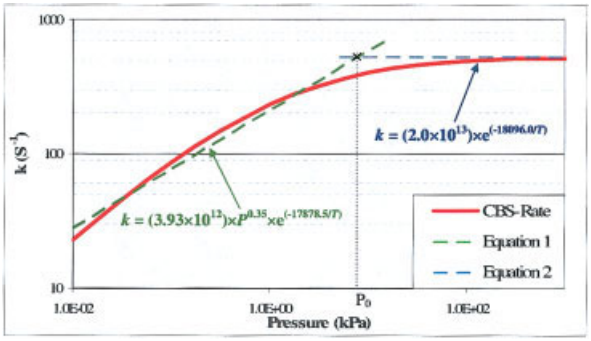


Figure 5. *Tert*-butyl radical decomposition reaction kinetic models at $T = 750$ K.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ship of $\log(k)$ with respect to $\log(P)$ and $1/T$ is introduced. The obtained kinetic model is shown below

$$k\,[\mathrm{s}^{-1}] = (3.93 \times 10^{12}) \times P^{0.35} \times e^{(-17878.5/T)} \quad \text{when } P \le P_0 \tag{1}$$

$$k\,[\mathrm{s}^{-1}] = (2.0 \times 10^{13}) \times e^{(-18096.0/T)} \quad \text{when } P > P_0 \tag{2}$$

where P is in units of kPa and T is in units of degrees Kelvin. Equation 1 describes the reaction rate in the fall-off region, while Eq. 2 applies in the high-pressure region and is derived from the high pressure limit CTST. P_0 is switching pressure where the reaction rates change from the fall off region to the high-pressure limit. This pressure was obtained by equalizing Eq. 1 and 2, leading to $P_0 = (1.04 \times 10^2) \times e^{(-621.43/T)}$. At $T = 750$ K, the model and the calculated results are shown in Figure 5. This figure shows the model to be a good description of the complicated quantum chemical-based kinetic simulation data. The advantages of this simple model are that it is extrapolated to nitrogen as the bath gas, which is more industrially common and can be easily applied even under conditions where pressure is a factor.

Conclusions

In this research, the theoretical reaction rate constants of the *tert*-butyl radical decomposition reaction were calculated using Gaussian-3 (G3) and complete basis set (CBS) composite energy methods, and the results were compared with the available experimental data. A kinetic model of this reaction with pressure and temperature effects is proposed, which can be easily applied to different reaction conditions without going into the complicated theoretical details. The CBS composite energy method has proven to give accurate energetic results for the *tert*-butyl radical decomposition reaction. This method is now applicable to hydrocarbon cracking reactions involving other species where computational demands are high.

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