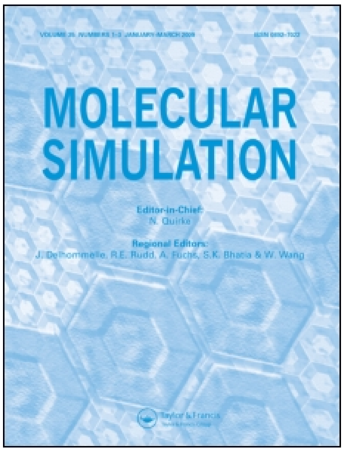

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# Application of compound models for estimating rate constants of hydrocarbon thermal cracking reactions: The neopentyl radical β-scission reaction

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# Application of compound models for estimating rate constants of hydrocarbon thermal cracking reactions: The neopentyl radical *β*-scission reaction

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In this work, neopentyl radical $\beta$-scission reaction kinetics and energetics are investigated using quantum chemical G3 and Complete Basis Set (CBS) compound models. Experimental thermodynamic and kinetic data are employed to assess the accuracy of these calculations. The CBS model 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 proposed. For $P \leq P_0$, $\mathbf{k}\,[\mathbf{s^{-1}}] = \mathbf{1.44 \times 10^{12}} \times P^{0.29} \times \exp(-13890.20/T)$; for $P > P_0$, $\mathbf{k}\,[\mathbf{s^{-1}}] = \mathbf{1.04 \times 10^{14} \times exp(-16075.80}/T)$, where $P$ is in the units of kPa, $T$ in the units of Kelvin, and $P_0 = 2.54 \times 10^6 \times \exp(-7536.55/T)$. These equations can be easily applied to different reaction conditions without performing additional costly calculations.

*Keywords*: Hydrocarbon cracking; Neopentyl radical; Rate constant; CBS method

## 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]. Understanding the kinetics of hydrocarbon cracking reactions has very important applications in the petroleum industry due to the large amounts of material processed yearly. There are three mechanisms for hydrocarbon cracking reactions: thermal cracking, catalytic cracking and hydrocracking [2]. In thermal cracking, high temperatures (typically in the range of 450–750°C) and pressures (up to about 70 atmospheres) are used to the break large hydrocarbons into smaller ones; in catalytic cracking, catalysts, usually zeolites, are used to break the large hydrocarbons; while in hydrocracking, the large hydrocarbons are broken into smaller ones by the addition of hydrogen in the presence of catalyst. Among them, thermal cracking is the dominant method for petroleum refining processes. 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.

In general, radicals are highly reactive species and have very short lifetimes, which make experimental study of their reaction kinetics very difficult. The experimental kinetic information for hydrocarbon radical cracking reactions is only available for several simple species [3–9]. Because under high temperatures, the lifetimes for radicals are very short and the product radicals are difficult to isolate before reacting further, even these experimental data are limited to moderate temperatures. In the petroleum industry, the cracking reactions always take place at high temperatures, where the measured data may not be applicable.

In this work, the focus will be on the neopentyl radical $\beta$-scission reaction:

$$^{\cdot}CH_2C(CH_3)_3 \rightarrow CH_2C(CH_3)_2 + {}^{\cdot}CH_3$$

This is a reaction where some limited experimental information is available [6]. Therefore, this reaction is applied as a benchmark to evaluate the accuracy of various theoretical methodologies. With the accuracy of methods proven by this reaction, the methods can be implemented

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for other hydrocarbon species where experimental data are currently unavailable.

Slagle *et al.* have studied the kinetics of the $\beta$-scission reaction using the master equation approach [6]. The master equation approach is one method to treat collisional energy transfer to obtain unimoleular reaction rates. $\langle \Delta E \rangle_{\mathrm{down}}$, the average energy transferred in deactivations, was derived with a large uncertainty of ± 30% and it requires the high pressure limit experiment reaction rates. $\langle \Delta E \rangle_{\mathrm{down}}$ 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.

## 2 Computational method

### *2.1 Compound models*

*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 [10–19]. *Ab initio* calculations, which are based on the Schrödinger equation, have the advantage of depending on the fundamental laws of physics and universal constants only. Therefore, no empirical constants are required in the calculations.

Electronic structure energy calculations traditionally consist of a single computation. However, in order to reach high accuracy compared to experimental molecular structures or energetics, the calculation generally requires a very large basis set and high level method, which takes a significantly long time to complete. Compound models, also referred to as composite energy methods, were proposed in order to reach a high level of energetic accuracy at a reduced computational cost. They are defined as a series of single point calculation steps where the results are combined to obtain the final electronic energy value. For instance, the G3 method developed by Pople and coworkers has shown great promise for predicting heats of reaction, ionization potentials and other phenomena [20–24] at a relatively low computational cost compared to its G2 ancestor. However, the single point calculation using the G3Large 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 [25–34]. 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. [35] 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)/6–31g* geometry optimization and frequency calculation method in the CBS-RAD method with the MP2(full)/6–31g* method and basis set, which provides similar accuracy at a reduced computational cost, only 32% of G3 [35]. 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 neopentyl radical $\beta$-scission reaction. All of the *ab initio* calculations were performed with the GAUSSIAN 98 [36] 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) calculations showed 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 [37].

### *2.2 Rice-Ramsberg-Kassel-Marcus (RRKM) theory*

RRKM theory is the most commonly used method for predicting reaction rate constant for unimolecular reactions of polyatomic molecules [38]. The reaction rate constant for a unimolecular reaction can be modeled as:

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

$$k_a(E^{*}) = \frac{L Q_1^{+} W(E^{+})}{h Q_1 \rho(E^{*})} \tag{2}$$

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 transition state $\mathrm{A}^{+}$; $Q_1$, the partition function for the rotation of reactant A; $Q_2$, the partition function for non-rotational modes of reactant A; $\beta_c$, the collision efficiency; $Z_{\mathrm{LJ}}$, the Lennard–Jones collision frequency; $k$, Boltzmann's constant; $h$, Pianck's constant; $[M]$, the concentration of bath gas; $W(E^{+})$, the sum of states; and $\rho(E^*)$, the density of states [39].

Recall, quantum mechanics considers the local environment. However, RRKM theory accounts for the larger environment surrounding the reactant through an averaged number of collisions that the reactant sees with other species in the Lennard–Jones parameter included in the integral. For this calculation of $Z_{\mathrm{LJ}}$, one has to select what the collisional partner is in order to do the calculation. Normally this species is the bath gas.

All the parameters listed can be obtained from quantum theory except for the collisional efficiency $\beta_c$, which is usually taken as a fitting parameter between zero and

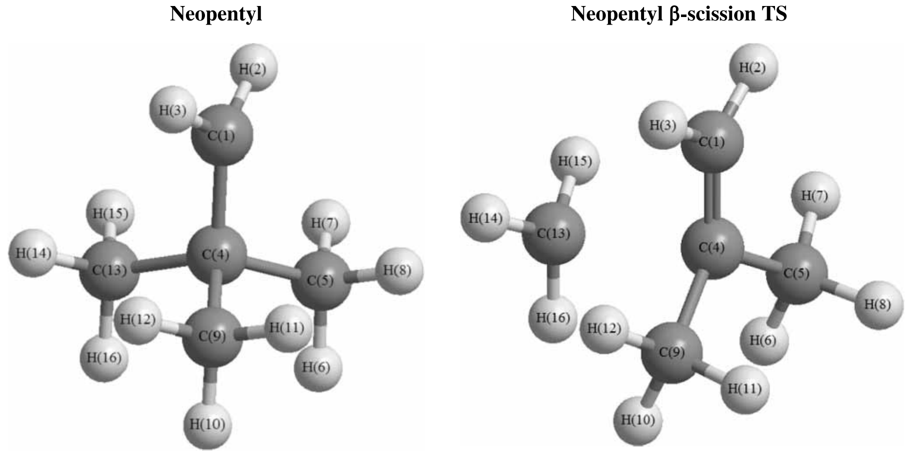
**Neopentyl** **Neopentyl β-scission TS**

Table 1. Comparison of the calculated geometry of neopentyl and the neopentyl $\beta$-scission transition state structure (Structures are optimized at MP2/6−31G* level. Units are inÅ for bond lengths and degrees for angles).

| | *Neopentyl* | *Transition State* |
|---|---|---|
| R(C1C4) | 1.497 | 1.349 |
| R(C5C4) | 1.537 | 1.510 |
| R(C13C4) | 1.537 | 2.255 |
| R(H2C1) | 1.085 | 1.085 |
| R(H7C5) | 1.095 | 1.092 |
| R(H14C13) | 1.094 | 1.083 |
| A(C5C4C1) | 109.8 | 119.9 |
| A(C13C4C1) | 109.4 | 100.6 |
| A(C5C4C9) | 109.6 | 115.1 |
| A(H2C1H3) | 117.2 | 116.7 |
| A(H7C5H8) | 108.1 | 108.1 |
| A(H14C13H15) | 108.1 | 115.6 |
| D(H9C4C1C5) | 120.5 | 153.3 |

unity. In this work, the sum of states $W(E^+)$ and the density of states $\rho(E^{\beta})$ were calculated using the Beyer–Swinehart algorithm [40]. Hindered rotor effects were ignored because they changed the rate constant by less than a few percent.

### *2.3 Canonical transition state theory (CTST)*

At high pressure limit conditions, the unimolecular rate constant does not depend on pressure and the expression simplifies to CTST:

$$k_\infty = L\frac{kT}{h}\frac{Q^+}{Q}\exp(-E_0/RT) \tag{3}$$

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

## 3 Results and discussions

Table 1 shows the structures of the neopentyl radical and the transition state of the neopentyl radical $\beta$-scission reaction optimized at the MP2/6−31G* level. For the neopentyl radical, the C1—C4 ($\alpha$) bond length is 1.497 Å and the C13—C4 ($\beta$) bond length, 1.537 Å, is slightly larger. This is an indication that the $\beta$-bond is weaker than the $\alpha$-bond and prone to break. As the reaction takes place, the $\beta$-bond length increases and reaches 2.255 Å at the transition state, revealing the bond rupture mode; the $\alpha$-bond length decreases and reaches 1.349 Å, which is close to 1.321 Å, the equilibrium bond length of isobutene. Meanwhile, the C1-C4-C5-C9 and C13 structures become mostly planar, suggesting the formation of isobutene and methyl radical products. Less experimental information is available for radicals because of their short residence time.

Table 2. Calculated energies of neopentyl $\beta$-scission reaction (Units are in Hartrees for the reactant, TS and products; Units are in kcal/mol for heat of reaction and activation energy).

| | Neopentyl | TS | Isobutene | Methyl | Heat of reaction | Activation energy |
|---|---|---|---|---|---|---|
| G3 | − 196.8761157 | − 196.8274672 | − 157.0549963 | − 39.791438 | 18.63 | 30.53 |
| CBS | − 196.6504753 | − 196.6025667 | − 156.8746801 | − 39.74397279 | 19.97 | 30.06 |
| Experiment | N/A | N/A | N/A | N/A | N/A | 29.81[42] |

Table 3. Computational cost comparison of the single point calculations using the G3 and CBS composite energy methods.

| | Neopentyl | Transition State | Isobutene |
|---|---|---|---|
| G3 | 8 hours 44 minutes | 9 hours 11 minutes | 3 hours 30 minutes |
| CBS | 2 hours 48 minutes | 3 hours 19 minutes | 1 hour 34 minutes |

Therefore, the calculated results cannot be compared directly to 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 [41].

Table 2 lists the calculated energies of the reactant, transition state and products as well as the heat of reaction and the activation energy. G3 and CBS compound models were chosen because of their proven compromise between accuracy and computational cost for hydrocarbon cracking reactions [35]. Figure 1 shows the calculated reaction pathway of the reaction. The activation energy of the neopentyl $\beta$-scission reaction is 30.53 kcal/mol using the G3 method and 30.06 kcal/mol using the CBS method. Compared with the experimental activation energy obtained by Tsang et al. [42], 29.81 kcal/mol, the relative error is only 0.83% for the CBS method and 2.4% for the G3 method. This proves that the CBS composite energy method can accurately predict reaction energetics. The heat of reaction is 18.63 kcal/mol using the G3 method and 19.97 kcal/mol using the CBS method. The activation energies of the reverse radical recombination results can be calculated as 11.90 and 10.09 kcal/mol using the G3 and CBS methods, respectively.

The supercomputer time cost for G3 and CBS composite energy calculations are listed in table 3. The calculations were performed using the IBM pSeries 690 and pSeries 655 at Boston University and the p4-long queue, which has 16GB of memory and 36GB of disk space. From the computational cost of the composite energy of neopentyl, transition state structure and isobutene species, the CBS compound method only takes one third of the supercomputer time compared to the G3 method. This difference will be crucial when investigating large hydrocarbon species in the future, not even considering that the accuracy of CBS method is better than that of G3.

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 600 K using the CBS compound model. The 600 K was chosen because it is in the middle of the experimental temperature range from previous work [6], 560–650 K. 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 is calculated using both G3 and CBS methods. The results, together with the available experimental data [6], are shown in figure 3. In this research, the collisional efficiency in the RRKM expression is taken as 0.1 and kept constant for all calculations. Three bath gases—He, $N_2$ and Ar—with

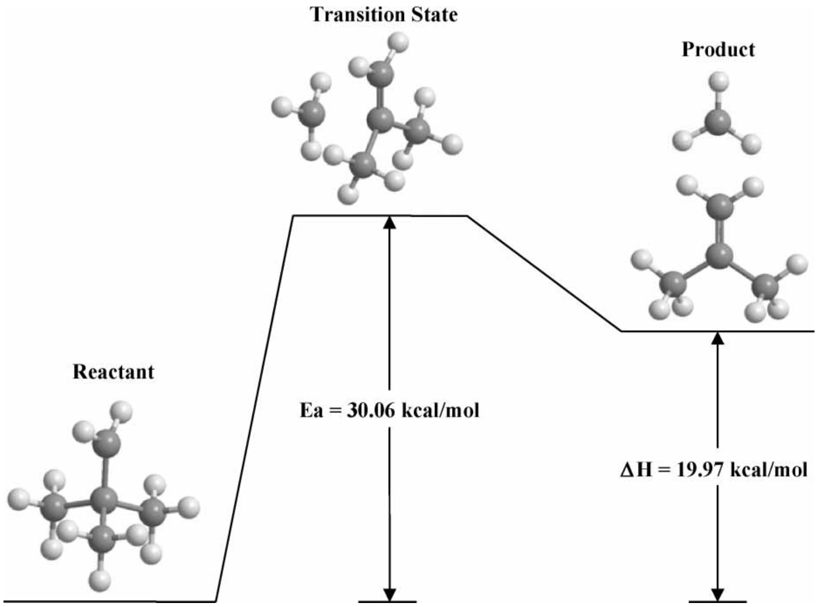

Figure 1. The calculated reaction coordinate of the neopentyl radical $\beta$-scission reaction using the CBS compound model (Structures are optimized at MP2(full)/6−31G* level and energies listed are calculated using the CBS method).

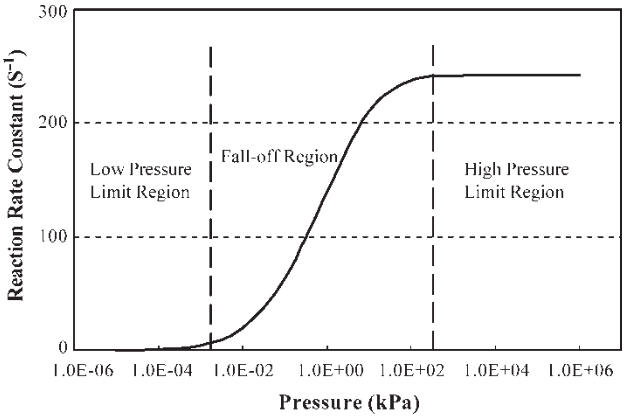

Figure 2. Neopentyl radical $\beta$-scission reaction rate results as a function of pressure at $T = 600\,\text{K}$.

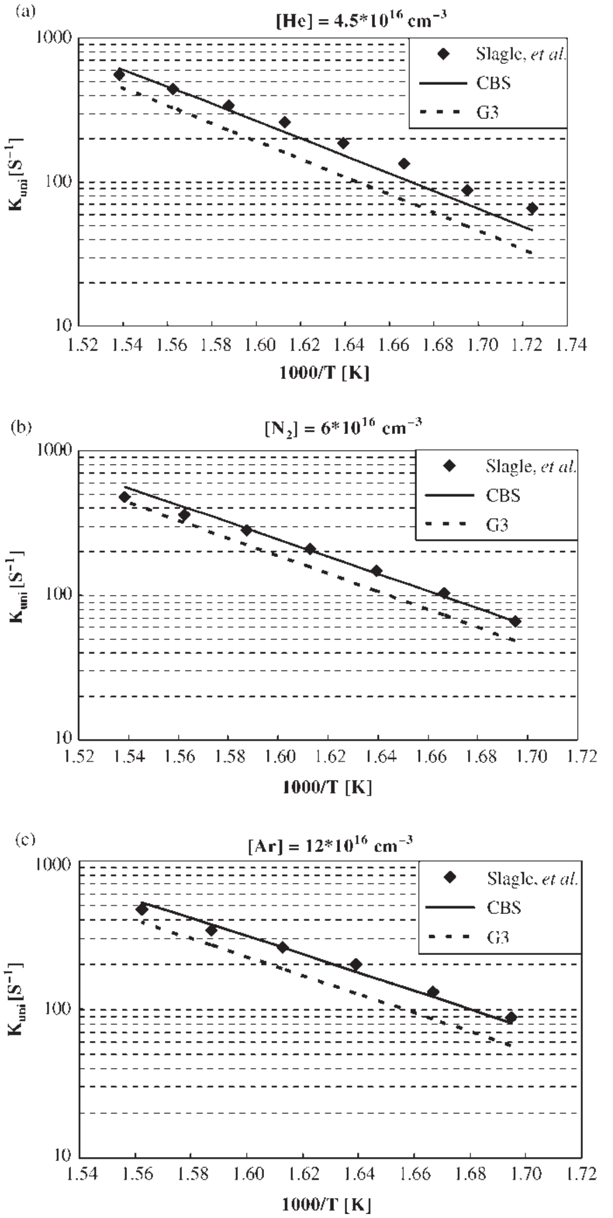

Figure 3. (a–c). RRKM theory reaction rate constants for the neopentyl $\beta$-scission reaction using different bath gases compared with experimental data from Slagel, *et al.* [6].

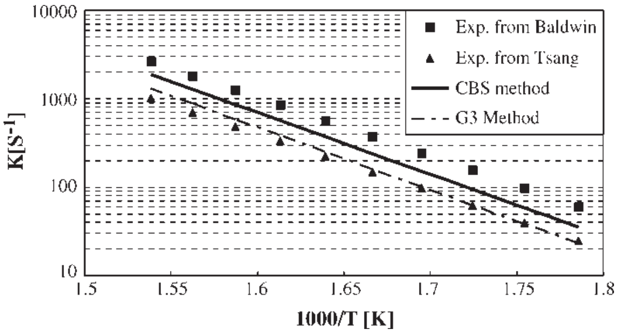

Figure 4. High pressure canonical transition state theory rate constant results for the neopentyl $\beta$-scission reaction compared with experimental data from Baldwin [43] and Tsang [42].

different concentrations are considered. The bath gas influences the reaction rate through the Lennard–Jones collision frequency term, $Z_{\text{LJ}}$. It can be seen from figure 3 that the CBS method successfully predicts the reaction rate under all conditions (different bath gases and concentrations), and the errors are almost negligible compared with the experimental results. The G3 method estimates a slightly lower reaction rate compared with the CBS method because the activation energy obtained by the G3 method is 0.47 kcal/mol higher than CBS.

In the high pressure region, the reaction rate is estimated using CTST and compared with experimental data from Tsang et al. [42] and Baldwin et al. [43]. As shown in figure 4, the CBS method results show very good agreement with the experiments, while the calculated results using the G3 method are relatively lower.

The reaction rate was then calculated in the pressure range of 0.1–1000 kPa and the temperature range of 500–1000 K using $N_2$ as the bath gas to extend the predictions to a wide range of conditions. In order to accommodate chemists and engineers who would like to utilize the kinetic calculation results without going into the details of the complicated theories, the data were regressed using the SAS software program package [44]. A linear relationship of log($k$) with respect to log($P$) and

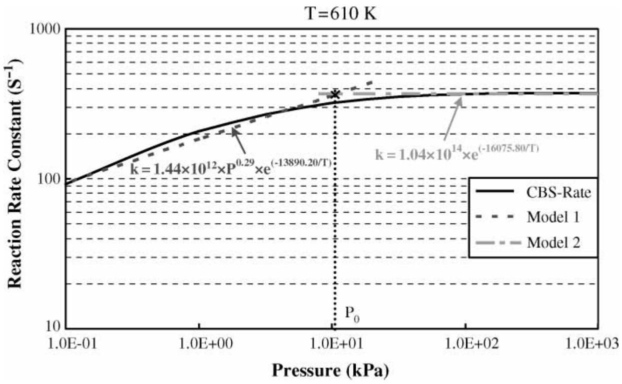

Figure 5. Neopentyl radical $\beta$-scission reaction kinetic models at $T = 610\,\text{K}$.

1/T is introduced. An R-square value of 0.995 indicates a good fit of the resulting model with the quantum chemical calculation results. The obtained models are shown below.

$$\mathrm{k}\,[\mathrm{s}^{-1}] = 1.44\times 10^{12}\times P^{0.29}\times \exp(-13890.20/T) \quad \text{when}\, P \le P_0 \tag{4}$$

$$\mathrm{k}\,[\mathrm{s}^{-1}] = 1.04\times 10^{14}\times \exp(-16075.80/T) \quad \text{when}\, P > P_0 \tag{5}$$

where $P$ is in kPa and $T$ is in degrees Kelvin. Model (4) describes the reaction rate in the fall-off region, while model (5) applies in the high pressure region and is derived from the high pressure limit CTST. $P_0$ is switching pressure where the behavior of the reaction changes from the fall off region to the high pressure limit region. This pressure was obtained by equalizing models (4) and (5), leading to $P_0 = 2.54\times 10^6\times \exp(-7536.55/T)$. At $T = 610\,\mathrm{K}$, the model and the calculated results are shown in figure 5.

The calculated results indicate the model is a good description of the complicated quantum chemical-based chemical kinetic simulation data. The advantage of this simple model is that it can be easily applied even under conditions where pressure is a factor, meaning it has broad applications to the petroleum industry.

## 4 Conclusions

In this research, the theoretical reaction rate constants of the neopentyl radical $\beta$-scission reaction were calculated using G3 and CBS compound models and compared with the available experimental data. A kinetic model of this reaction with pressure and temperature effects, which can be easily applied to different reaction conditions without going into the complicated theory details, is proposed. The CBS compound model has proven to give accurate energetic results for the neopentyl hydrocarbon cracking reaction. This method is now applicable to hydrocarbon cracking reactions involving other species where computational demands are high.

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