Kinetics and Product Distribution of *n*-Hexadecane Pyrolysis

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Pyrolysis experiments on n-hexadecane (n-C_{16}) were conducted at 673−723 K and n-C_{16} concentrations of 0.07−1.47 mol/L by using batch type reactors. The main products of n-C_{16} pyrolysis were n-alkanes and 1-alkenes at all the reaction conditions. The 1-alkene/n-alkane ratio decreased with increasing n-C_{16} concentration at all the reaction temperatures. The rate of n-C_{16} pyrolysis increased to a maximum and then decreased with increasing n-C_{16} concentration. The activation energy of the overall rate constant of n-C_{16} pyrolysis was 196 kJ/mol at 0.07 mol/L of n-C_{16} concentration and 263 kJ/mol at 0.22 mol/L. To describe these phenomena, a mathematical model for the pyrolysis that expresses the radical network reaction, including initiation, isomerization, β-scission, H abstraction, and termination, was developed. The effect of radical size on the rates of bimolecular reactions (H abstraction and termination) was important for a correct quantitative description. Comparison between the experimental data and the model showed that the rates of bimolecular reactions were inversely proportional to the carbon number i of radical R_i. The model can predict product distribution and n-C_{16} pyrolysis rate in a wide range of temperatures (603−893 K) and n-C_{16} concentrations (6.86×10^{-3} 2.48 mol/L). Furthermore, the model can describe the pyrolysis kinetics of n-C_{10}−n-C_{25} by considering the carbon number of the hydrocarbon.

Introduction

Rice and Herzfeld (1934) suggested that hydrocarbon pyrolysis occurs through a free-radical chain reaction. This reaction is initiated via C−H or C−C bond cleavage of the given hydrocarbon to form two radicals. The radicals subsequently propagate β-scission or H abstraction. The pyrolysis proceeds via these reactions and terminates by reaction between two radicals. Kossiakoff and Rice (1943) added isomerization into the mechanism of Rice and Herzfeld. This mechanism, which was proposed by Kossiakoff and Rice, is called KR theory and is widely accepted by many researchers.

Based on the KR theory, numerous models for explaining the product distribution and the reaction rate of hydrocarbon pyrolysis have been developed (Gavalas, 1966; Murata et al., 1973; Domine et al., 1990; Khorasheh and Gray, 1993; Nigam and Klein, 1993; and Song et al., 1994). All the models mainly considered five elementary reaction groups—initiation, isomerization, β-scission, H abstraction, and termination—at low overall conversions.

In the model of Nigam and Klein (1993), the type of radical in the β-scission rate constant (k_β) and H abstraction rate constant (k_H) were taken into account. Activation energies of k_β and k_H were assumed to be proportional to an enthalpy of each radical reaction. Overall rate constants of hydrocarbon pyrolysis over a wide range of temperatures and pressures were predicted with their model. Domine et al. (1990) and Khorasheh and Gray (1993) developed a model with constant kinetic parameters for each reaction group. They demonstrated that overall hydrocarbon pyrolysis rate could be explained by using five constant parameters for the elementary reaction groups. These results of Domine et al. (1990), Khorasheh and Gray (1993), and Nigam and Klein (1993) suggested that the sensitivity of the radical size on the kinetic parameter was relatively low for predicting the overall rate.

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Recently, Wu et al. (1996) reported that the ratio of k_β to k_H [n-C$_i$], which was defined as the concentration of the starting hydrocarbon, n-C$_i$, increases with radical carbon-number-based experimentally determined product distributions of n-hexadecane (n-C$_{16}$) pyrolysis. Their results suggest that the radical-size dependence of k_H and k_β is essential for explaining of product distribution.

The size dependence of species on the rate constant of elementary reaction of free radical has been evaluated through direct measurement (Cohen and Benson, 1987a,b; Bott and Cohen, 1991; Cohen, 1991; Koffend and Cohen, 1996). Cohen and Benson (1987b) and Cohen (1991) reported that the rate constant of H abstraction between OH radical and n-alkane (n-C$_i$) decreased with increasing carbon number (i) of n-C$_i$. Direct measurement of the rate constant of the elementary reactions of a shorter chain alkyl radical also has been reported (reviewed by Allara and Shaw, 1980). Cohen (1991) explained the size dependence of n-alkane on the rate constant of H abstraction using transition-state theory (TST). However, for long chain alkyl radicals, the direct measurement of the radical-size dependence on the rate constant has not been reported so far.

Experimental data on n-C$_{16}$ pyrolysis is most abundant among the hydrocarbon pyrolysis studies performed. Pyrolysis experiments of n-C$_{16}$ in the gas phase have been conducted for industrial interests (Voge and Good, 1949; Panchenkov and Branov, 1958; Tilicheev and Zimina, 1956; Fabuss et al., 1962, 1964; Groenendyk et al., 1970; Rebick, 1981; Fairburn et al., 1990; Wu et al., 1996, 1997). Liquid-phase pyrolysis experiments of n-C$_{16}$ have also been conducted for mainly geochemical interests (Blouri et al., 1984; Ford, 1986; Khorasheh and Gray, 1993; Song et al., 1994; and Jackson et al., 1995). Unfortunately, few data exist over the continuous range of conditions from the liquid to the gas and supercritical phase.

A compound above its critical temperature is noncondensable. Thus, the supercritical condition offers an excellent environment for understanding pyrolysis, since the density of the reacting phase can be varied continuously over the range of conditions of interest. Our objective was to examine the pyrolysis of n-C$_{16}$ at sub- and supercritical conditions and to develop a new model that could describe the kinetics and product distribution.

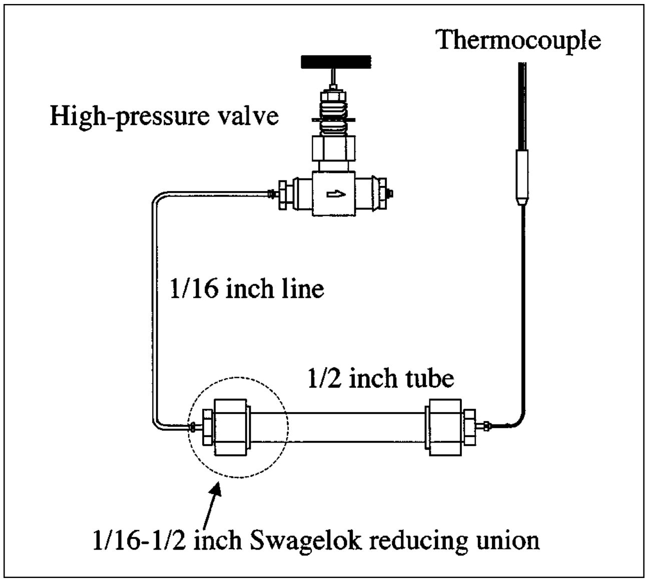

Figure 1. Batch reactor.

Experimental Studies

The n-hexadecane used had a purity of +98.0% and was obtained from Wako Chemicals (Osaka, Japan). The analytical reagents used were tetrahydrofuran (THF, +97%) with 2,6-di-t-butyl-4-methylphenol inhibitor and naphthalene (+99%) and also were obtained from Wako Chemical. All chemicals were used without further purification.

Pyrolysis experiments were carried out at temperatures of 673 K, 693 K, and 723 K. Experiments at 673 K were conducted with stainless-steel (SS 316) batch type reactors (6 cm^3) with a high-pressure valve (Whitey, model SS-3NBF2), as shown in Figure 1. The batch type reactors were made of an SS 316 tube (length: 105 mm; ID: 8.5 mm; OD: 12.7 mm) and had two SS316 1/16−1/2-inch Swagelok reducing unions. One of the reducing unions had a 1/16-inch SS 316 line (length: 100 mm; ID: 0.588 mm; OD: 1.588 mm) that was connected to the high-pressure valve, and the another had a thermocouple that was inserted into the reactor to measure the reaction temperature. Experiments at 693 K and 723 K were conducted without the high-pressure valve. The reaction times were at 10 min or 60 min, as indicated in Tables 1 and 2. Air in the reactor was displaced with Argon (Ar). The reactor was loaded with 0.1 g (0.07 mol/L) or 0.3 g (0.22 mol/L) of n-C$_{16}$ for experiments at 673 K and 693 K. For 723 K experiments (above the critical temperature of n-C$_{16}$), loadings of 0.6 g (0.44 mol/L) and 2.0 g (1.47 mol/L) of n-C$_{16}$ were used in addition to the loadings of 673 K and 693 K experiments. At 673 K, gas-phase concentration is 0.22 mol/L and liquid-phase concentration is 2.1 mol/L, and at 693 K, gas-phase concentration and liquid-phase concentration is 0.33 mol/L

Table 1. Experimental Results at 673 K

[n-C$_{16}$], mol/L	0.07	0.22
Reaction Time, min	60	60
Conversion, %	8.7	10

Carbon No.	Product Distribution					
	Molar Selectivity, mol. %			Molar Selectivity, mol %		
	n-Alkane	1-Alkene	$\theta_{i(\exp)}$	n-Alkane	1-Alkene	$\theta_{i(\exp)}$
1	5.4	—	—	3.2	—	—
2	9.6	5.0	0.5	5.5	1.9	0.3
3	7.6	7.8	1.0	4.6	4.2	1.0
4	6.0	7.4	1.2	5.0	5.2	1.0
5	4.5	2.5	0.6	6.3	3.0	0.5
6	2.8	4.1	1.5	3.7	5.5	1.5
7	2.1	5.5	2.6	4.7	6.3	1.3
8	1.4	3.9	2.8	3.6	5.2	1.5
9	1.2	3.6	3.1	3.1	4.8	1.5
10	0.9	3.2	3.7	3.1	4.6	1.5
11	1.0	3.4	3.5	2.7	4.4	1.6
12	0.8	2.7	3.5	2.3	4.0	1.7
13	1.0	3.0	2.9	2.5	3.6	1.4
14	0.7	2.8	4.1	0.5	3.5	6.7
15	nd*	1.0	—	0.2	1.1	4.8

*Not detected.

Table 2. Experimental Results at 693 and 723 K

$[n\text{-C}_{16}]$, mol/L	0.07	0.22	0.07	0.22	0.44	1.47
Temp. K	693	693	723	723	723	723
Reaction Time, min	10	10	10	10	10	10
Conversion, %	4.2	5.7	15.7	27.6	30.2	29.9
CN	1-Alkene/n-Alkane Ratio ($\theta_{i(\mathrm{exp})}$)					
6	1.7	1.2	1.6	1.3	1.1	0.6
7	2.3	1.8	3.6	2.2	1.6	0.7
8	2.8	2.0	4.3	2.5	1.7	0.7
9	2.9	1.9	4.3	2.5	1.7	0.7
10	2.9	2.0	4.7	2.7	1.7	0.7
11	3.3	2.0	4.7	2.6	1.8	0.7
12	3.5	2.0	4.7	2.7	1.8	0.8
13	3.0	1.4	4.2	2.3	1.6	0.6
14	17.3	3.0	30.7	14.6	10.6	3.1
15	4.6	4.2	11.6	8.8	6.7	1.5

and 2 mol/L, respectively, (Peng and Robinson, 1976; Marano and Holder, 1997). Therefore, the reaction phases under all reaction conditions were homogeneous phases.

The reactor was submerged in a fluidized sand bath (Takabayashi Riko Co., model TK-3) whose temperature was controlled to be a reaction temperature. Heatup time of the inside of a reactor was around 3 min. After the reaction time, exclusive of the heatup time, the reactor was taken out of the bath and rapidly quenched (in several seconds) in a water bath.

After the cooling, the reactor was connected to a syringe that was equipped with gas samplers to collect produced gas and measure its volume. Typical gas volumes were 20 mL ~ 60 mL at STP. The produced gases were analyzed by GC-TCD (Shimadzu, model GC-7A) with an He carrier after measuring its volume.

After sampling or displacing the produced gases, the reactor was opened and washed with THF. The THF solution contained $C_5 \sim C_{16}$ hydrocarbons. The concentration of each product in the THF solution was quantified by GC-FID (Hewlett-Packard, model 5890, series II) and evaluated with naphthalene as the internal standard. The response factors for several hydrocarbon standard (1-C_7, n-C_7, 1-C_9, n-C_9, 1-C_{11}, n-C_{12}, n-C_{13}, 1-C_{14}, and n-C_{14}; purity of all the standards was over 99%) were evaluated to be $0.98 \sim 1.04$. The compounds in the THF solutions were identified by the GC-FID and GC-MS (Japan Electron Optics Laboratory, model Automass 20).

Conversion of n-C_{16} ($X_{n\text{-C}_{16}}$) was evaluated as

$$X_{n-\mathrm{C}_{16}} = \left(1 - \frac{[n-\mathrm{C}_{16}]_f(\mathrm{mol})}{[n-\mathrm{C}_{16}]_0(\mathrm{mol})}\right) \times 100\,[\%], \tag{1}$$

where $[n\text{-C}_{16}]_0$ is the amount of n-C_{16} loaded, and $[n\text{-C}_{16}]_f$ is the amount of n-C_{16} recovered. The apparent first-order rate constant ($k_{(16)}$) was evaluated by

$$k_{(16)} = -\frac{\ln\left(1 - X_{n\text{-C}_{16}}/100\right)}{\tau}, \tag{2}$$

where τ is the reaction time. Molar selectivity was evaluated as

$$\text{Molar selectivity} = \frac{[n\text{-C}_i]}{\sum_{j=1}^{15}\left\{[n\text{-C}_j] + [\mathrm{Ol}_j]\right\}} \times 100\,[\%] \quad \text{or}$$

$$= \frac{[\mathrm{Ol}_i]}{\sum_{j=1}^{15}\left\{[n\text{-C}_j] + [\mathrm{Ol}_j]\right\}} \times 100\,[\%] \tag{3}$$

where $[n\text{-}C_i]$ is the amount of n-alkane (n-C_i, where i is a carbon number) and $[\mathrm{Ol}_i]$ is the amount of 1-alkene produced (Ol_i, where i is also a carbon number). The 1-alkene/n-alkane ratio ($\theta_{i(\mathrm{exp})}$) at carbon number of i was defined by

$$\theta_{i(\mathrm{exp})} = \frac{[\mathrm{Ol}_i]}{[n\text{-C}_i]}. \tag{4}$$

Results

Product distribution

Tables 1 and 2 show experimental results. The experiments were repeated at least three times for all the data points, and the mean values are shown in these tables. The experimental errors were ±0.1% for the molar selectivities and ±1% for the conversions.

C_1, C_2, and C_3 are gas products, and these yields seemed a little low in quantity because of the difficulty in taking complete samples and the accurate analysis gas products. Moreover, since C_4 and C_5 existed in both gas and liquid products, the quantification of C_4 and C_5 compounds seemed incomplete. Furthermore, since the peak of the C_6 and C_7 species on the FID chromatogram was partly merged, the analysis of the C_6 compounds was also incomplete. The carbon balance was 80 ~ 90% in all experiments conducted at 673 K for these reasons. The amount of hydrogen in the product gas is negligibly small at 673 K. The gas product was not analyzed since a high-pressure valve was not used for the 693 K and 723 K experiments. Carbon balance was not evaluated in all experiments conducted at 693 K and 723 K.

We used GC-MS to identify all the peaks detected on the chromatogram. As shown in Tables 1 and 2, the primary products of n-C_{16} pyrolysis were n-alkanes from C_1 to C_{15} and 1-alkenes from C_2 to C_{15}. Khorasheh and Gray (1993) reported that a series of 2-alkenes was produced through n-C_{16} pyrolysis. According to them, the GC peak of a series of 2-alkene (2-Ol_i) was located between that of Ol_i and n-C_i. Although our GC analytical procedures were almost the same as theirs, there was no peak or negligibly small peak between Ol_i and n-C_i. A series of branched alkane was also formed through n-C_{16} pyrolysis at high n-C_{16} concentration conditions (Ford, 1986; Khorasheh and Gray, 1993; Wu et al., 1996). According to Khorasheh and Gray (1993), the GC peak of a series of branched alkane (branch-C_i) appeared between that of n-C_i and n-C_{i+1}. In the experiments, we recognized the existence of branched alkanes only at the highest n-C_{16} concentration (723 K and 1.47 mol/L of n-C_{16} concentration). Therefore, we consider that, except for the 723 K condition and a concentration of 1.47 mol/L of n-C_{16}, only n-alkane and 1-alkene were products in the experimental conditions.

As shown in Table 1, the 1-alkene/n-alkane ratio varied from 0.3 to 6.7. The molar selectivity of shorter chain hydrocarbons ($C_1 \sim C_4$) at 0.07 mol/L of n-C_{16} concentration was higher than that at 0.22 mol/L of n-C_{16} concentration. The 1-alkene/n-alkane ratios at 0.07 mol/L of n-C_{16} concentration was higher than that at 0.22 mol/L of n-C_{16} concentration.

From KR theory, n-alkanes are produced from H abstraction and 1-alkenes are formed via β-scission. Therefore, as shown in Table 1, the higher molar selectivity of n-alkanes at a higher n-C_{16} concentration (0.22 mol/L) indicates that H abstraction is predominant against β-scission, as has been elucidated in earlier works (Watanabe et al., 1998).

Table 2 shows 1-alkene/n-alkane ratios ($\theta_{i(\exp)}$) for runs made at 693 K and 723 K. The $\theta_{i(\exp)}$ is higher than unity at any carbon number i ($= 6 \sim 15$), except for the results obtained at 723 K and 1.47 mol/L. We also obtained additional products (C_{16}^{+}) at 723 K and 1.47 mol/L. This molecular compound, which is larger than n-C_{16} was produced by adding the n-hexadecyl radical to 1-alkene (Ford, 1986; Khorasheh and Gray, 1993; Wu et al., 1996). 1-Alkene disappears as a result of this addition reaction. In the results, the ratio of 1-alkene to n-alkane was below unity. At both 693 K and 723 K, 1-alkene/n-alkane ratios increased with the decreasing n-C_{16} concentration.

The 1-alkene/n-alkane ratio clearly increased as the carbon number increased at both concentrations at 673 K, as shown in Table 1. The 1-alkene/n-alkane ratio in the 693 K and 723 K experiments also increased with increasing carbon number at all concentrations, as shown in Table 2. Therefore, the carbon number dependence on the formation rate of the n-alkanes and 1-alkenes must be taken into account.

Apparent first-order rate constant

The overall activation energies obtained from an Arrhenius plot of the apparent first-order rate constants were 196 kJ/mol and 263 kJ/mol for n-C_{16} concentration of 0.07 mol/L and 0.22 mol/L, respectively. This difference is mostly due to the change between β-scission and H abstraction with changing n-C_{16} concentration and is discussed later.

Model

Elementary reactions

The model is based on the KR theory, and thus the following five elementary reaction groups were considered:

1. *Initiation*: A reaction of a C−C bond cleavage of n-C_{16}.
2. *Isomerization*: A reaction of an odd electron transfer in an alkyl radical.
3. *β-scission*: A reaction of an alkyl radical decomposition.
4. *H abstraction*: A reaction of an odd electron transfer between n-C_{16} and an alkyl radical.
5. *Termination*: A reaction of the recombination of two alkyl radicals.

A set of the rate constants of the reactions used in this analysis is from earlier work. In this model, however, the following additional assumption was incorporated: for the rates of bimolecular reactions 4 and 5 the radical-size dependence is taken into account and can be expressed as

(a) $k_{\mathrm{H}}(i) = f(i) k_{H_0}$ for 4

(b) $k_{\mathrm{term}}(i)(j) = g(i) g(j) k_{\mathrm{term}_0}$ for 5,

due to the recently reported experimental results by Wu et al. (1996). The basic concept of this model (based on the models of Fabuss et al., 1964; Doue and Guiochon, 1968; Murata et al., 1973; Khorasheh and Gray, 1993; Nigam and Klein, 1993; and Wu et al., 1996, plus preceding two assumptions) is summarized below.

1. Initiation. In the model, as in the models of Fabuss et al. (1964), Khorasheh and Gray (1993), and Nigam and Klein (1993), initiation occurs only for n-C_{16}, because the amount of n-C_{16} is much greater than that of the other species at a lower conversion level. The formation of hydrogen atm through initiation was neglected, as in the models of Fabuss et al. (1964) and Khorasheh and Gray (1993), for the following reasons. The activation energy of initiation is equal to bond dissociation energy (Nigam and Klein (1993)). The activation energy of the rate constant of initiating the formation of the methyl radical ($k_{\mathrm{init}(M)}$) should be 13 kJ/mol higher than that of the formation of the other radicals ($k_{\mathrm{init}(O)}$), and that of forming hydrogen atm ($k_{\mathrm{init}(H)}$) should be 69 kJ/mol higher than that of $k_{\mathrm{init}(O)}$ (Benson, 1976). The frequency factor is the same for $k_{\mathrm{init}(M)}$ and $k_{\mathrm{init}(O)}$ (Nigam and Klein, 1993).

2. Isomerization. As in the models of Fabuss et al. (1964), Khorasheh and Gray (1993), and Wu et al. (1996), an odd electron position on an alkyl radical is evaluated statistically, because the rate of isomerization is much faster than that of the other propagation reaction, even at a lower temperature and higher concentration, where bimolecular reaction is assumed to predominate (Khorasheh and Gray, 1993; Wu et al., 1996). In this model, we employed isomerization through 6- or 7-ring formation (1,5-shift or 1,6-shift, respectively), as proposed by Fabuss et al. (1964). For the statistical evaluation of the odd-electron position, a possible site for the electron transfer through 6- and 7-ring formation and its rate were taken into consideration (see the Appendix for more details). The kinetic data were from Fabuss et al. (1964) and Murata et al. (1973). The activation energy of the rate constant of the intramolecular H abstraction from the primary carbon ($k_{H(P)}$) is 16.7 kJ/mol higher than that from the secondary carbon ($k_{H(S)}$) (Fabuss et al., 1964; Murata et al., 1973), and the frequency factor of both $k_{H(P)}$ and $k_{H(S)}$ is the same (Fabuss et al., 1964; Murata et al., 1973.

3. β-Scission. The formation of hydrogen atm through β-scission was not considered and both the frequency factors of the rate constants of β-scission forming the methyl radical ($k_{\beta(M)}$) and that for forming the other alkyl radicals ($k_{\beta(O)}$) were the same as in the other models (Fabuss et al., 1964; Khorasheh and Gray, 1993). In this analysis, the kinetic data used were the same as in these models. The activation energy of the rate constants of β-scission of the forming hydrogen atm ($k_{\beta(H)}$) is 42 kJ/mol higher than that for forming the other radicals ($k_{\beta(O)}$), and that of forming the methyl radical ($k_{\beta(M)}$) is 8.4 kJ/mol higher than that for $k_{\beta(O)}$ (Murata et al., 1973; Allara and Shaw, 1980; Khorasheh and Gray, 1993).

4. H Abstraction. As in the models of Fabuss et al. (1964), Khorasheh and Gray (1993), and Wu et al. (1996), H abstraction occurs only for n-C$_{16}$, because n-C$_{16}$ is the most abundant in the system at a low conversion level. In this model, assumption (a) has been adopted: the rate constant of H abstraction between n-C$_{16}$ and an alkyl radical, which has i carbon atm (R_i), is assumed to be expressed by $k_{H_0} f(i)$, where $f(i)$ is the function of the carbon number of R_i and k_{H_0} is the intrinsic rate constant of H abstraction.

5. Termination. As reported by Allara and Shaw (1980), the radical reaction network of n-C$_{16}$ pyrolysis is assumed to terminate by only recombination of two radicals, because a disproportionate contribution between the two alkyl radicals is negligible. Here assumption (b) has been incorporated: the termination rate constant between R_i and R_m is assumed to be expressed by $k_{\text{term}_0} g(i) g(m)$, where $g(i)$ and $g(m)$ are the function of the carbon number of radicals (R_i and R_m) and k_{term_0} is the intrinsic rate constant.

Radical concentration

The net formation rate of a radical is evaluated by the formation rate minus the disappearance rate of the radical. Except for R_{16}, alkyl radicals are produced by initiation and β-scission, and disappear via β-scission, H abstraction, and termination. Therefore, the net formation rate R_i $(1 \le i \le 15)$ is described by

$$\begin{aligned}\frac{d[R_i]}{dt} &= 2k_{\text{init}(X)}[n\text{-C}_{16}] + k_{\beta(X)}\left[\sum_{j=i+2}^{16} \omega_j [R_j]\right] \\ &\quad - k_{\beta(i)}[R_i] - k_{H_0} f(i)[R_i][n\text{-C}_{16}] \\ &\quad - k_{\text{term}_0} g(i)[R_i]\sum_{j=1}^{16} g(j)[R_j], \qquad (5)\end{aligned}$$

where

$$\omega_j = P_{\text{iso}}(j, j-i-1) + P_{\text{iso}}(j, i+2). \qquad (6)$$

The first term on righthand side of Eq. 5 is the formation of R_i via initiation, where X is M ($i = 1$ or 15) or O ($2 \le i \le 14$). The second term is the formation of R_i via β-scission after isomerization, where X is M ($i = 1$) or O ($2 \le i \le 14$), and $P_{\text{iso}}(j,\ j-i-1)$ and $P_{\text{iso}}(j,\ i+2)$ are probabilities of an odd electron position on R_i (see the Appendix). The third term is the disappearance rate of R_i via β-scission, where $k_{\beta(i)}$ is disappearance rate constant of β-scission of R_i (see the Appendix). The fourth term is the disappearance rate of R_i via H abstraction and the last term is the disappearance rate of R_i via termination.

The hexadecyl radical (R_{16}) forms only through the H abstraction of n-C$_{16}$. This radical also disappears through β-scission, H abstraction, and termination, as well as the other alkyl radicals. Thus, the net formation rate of R_{16} is

$$\begin{aligned}\frac{d[R_{16}]}{dt} &= k_{H_0}[n\text{-C}_{16}]\sum_{j=1}^{16} f(j)[R_j] \\ &\quad - k_{\beta(16)}[R_{16}] - k_{H_0} f(16)[n\text{-C}_{16}][R_{16}] - \\ &\quad - k_{\text{term}_0} g(16)[R_{16}]\sum_{j=1}^{16} g(j)[R_j]. \qquad (7)\end{aligned}$$

In order to calculate the radical concentration, the quasi-steady-state approximation is employed for Eqs. 5 and 7:

$$\frac{d[R_i]}{dt} = 0. \qquad (8)$$

The concentration of R_i is thus described as

$$[R_i] = \frac{2k_{\text{init}(X)}[n\text{-C}_{16}] + k_{\beta(X)}\left[\sum_{j=i+2}^{16} \omega_j [R_j]\right]}{k_{\beta(i)} + k_{H_0} f(i)[n\text{-C}_{16}] + k_{\text{term}_0} g(i)\sum_{j=1}^{16} g(j)[R_j]}. \qquad (9)$$

Product distribution

Formation Rate of n-Alkane and 1-Alkene. At a lower conversion level, the reaction of Ol$_i$ with n-C$_i$ can be neglected (Fabuss et al., 1964; Nigam and Klein, 1993). Therefore, the formation rate of both n-C$_i$ and Ol$_i$ are evaluated only from the disappearance rate of an alkyl radical via H abstraction and β-scission, because H abstraction of an alkyl radical produces n-C$_i$ and an alkyl radical, while β-scission of an alkyl radical produces Ol$_i$ and an alkyl radical.

As just described, H abstraction occurs only for n-C$_{16}$ because n-C$_{16}$ is the most abundant in the system at a low conversion level. Thus, the formation rate of n-C$_i$ is

$$\frac{d[n\text{-C}_i]}{dt} = k_{H_0} f(i)[n\text{-C}_{16}][R_i]. \qquad (10)$$

The concentration of R_i, $[R_i]$, can be calculated by Eq. 9. Substituting Eq. 9 into Eq. 10, the formation rate of n-C$_i$ is

$$\begin{aligned}\frac{d[n\text{-C}_i]}{dt} &= k_{H_0} f(i)[n\text{-C}_{16}] \\ &\quad \times \left\{\frac{2k_{\text{init}(X)}[n\text{-C}_{16}] + k_{\beta(X)}\left[\sum_{j=i+2}^{16} \omega_j [R_j]\right]}{k_{\beta(i)} + k_{H_0} f(i)[n\text{-C}_{16}] + k_{\text{term}_0} g(i)\sum_{j=1}^{16} g(j)[R_j]}\right\}. \qquad (11)\end{aligned}$$

A 1-alkene that has i carbon atm (Ol$_i$) forms through the β-scission of larger radicals, R_{i+n} ($i + n \le 16$), since Ol$_i$ does not disappear at a lower conversion. In the case where $n = 1$, Ol$_i$ forms with a methyl radical, in which the rate $k_{\beta(M)}$ is employed. In the case where $n \ge 2$, the rate constant of β-scission is $k_{\beta(O)}$. Therefore, the formation rate of Ol$_i$ is

$$\frac{d[\text{Ol}_i]}{dt} = k_{\beta(M)}\zeta_{i+1}[R_{i+1}] + k_{\beta(O)}\left[\sum_{j=i+2}^{16} \xi_j [R_j]\right] \qquad (12)$$

where

$$\zeta_{i+1} = P_{\text{iso}}(i+1,3) + P_{\text{iso}}(i+1,i-1) \tag{13}$$

$$\xi_j = P_{\text{iso}}(j,j-i+2) + P_{\text{iso}}(j,i-1). \tag{14}$$

1-Alkene/n-Alkane Ratio. The reaction of Ol_i with $n\text{-C}_i$ can be neglected at a lower conversion level (Fabuss et al., 1964; Nigam and Klein, 1993), as mentioned earlier. Therefore, $d[n\text{-C}_i]/dt$ and $d[\text{O}l_i]/dt$ are considered to be constant at a lower conversion level, as shown in Eqs. 11 and 12. Thus, the 1-alkene/n-alkane ratio at carbon number $i(\theta_{i(\text{model})})$ is described by the following equation at a steady state and a lower conversion level:

$$\theta_{i(\text{model})} = \frac{\dfrac{d[Ol_i]}{dt}}{\dfrac{d[n\text{-C}_i]}{dt}}. \tag{15}$$

The rate of n-alkane formation was defined by Eq. 11, and that of 1-alkene by Eq. 12. Equation 12 can be rewritten as

$$\frac{d[Ol_i]}{dt} = k_{\beta(O)} \times \left[\sum_{j=i+1}^{16} \xi_j [R_j] + \exp\left(-\frac{8.4 \text{ kJ/mol}}{RT} \right) \zeta_{i+1} [R_{i+1}] \right]. \tag{16}$$

Combining Eqs. 11, 15, and 16 gives the 1-alkene/n-alkane ratio $\theta_{i(\text{model})}$ as

$$\theta_{i(\text{model})} = \frac{\dfrac{d[Ol_i]}{dt}}{\dfrac{d[n\text{-C}_i]}{dt}} = \frac{k_{\beta(O)} \left[\displaystyle\sum_{j=i+1}^{16} \xi_j [R_j] + \exp\left(-\frac{8.4 \text{ kJ/mol}}{RT} \right) \zeta_{i+1} [R_{i+1}] \right] \cdot \left[k_{\beta(i)} + k_{H_0} f(i)[n\text{-C}_{16}] + k_{\text{term}_0} g(i) \displaystyle\sum_{j=1}^{16} g(j)[R_j] \right]}{\left(k_{H_0} f(i)[n\text{-C}_{16}] \right) \cdot \left\{ 2k_{\text{init}(X)}[n\text{-C}_{16}] + k_{\beta(X)} \left[\displaystyle\sum_{j=i+2}^{16} \omega_j [R_j] \right] \right\}}. \tag{17}$$

Since the rate of initiation and termination is negligibly smaller than that of propagation, Eq. 17 can be simplified to

$$\theta_{i(\text{model})} = \frac{k_{\beta(O)} \left[\displaystyle\sum_{j=i+1}^{16} \xi_j [R_j] + \exp\left(-\frac{8.4 \text{ kJ/mol}}{RT} \right) \zeta_{i+1} [R_{i+1}] \right] \cdot \left[k_{\beta(i)} + k_{H_0} f(i)[n\text{-C}_{16}] \right]}{\left(k_{H_0} f(i)[n\text{-C}_{16}] \right) \cdot k_{\beta(X)} \left[\displaystyle\sum_{j=i+2}^{16} \omega_j [R_j] \right]}. \tag{18}$$

Apparent first-order rate constant of n-C_{16} pyrolysis

At the low $n\text{-C}_{16}$ pyrolysis conversion level, $n\text{-C}_{16}$ disappears through initiation and H abstraction. Each bond of $n\text{-C}_i$ can split with a rate constant of $k_{\text{init}(O)}$ or $k_{\text{init}(M)}$. Thus, the overall rate constant of initiation for $n\text{-C}_{16}$ pyrolysis is

$$k_{\text{init}(16)} = 2k_{\text{init}(M)} + 13k_{\text{init}(O)}. \tag{19}$$

H abstraction of $n\text{-C}_{16}$ by R_{16} forms $n\text{-C}_{16}$ as a product. Thus, $n\text{-C}_{16}$ does not disappear through this reaction. Contribution of H abstraction for the disappearance of $n\text{-C}_{16}$ is thus $k_{H_0}\sum_{i=1}^{15} f(i)[R_i]$. The apparent first-order rate constant of the $n\text{-C}_{16}$ disappearance $(k_{(16)})$ is expressed as

$$k_{(16)} = k_{\text{init}(16)} + k_{H_0} \sum_{i=1}^{15} f(i)[R_i]. \tag{20}$$

The preceding equation can be rewritten as

$$k_{(16)} = k_{\text{init}(16)} + k_{H_0} \sum_{i=1}^{16} f(i)[R_i] - k_{H_0} f(16)[R_{16}]. \tag{21}$$

The concentration of R_{16} can be evaluated from Eqs. 7 and 8 as

$$[R_{16}] = \frac{k_{H_0}[n\text{-C}_{16}] \displaystyle\sum_{i=1}^{16} f(i)[R_i]}{k_{\beta(16)} + k_{H_0} f(16)[n\text{-C}_{16}] + k_{\text{term}_0} g(16) \displaystyle\sum_{j=1}^{16} g(j)[R_j]}. \tag{22}$$

The following equation is obtained by substituting Eq. 22 into

Eq. 21:

$$k_{(16)} = k_{\text{init}(16)} + \frac{k_{\beta(16)} k_{H_0} \sum_{i=1}^{16} f(i)[R_i] + \left(k_{H_0} \sum_{i=1}^{16} f(i)[R_i] \right) \left(k_{\text{term}_0} g(16) \sum_{j=1}^{16} g(j)[R_j] \right)}{k_{\beta(16)} + k_{H_0} f(16)[n\text{-C}_{16}] + k_{\text{term}_0} g(16) \sum_{j=1}^{16} g(j)[R_j]}. \tag{23}$$

Since the initiation and termination terms in this equation can be eliminated the same as transferring Eq. 17 into Eq. 18, Eq. 23 can be simplified to

$$k_{(16)} = \frac{k_{\beta(16)} k_{H_0} \sum_{i=1}^{16} f(i)[R_i]}{k_{\beta(16)} + k_{H_0} f(16)[n\text{-C}_{16}]}. \tag{24}$$

For the description of Eq. 24, the summation term needs to be evaluated. The formation rates of alkyl radicals $R_1 \sim R_{16}$ (Eqs. 5 and 7) were calculated by applying the pseudo-steady-state approximation (Eq. 8):

$$\sum_{i=1}^{16} \frac{d[R_i]}{dt} = 2 k_{\text{init}(16)}[n\text{-C}_{16}] - k_{\text{term}_0} \left(\sum_{i=1}^{16} g(i)[R_i] \right)^2 = 0. \tag{25}$$

We obtain Eq. 26 from Eq. 25:

$$\sum_{i=1}^{16} g(i)[R_i] = \sqrt{\frac{2 k_{\text{init}(16)}[n\text{-C}_{16}]}{k_{\text{term}_0}}}. \tag{26}$$

Since $g(i)$ is a function of only carbon number i, the function of F can be defined as $\sum_{i=1}^{16} f(i)[R_i] = F(\sum_{i=1}^{16} g(i)[R_i])$. Using the function of F, Eq. 24 can be rewritten as

$$k_{(16)} = \frac{k_{\beta(16)} k_{H_0} \cdot F\left(\sum_{i=1}^{16} f(i)[R_i] \right)}{k_{\beta(16)} + k_{H_0} f(16)[n\text{-C}_{16}]}$$

$$= \frac{k_{\beta(16)} k_{H_0} \cdot F\left(\sqrt{\frac{2 k_{\text{init}(16)}[n\text{-C}_{16}]}{k_{\text{term}_0}}} \right)}{k_{\beta(16)} + k_{H_0} f(16)[n\text{-C}_{16}]}. \tag{27}$$

If $f(i)$ is proportional to $g(i)$ ($f(i) = \sigma \times g(i)$, where σ is a proportional constant, Eq. 27 can be rewritten as

$$k_{(16)} = \frac{\sigma k_{\beta(16)} k_{H_0} \sqrt{\frac{2 k_{\text{init}(16)}[n\text{-C}_{16}]}{k_{\text{term}_0}}}}{k_{\beta(16)} + k_{H_0} f(16)[n\text{-C}_{16}]}. \tag{28}$$

Discussion

Evaluation of f(i)

According to Eq. 18, the radical-size dependence of the rate constant of H abstraction ($f(i)$) needs to be known to evaluate the radical-size dependence on the 1-alkene/n-alkane ratio (θ_i). Rewriting Eq. 18 gives

$$\left(\theta_{i(\text{model})} \cdot \frac{\left[\sum_{j=i+2}^{16} \omega_j [R_j] \right]}{\left[\sum_{j=i+1}^{16} \{ \xi_j [R_j] \} + \exp\left(- \frac{8.4\ \text{kJ/mol}}{RT} \right) \zeta_{i+1} [R_{i+1}] \right]} - 1 \right) \cdot \frac{k_{H_0}[n\text{-C}_{16}]}{k_{\beta(i)}} = \frac{1}{f(i)}. \tag{29}$$

When $f(i)$ is αi^n, this equation can be converted into logarithmic form as

$$\ln \left(\theta_{i(\text{model})} \cdot \frac{\left[\sum_{j=i+2}^{16} \omega_j [R_j] \right]}{\left[\sum_{j=i+1}^{16} \{ \xi_j [R_j] \} + \exp\left(- \frac{8.4\ \text{kJ/mol}}{RT} \right) \zeta_{i+1} [R_{i+1}] \right]} - 1 \right)$$

$$+ \ln \frac{A_{H_0}[n\text{-C}_{16}]}{A_{\beta(i)}} - \frac{E_H - E_\beta}{RT} = \ln \left(\frac{1}{f(i)} \right) = n \ln i + \ln \alpha, \tag{30}$$

where $A_{\beta(i)}$ and E_β are described in the Appendix.

The 1-alkene/n-alkane ratio at carbon number i obtained from experiments was

$$\theta_{i(\exp)} = \bar{\theta}_i = \frac{\displaystyle\int_0^t \left(\frac{d[\mathrm{O}l_i]}{dt}\right) dt}{\displaystyle\int_0^t \left(\frac{d[n\text{-}\mathrm{C}_i]}{dt}\right) dt}, \tag{31}$$

where t is the reaction time. At a lower conversion level, where the reaction of $\mathrm{O}l_i$ and n-C_i can be neglected, $d[n-\mathrm{C}_i]/dt$ and $d[\mathrm{Ol}_i]/dt$ are considered to be constant. Thus, if $\int_0^{tr} dt$ (where tr is the time up to reaching steady state) were much smaller than $\int_{tr}^{t} dt$, $\theta_{i(\mathrm{model})}$ is nearly equal to $\theta_{i(\exp)}$. In general, $\int_0^{tr} dt$ is much smaller than $\int_{tr}^{t} dt$ in the conversion range around several percent. Although it was not confirmed by the experiments, in the following analysis, the relation between $\theta_{i(\exp)}$ and i is examined by considering the relation between $\theta_{i(\mathrm{model})}$ and i.

The slope of a plot of $\ln(1/f(i))$ against $\ln(i)$ indicates an order of carbon number, n, with an intercept of α. Parameter sets for $A_{\beta(i)}$, A_H, E_β, and E_{H_0} were evaluated from Doue and Guiochon (1968), Allara and Shaw (1980), Ranzi et al. (1983), Willems and Froment (1998a,b), Khorasheh and Gray (1993), and Nigam and Klein (1993). As shown in Figure 2, Doue and Guiochon's parameters (1968) (see in Table 3) had the highest correlation coefficient for Eq. 30. Determined α was almost 1 and n was about -1.

For a biomolecular reaction such as H abstraction to occur, two molecules must collide. According to collision theory, the rate constant of the biomolecular reaction between A and B is expressed by the following equation (Benson, 1976):

$$k_{AB} = pZ_{AB} \exp\left(-\frac{E_{AB}}{RT}\right), \tag{32}$$

where p is probability for geometry reason, Z_{AB} is the collision frequency between A and B; E_{AB} is the activation energy; R is the gas constant; and T is the absolute temperature. Here, collision frequency, Z_{AB}, can be described as

$$Z_{AB} = \pi r_{AB}^2 \sqrt{\frac{8RT}{\pi \mu_{AB}}}, \tag{33}$$

where π is a circular constant; r_{AB} is the distance between the centers of A and B in the collision complex ($r_{AB} = r_A + r_B$, where r_A and r_B are almost equal to the radius of molecule A and B, respectively); and μ_{AB} is the reduced molecular weight of A and B, which is expressed by

$$\mu_{AB} = \frac{M_A M_B}{M_A + M_B}, \tag{34}$$

where M_A and M_B are molecular weights of A and B, respectively. An r_{AB} ($r \propto M^{1/3}$) increases as the molecular weights of A and B increase. A μ_{AB} ($\mu \propto M$) also increased as the molecular weights of A and B increased. Therefore, the dependence of Z_{AB} on the molecular weight is small ($Z \propto M^{1/6}$). An $f(i)$ corresponds to the probability, p, of the reaction in Eq. 32. If we consider the probability of an odd electron being at the collision site, it is inversely proportional to the carbon number of alkyl radical, $1/i$. Thus, evaluated α $(=1)$ and n $(=-1)$ can be reasonably explained.

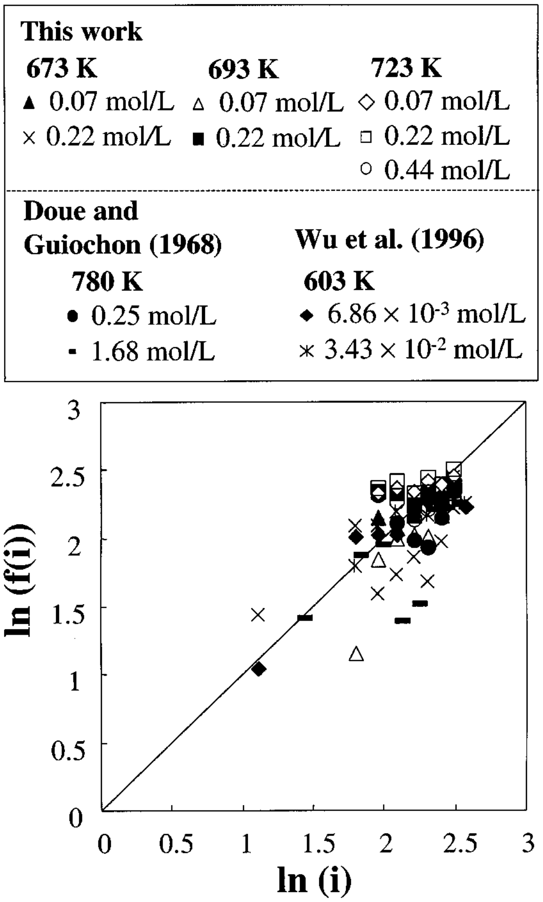

Figure 2. Evaluation of $f(i)$.

Cohen (1991) measured the rate constant of H abstraction between the OH radical and n-alkane and found that the rate constant decreased with increasing n-alkane size. He used transition-state theory (TST) to explain that the rate constant decreased with n-alkane size. According to Cohen (1991), the translational degree of freedom affects the size of the alkyl radical the most among all the contributions for the entropy of activation. Thus, $f(i)$ corresponds to

$$f(i) \propto \left(\frac{M^{\neq}}{M}\right)^{1.5}, \tag{35}$$

where $M^{\neq}$ is the molecular weight of the activated complex and M is the molecular weight of the reactants. In this study, since we assumed that the alkyl radical only abstracted hydrogen from n-C_{16}, reaction entropy, $S(n\text{-}\mathrm{C}_{16})$, is constant for any n-$\mathrm{C}_{16} + R_i$ reaction. Thus, $M^{\neq}$ is equals 226 (molecular weight of n-C_{16}) plus $12i + 2i + 1$ [molecular weight of alkyl radical (R_i), M], and Eq. 34 can be rewritten as

Table 3. Kinetic Parameter Reported

k	A	E
Doue and Guiochon (1968)		
$k_{\text{init}(O)}$	$A_{\text{init}} = 10^{18.7}\text{h}^{-1}$	$E_{\text{init(O)}} = 343$ kJ/mol
$k_{\beta(O)}$	$A_{\beta} = 10^{15.9}\text{h}^{-1}$	$E_{\beta(\text{O})} = 100.4$kJ/mol
k_{H0}	$A_H = 10^{13.4}$L/mol/h	$E_{\text{H0}} = 41.8$kJ/mol
k_{term0}	$A_{\text{term}} = 10^{14.3}$L/mol/h	$E_{\text{term0}} = 0$ kJ/mol
Allara and Shaw (1980)		
$k_{\text{init}(O)}$	$A_{\text{init}} = 10^{20.3}\text{h}^{-1}$	$E_{\text{init(O)}} = 343$ kJ/mol
$k_{\beta(O)}$	$A_{\beta} = 10^{16.3}\text{h}^{-1}$	$E_{\beta(\text{O})} = 117.2$ kJ/mol
k_{H0}	$A_H = 10^{12.1}$L/mol/h	$E_{H0} = 40$ kJ/mol
k_{term0}	$A_{\text{term}} = 10^{14}$L/mol/h	$E_{\text{term0}} = 0$ kJ/mol
Ranzi et al. (1983)		
$k_{\text{init}(O)}$	—	—
$k_{\beta(O)}$	$A_{\beta} = 10^{17.6}\text{h}^{-1}$	$E_{\beta(\text{O})} = 125.5$ kJ/mol
k_{H0}	$A_H = 10^{11.9}$L/mol/h	$E_{H0} = 58.6$ kJ/mol
k_{term0}	—	—
Willems and Froment (1988a,b)		
$k_{\text{init}(O)}$	$A_{\text{init}} = 10^{20.6}\text{h}^{-1}$	$E_{\text{init(O)}} = 343$ kJ/mol
$k_{\beta(O)}$	$A_{\beta} = 10^{17.6}\text{h}^{-1}$	$E_{\beta(\text{O})} = 90$ kJ/mol
k_{H0}	$A_H = 10^{12.7}$L/mol/h	$E_{\text{H0}} = 45.9$ kJ/mol
k_{term0}	—	—
Nigam and Klein (1993)		
$k_{\text{init}(O)}$	$A_{\text{init}} = 10^{19.6}\text{h}^{-1}$	$E_{\text{init(O)}} = 343$ kJ/mol
$k_{\beta(O)}$	$A_{\beta} = 10^{16.6}\text{h}^{-1}$	$E_{\beta(\text{O})} = 104$ kJ/mol
k_{H0}	$A_H = 10^{12.1}$L/mol/h	$E_{\text{H0}} = 66$ kJ/mol
k_{term0}	$A_{\text{term}} = 10^{12.6}$L/mol/h	$E_{\text{term0}} = 0$ kJ/mol
Khorasheh and Gray (1993)		
$k_{\text{init}(O)}$	$A_{\text{init}} = 10^{16.2}\text{h}^{-1}$	$E_{\text{init(O)}} = 280$ kJ/mol
$k_{\beta(O)}$	$A_{\beta} = 10^{17.6}\text{h}^{-1}$	$E_{\beta(\text{O})} = 130$ kJ/mol
k_{H0}	$A_H = 10^{11}$L/mol/h	$E_{\text{H0}} = 49$ kJ/mol
k_{term0}	$A_{\text{term}} = 10^{13.6}$L/mol/h	$E_{\text{term0}} = 0$ kJ/mol

$$f(i) \propto \left(\frac{12i+2i+1+226}{12i+2i+1}\right)^{1.5} \approx \left(\frac{i+16}{i}\right)^{1.5}. \qquad (36)$$

The size dependence of $f(i)$ is between 0th order and -1.5th order. We examined the $f(i)$ (Eq. 36) by comparing with the experimental results and found that $f(i)$ was nearly equal to $(1/i)$.

Estimation of product distribution

Figure 3 shows calculated results using the model. Figure 3A shows the molar selectivity, and Figure 3B shows the 1-alkene/n-alkane ratio at 673 K of reaction temperature and 0.07 mol/L of n-C_{16} concentration. As shown in Figure 3, the model can describe the experimental results successfully.

Although 6- or 7-member ring isomerization was employed in our model, Benson (1970) and Ranzi et al. (1983) suggested that isomerization through the formation of a 5- or larger-member ring is faster than that of a smaller-member ring. We also calculated the product distribution, assuming a 5-member ring. However, experimental result could not be fairly explained by this model. The correlation of the calculated result and the experimental result was much poorer than that shown in Figure 3.

At lower conversions of n-C_{16} pyrolysis, it can be assumed that the n-alkane and 1-alkene that are produced do not disappear as shown in Table 1. Therefore, the 1-alkene/n-alkane ratio ($\theta_{i(\exp)}$) shows the product distribution of n-C_{16} pyrolysis. Figures 4 and 5 show the parity plot for the 1-alkene/n-alkane ratio. The range of the reaction temperatures of the data used is from 603 K to 780 K, and that of n-C_{16} concentrations is from 6.86×10^{-3} mol/L to 2.32 mol/L. As shown in Figures 4 and 5, the model can describe $\theta_{i(\exp)}$ over the full range of conditions measured in the literature and this work.

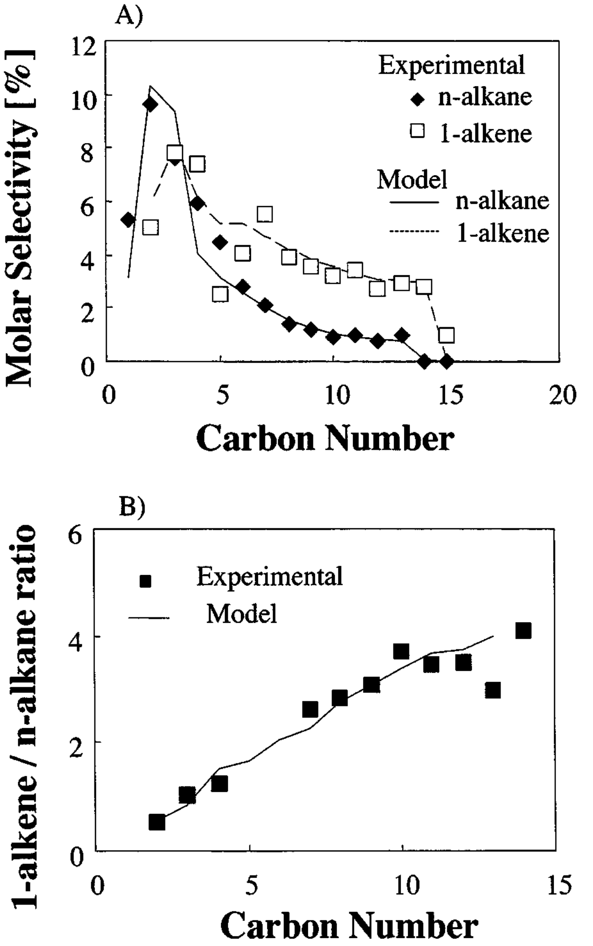

Figure 3. Product distribution of n-C_{16} pyrolysis at $T = 673$ K, $[n\text{-}C_{16}] = 0.07$ mol/L, and conversion $= 8.7\%$.

Apparent first-order rate constant

In the preceding analysis, radical-size dependence for the bimolecular reaction could be explained similarly by the TST and collision model. For simplicity in the following analysis, we use the expression of probability from the collision model. Even though the two radicals collide, if both odd electrons are not on the collision sites, termination does not take place. Therefore, the probability of radical recombination between R_i and R_j is assumed to be $(1/i) \times (1/j)$ as well as H abstraction. Thus, $g(i)$ is also equal to $1/i$. As described in Eq. 28, the apparent first-order rate constant can be expressed as

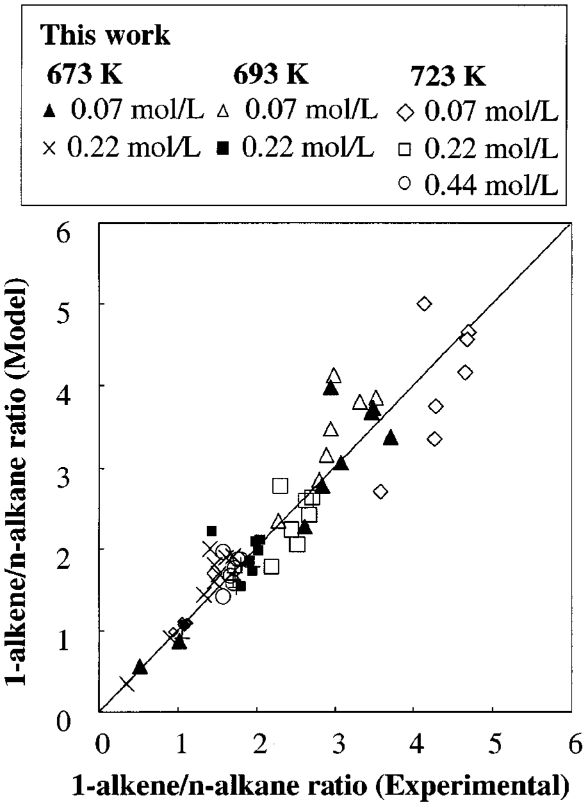

Figure 4. Parity plot of 1-alkene/*n*-alkane ratio of *n*-C_{16} pyrolysis obtained in this study.

$$k_{(16)} = \frac{k_{\beta(16)} k_{H_0} \sqrt{\dfrac{2k_{\text{init}(16)}[n\text{-}C_{16}]}{k_{\text{term}_0}}}}{k_{\beta(16)} + k_{H_0}(1/16)[n\text{-}C_{16}]}. \tag{37}$$

According to Eq. 37, the difference in the overall activation energies can be explained by *n*-C_{16} concentration. At a lower *n*-C_{16} concentration, the apparent first-order rate constant of *n*-C_{16} pyrolysis can be expressed as

$$\begin{aligned} k_{(16)} &= k_{H_0}\sqrt{\frac{2k_{\text{init}(16)}[n\text{-}C_{16}]}{k_{\text{term}_0}}} \\ &= A_{H_0}\sqrt{\frac{2A_{\text{init}(16)}[n\text{-}C_i]}{A_{\text{term}_0}}} \\ &\quad \times \exp\left(-\frac{E_H + E_{\text{init}}/2 - E_{\text{term}}/2}{RT}\right). \end{aligned} \tag{38}$$

Therefore the apparent activation energy (E) of *n*-C_i pyrolysis is

$$E = E_H + \frac{E_{\text{init}}}{2} - \frac{E_{\text{term}}}{2}. \tag{39}$$

On the other hand, at higher *n*-C_{16} concentrations, the apparent first-order rate constant of *n*-C_{16} pyrolysis can be expressed as

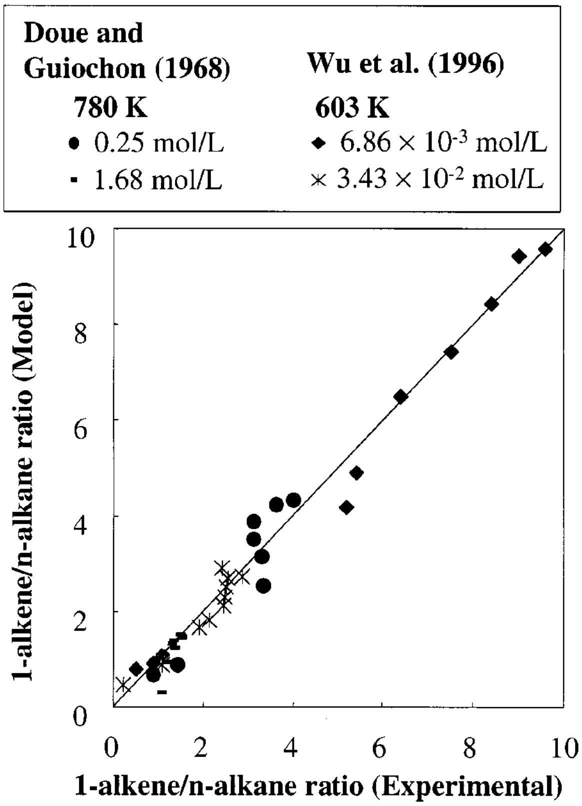

Figure 5. Parity plot of 1-alkene/*n*-alkane ratio of *n*-C_{16} pyrolysis from literatures.

$$\begin{aligned} k_{(16)} &= 16k_{\beta(16)}\sqrt{\frac{2k_{\text{init}(16)}}{k_{\text{term}_0}[n\text{-}C_i]}} \\ &= 16A_{\beta(16)}\sqrt{\frac{2A_{\text{init}(16)}}{A_{\text{term}_0}[n\text{-}C_i]}} \\ &\quad \times\left(-\frac{E_\beta + E_{\text{init}}/2 - E_{\text{term}}/2}{RT}\right). \end{aligned} \tag{40}$$

Thus the apparent activation energy (E) of *n*-C_i pyrolysis is

$$E = E_\beta + \frac{E_{\text{init}}}{2} - \frac{E_{\text{term}}}{2}. \tag{41}$$

Substituting the kinetic parameters of Doue and Guiochon (1968) (see Table 3) into Eq. 39, the apparent activation energy at lower *n*-C_{16} concentration is 192 kJ/mol. Similarly, substituting their parameters into Eq. 41, the apparent activation energy at higher *n*-C_{16} concentration is 217 kJ/mol. Thus, the change in the apparent activation energy of *n*-C_{16} pyrolysis with *n*-C_{16} concentration can be explained by the change that occurs in the amount at β-scission or *H* abstraction.

Further, the apparent first-order rate constant of *n*-C_{16} pyrolysis $(k_{(16)})$ that can be obtained from 6.86×10^{-3} mol/L

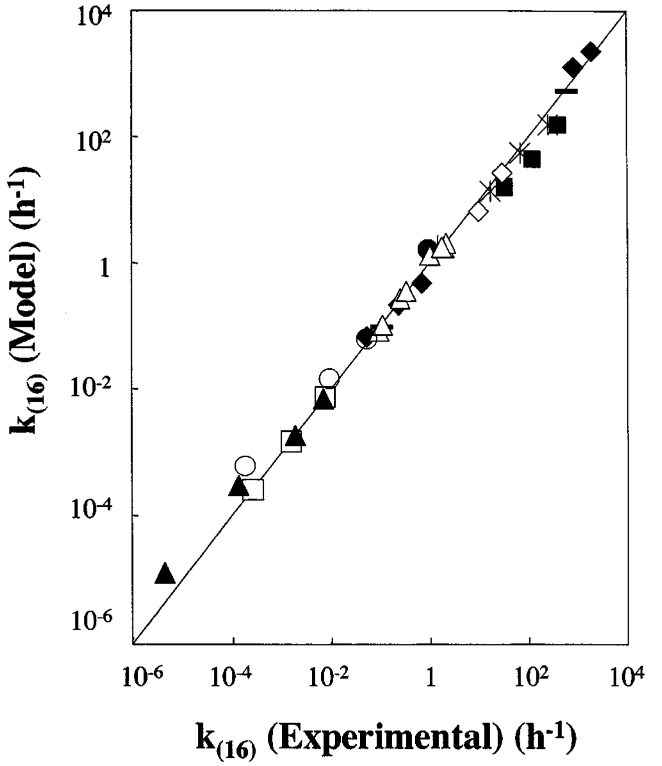

Figure 6. Parity plot of apparent first-order rate constants of n-C_{16} pyrolysis.

Conditions: △ This work, 673–723 K and 0.07–1.47 mol/L; ◇ Voge and Good (1949), 773 K and 1.6×10^{-2}–0.62 mol/L; ■ Panchenkov and Branov (1958), 794–855 K and 1.6×10^{-2}–1.4×10^{-2} mol/L; * Groenendyk et al. (1970), 790–856 K and 1.6×10^{-2}–1.4×10^{-2} mol/L; ◆ Fabuss et al. (1962), 700–883 K and $1.6\times10^{-2}-0.65$ mol/L; ● Mushrsush and Hazlett (1984), 723 K and 2.46 mol/L; □ Ford (1986), 603–643 K and 2.12 mol/L; — Zhou et al. (1987), 893 K and 1.4×10^{-2} mol/L; ▲ Jackson et al. (1995), 572–643 K and 2.27 mol/L ~ 2.48 mol/L; ○ Wu et al. (1996, 1997), 603–673 K and 3.4×10^{-2} mol/L.

to 2.12 mol/L of n-C_{16} concentrations and from reaction temperatures of 603 K to 893 K was calculated using the kinetic parameters of Doue and Guiochon (1968). As shown in Figure 6, the model can estimate the experimental results.

We also tried to estimate the first-order rate constant for the other n-alkane pyrolysis (n-$C_{10} \sim n-C_{25}$). Here, the function of the carbon number for bimolecular reaction ($f(i) = g(i) = 1/i$) is assumed to be the same for the other n-alkane pyrolysis. Therefore, the apparent first-order rate constant of n-C_i pyrolysis can be expressed as

$$k_{(i)} = \frac{k_{\beta(i)} k_{H_0} \sqrt{\dfrac{2k_{\mathrm{init}(i)}[n\text{-}C_i]}{k_{\mathrm{term}_0}}}}{k_{\beta(i)} + k_{H_0}(1/i)[n\text{-}C_i]}. \qquad (42)$$

For the initiation, we assumed that the overall initiation of rate constant of n-C_i, $k_{\mathrm{init}(i)}$, is

$$k_{\mathrm{init}(i)} = 2k_{\mathrm{init}(M)} + (i-3)k_{\mathrm{init}(O)}, \qquad (43)$$

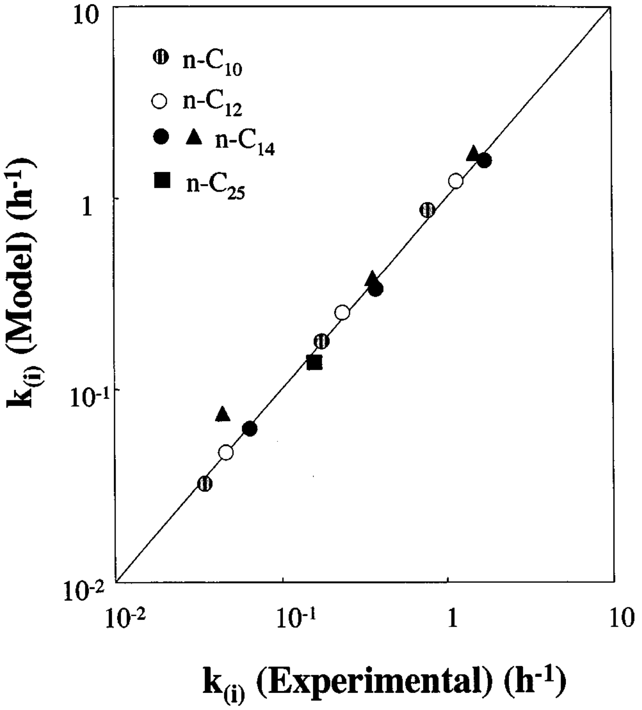

Figure 7. Parity plot of apparent first-order rate constants of n-C_{10}–n-C_{25} pyrolysis.

Conditions: ▲ Song et al. (1994), 673–723 K and 0.77 mol/L; ■ Behar and Vandenbroucke (1996), 673 K and 1.52 mol/L, ○ Yu and Eser (1997), 673–723 K and 1.38–1.84 mol/L.

where the rate constant of the C–C bond rupture of n-alkane was assumed to be the same for any n-alkane.

Figure 7 shows the results of the comparison between the experimental results of $n-C_{10} \sim n$-C_{25} pyrolysis reported by Song et al. (1994), Behar and Vandenbroucke (1996), and Yu and Eser (1997) and the calculated results. As shown in Figure 7, the model can estimate the experimental data.

Conclusions

A kinetic model for n-C_{16} pyrolysis at a low conversion level was developed that takes radical size dependence into account. A comparison of the experimental data and the model showed that, the rate of H abstraction, which is bimolecular reaction, is inversely proportional to carbon number, i, of radical R_i; namely $k_{H(i)} = k_{H_0}(1/i)$. The new model correlated the product distribution of n-C_{16} pyrolysis at 673 K accurately and predicted the product distribution and the 1-alkene/n-alkane ratio over a wide range of reaction conditions at a low conversion level.

The apparent first-order rate constant of n-C_i pyrolysis can be expressed as a simple expression, and the proposed model provides an accurate estimation of the apparent first-order rate constant for pyrolysis of n-alkanes in the n-$C_{10} \sim n$-C_{25} range.

Acknowledgment

The authors thank for Grants-in-Aid for Scientific Research on Priority Areas (09450281 and 10555270) of the Ministry of Education and Culture.

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Appendix: Details of Model Development

Probability of an odd electron position on R_i

Since an odd electron is transferred on the other side of the ring by forming a 6- or 7-ring for geometrical reason (Fabuss et al., 1964), the possibility of for an odd electron being transferred is limited.

$$R_i^j \xrightarrow{k_{\text{iso}}(6 \text{ or } 7 \text{ ring})} R_i^l, \tag{A1}$$

where i is the carbon number of a radical, and j and l are the position of an odd electron in a radical $(1 \leq j \leq i, 1 \leq l \leq i, l = j \pm 5$ or 6). Isomerization does not take place for R_1, R_2, R_3, R_4, and R_5, since these radicals cannot form a 6 or 7 ring. Thus,

$$P_{\text{iso}}(1,1) = 1 \tag{A2}$$

$$P_{\text{iso}}(i,1) = P_{\text{iso}}(i,i) = 0.5 \qquad (2 \leq i \leq 5) \tag{A3}$$

$$P_{\text{iso}}(i,\, j) = 0 \qquad (2 \leq i \leq 5,\ j < i), \tag{A4}$$

where $P_{\text{iso}}(i,j)$ is the probability of an odd electron position (j) on an alkyl radical (R_i). For R_6 and R_7, the possible position for an odd electron to be transferred is limited. For radicals larger than R_8, an odd electron can be transferred to any position by the isomerization forming a 6 or 7 ring.

In the isomerization, the intramolecular H abstraction rates from primary carbon and from secondary carbon are different, which also results in the difference in the probability of finding an odd electron position.

$$k_{H(P)} = A_H \exp\left(- \frac{(E_H + 16.7)\ \text{kJ/mol}}{RT} \right) \tag{A5}$$

$$k_{H(S)} = A_H \exp\left(- \frac{E_H\ \text{kJ/mol}}{RT} \right), \tag{A6}$$

where A_H is the frequency factor, and E_H is the activation energy of the rate constant of the intramolecular secondary H abstraction. Thus, the probability of an odd electron being on a certain position on a radical can be expressed as follows.

Isomerization of R_i produces R_i^1 and R_i^i as primary radicals and R_i^j $(2 \le j \le i-1)$ as secondary radicals. There are six possible positions on two primary carbons for an odd electron, since each of two primary carbons has three hydrogens. There are $2 \times (i-2)$ possible positions on $(i-2)$ secondary carbons, since each of $(i-2)$ secondary carbons has two hydrogens. Thus, the probability of forming a primary radical $(R_i^1$ or $R_i^i)$ is

$$P_{\text{iso}}(i,1) = P_{\text{iso}}(i,i) = \frac{3k_{H(P)}}{6k_{H(P)} + 2(i-2)k_{H(S)}}$$

$$= \frac{3\dfrac{k_{H(P)}}{k_{H(S)}}}{6\dfrac{k_{H(P)}}{k_{H(S)}} + 2(i-2)} = \frac{3\exp\left(\dfrac{-16.7\ \text{kJ/mol}}{RT}\right)}{6\exp\left(\dfrac{-16.7\ \text{kJ/mol}}{RT}\right) + 2(i-2)} \tag{A7}$$

The probability of forming a secondary radical (R_i^j) $(2 \le j \le i-1)$, $P_{\text{iso}}(i,j)$, can be expressed as

$$P_{\text{iso}}(i,j) = \frac{2k_{H(S)}}{6k_{H(P)} + 2(i-2)k_{H(S)}} = \frac{2}{6\dfrac{k_{H(P)}}{k_{H(S)}} + 2(i-2)}$$

$$= \frac{2}{6\exp\left(\dfrac{-16.7\ \text{kJ/mol}}{RT}\right) + 2(i-2)} \tag{A8}$$

Since R_6^3 or R_6^4 cannot be formed due to the limitation of the ring formation in the R_6 isomerization ($P_{\text{iso}}(6,3) = P_{\text{iso}}(6,4) = 0$), only two possible positions among four secondary carbons of R_6 are available. Therefore the probability of R_6^1 and R_6^6 ($P_{\text{iso}}(6,1)$ and $P_{\text{iso}}(6,6)$) can be expressed as

$$P_{\text{iso}}(6,1) = P_{\text{iso}}(6,6) = \frac{3k_{H(P)}}{6k_{H(P)} + 4k_{H(S)}}$$

$$= \frac{3\dfrac{k_{H(P)}}{k_{H(S)}}}{6\dfrac{k_{H(P)}}{k_{H(S)}} + 4} = \frac{3\exp\left(\dfrac{-16.7\ \text{kJ/mol}}{RT}\right)}{6\exp\left(\dfrac{-16.7\ \text{kJ/mol}}{RT}\right) + 4} \tag{A9}$$

Similarly, the probability of forming a radical of R_6^2 and R_6^5 can be expressed as

$$P_{\text{iso}}(6,2) = P_{\text{iso}}(6,5) = \frac{2k_{H(S)}}{6k_{H(P)} + 4k_{H(S)}} = \frac{2}{6\dfrac{k_{H(P)}}{k_{H(S)}} + 4}$$

$$= \frac{2}{6\exp\left(\dfrac{-16.7\ \text{kJ/mol}}{RT}\right) + 4} \tag{A10}$$

Through the isomerization of R_7, primary radicals, R_7^1 and R_7^7, and secondary radicals, R_7^2, R_7^3, R_7^5, and R_7^6, can be formed, but R_7^4 cannot, due to the limitation of the ring formation. By counting the number of possible positions and taking the intramolecular H abstraction rate (Eqs. A5 and A6) into account,

$$P_{\text{iso}}(7,1) = P_{\text{iso}}(7,7) = \frac{3k_{H(P)}}{6k_{H(P)} + 8k_{H(S)}} = \frac{3\dfrac{k_{H(P)}}{k_{H(S)}}}{6\dfrac{k_{H(P)}}{k_{H(S)}} + 8}$$

$$= \frac{3\exp\left(\dfrac{-16.7\ \text{kJ/mol}}{RT}\right)}{6\exp\left(\dfrac{-16.7\ \text{kJ/mol}}{RT}\right) + 8} \tag{A11}$$

$$P_{\text{iso}}(7,2) = P_{\text{iso}}(7,3) = P_{\text{iso}}(7,5) = P_{\text{iso}}(7,6) = \frac{2k_{H(S)}}{6k_{H(P)} + 8k_{H(S)}}$$

$$= \frac{2}{6\dfrac{k_{H(P)}}{k_{H(S)}} + 8} = \frac{2}{6\exp\left(\dfrac{-16.7\ \text{kJ/mol}}{RT}\right) + 8} \tag{A12}$$

$$P_{\text{iso}}(7,4) = 0. \tag{A13}$$

Overall rate constant of disappearance of R_i through $\boldsymbol{\beta}$-scission

For the β-scission, the rate constant of the C−C bond rupture of the alkyl radical is assumed to be the same for any alkyl radical. Therefore, we took into the case of the number of the C−C bond for the overall rate constant of β-scission.

Since there is only one β-position for R_i^1 (and R_i^i) and R_i^2 (and R_i^{i-1}), β-scission takes place only on that site. The other radicals have two β-positions, and thus there are two possible positions for the β-scission.

$$R_i^j \xrightarrow{k_\beta} R_{i-j-1}^1 + \mathrm{Ol}_{j+1} \qquad (j = 1,\ 2,\ i-1,\ \text{or}\ i) \tag{A14}$$

$$R_i^j \xrightarrow{k_\beta} R_{j-2}^1 + \mathrm{Ol}_{i-j+2} \qquad \text{or} \qquad R_{i-j-1}^1 + \mathrm{Ol}_{j+1} \qquad (3 < j < i-2). \tag{A15}$$

The activation energy of the β-scission rate constants of forming the methyl radical is 8.4 kJ/mol higher than that for forming other radicals (Murata et al., 1973; Khorasheh and Gray, 1993). Therefore, the β-scission rate constant of forming methyl radical ($k_{\beta(M)}$) and that for forming the other radicals ($k_{\beta(O)}$) are

$$k_{\beta(M)} = A_\beta \exp\left\{\frac{-(E_\beta + 8.4)\,\text{kJ/mol}}{RT}\right\} \tag{A16}$$

$$k_{\beta(O)} = A_\beta \exp\left\{\frac{-E_\beta\,\text{kJ/mol}}{RT}\right\}, \tag{A17}$$

where A_β is the frequency factor and E_β is the activation energy. Both frequency factors of $k_{\beta(\mathrm{M})}$ and $k_{\beta(O)}$ were assumed to be the same. For R_i^j, when j is equal to 3 or $i-2$, the methyl radical is produced by the β-scission at one of two possible positions. The β-scission rate constant to form the methyl radical is $k_{\beta(\mathrm{M})}$; the other rate constant is $k_{\beta(\mathrm{O})}$. The overall disappearance rate constant of R_i through β-scission ($k_{\beta(i)}$) is

$$\begin{aligned} k_{\beta(i)} = {} & k_{\beta(M)}\{P_{\text{iso}}(i,3) + P_{\text{iso}}(i,i-2)\} \\ & + k_{\beta(O)}\Bigg[\{P_{\text{iso}}(i,3) + P_{\text{iso}}(i,i-2)\} + 2 \sum_{j=1 \neq 3,\, i-2}^{i} \{p_{\text{iso}}(i,j)\} \\ & - \{P_{\text{iso}}(i,1) + P_{\text{iso}}(i,i)\} \text{-} \{P_{\text{iso}}(i,2) + P_{\text{iso}}(i,i-1)\}\Bigg]. \end{aligned} \tag{A18}$$

Substituting Eqs. A7, A8, A16 and A17 into Eq. A18, $k_{\beta(i)}$ becomes

$$\begin{aligned} k_{\beta(i)} = {} & A_\beta \exp\left(-\frac{E_{\beta(O)}}{RT}\right) \\ & \times \left\{ \frac{4}{6\exp\left(-\frac{16.7\ \text{kJ/mol}}{RT}\right) + 2(i-2)} \exp\left(-\frac{8.4\ \text{kJ/mol}}{RT}\right) \right. \\ & \left. + \frac{2 \times 3 \exp\left(\frac{-16.7\ \text{kJ/mol}}{RT}\right) + 2 \times 2(i-4)}{6\exp\left(-\frac{16.7\ \text{kJ/mol}}{RT}\right) + 2(i-2)} \right\} \\ & \equiv A_{\beta(i)} \exp\left(-\frac{E_{\beta(O)}}{RT}\right), \end{aligned} \tag{A19}$$

where $i \geq 3$ and $A_{\beta(i)}$ is defined as

$$\begin{aligned} A_{\beta(i)} = {} & \left\{ \frac{4}{6\exp\left(-\frac{16.7\ \text{kJ/mol}}{RT}\right) + 2(i-2)} \exp\left(-\frac{8.4\ \text{kJ/mol}}{RT}\right) \right. \\ & \left. + \frac{2 \times 3 \exp\left(\frac{-16.7\ \text{kJ/mol}}{\mathrm{RT}}\right) + 2 \times 2(i-4)}{6\exp\left(-\frac{16.7\ \text{kJ/mol}}{RT}\right) + 2(i-2)} \right\}. \end{aligned} \tag{A20}$$

Here, $k_{\beta(\mathrm{l})}$ and $k_{\beta(2)}$ are zero.

Manuscript received May 24, 1999, and revision received Nov. 16, 1999.