

# CARBON NUMBER CORRELATION OF OVERALL RATE CONSTANT OF PYROLYSIS OF N-ALKANES

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## Introduction

A lot of studies have been reported so far on pyrolysis of n-alkanes. From the literature, the overall rate constant of pyrolysis of n-alkanes is well known to affect on reaction condition (pressure and temperature) and carbon number of n-alkane.

The pressure dependence of reaction rate can be predicted by Rice and Herzfeld theory<sup>1</sup>. However, carbon number dependence of overall rate constant of n-alkane has not been explained by theoretical base, yet.

For carbon number dependence of the overall pyrolysis rate constant, two correlations were reported<sup>2,3</sup>. Voge and Good's correlation<sup>3</sup> is as:

$$k_{(i)} [s^{-1}] = (i - 1) (1.57i - 3.9) \times 10^{-5} \quad (1)$$

Herein,  $k_{(i)} [s^{-1}]$  is the pseudo first order rate constant of pyrolysis of n-alkanes and  $i$  is carbon number of n-alkane. This equation can be applied for the pyrolysis of n-C<sub>4</sub> ~ n-C<sub>16</sub> at 773 K and 0.1 MPa. Tilicheev's correlation<sup>2</sup> obtained for n-C<sub>12</sub> ~ n-C<sub>32</sub> at 698 K and 15 MPa has a different function of  $i$ .

$$k_{(i)} [s^{-1}] = (2.3i - 15.6) \times 10^{-5} \quad (2)$$

On the other hand, Yu and Eser<sup>4</sup> proposed the normalized expression of the overall rate constant of n-alkanes (n-C<sub>8</sub> ~ n-C<sub>16</sub>) using the overall rate constant of n-dodecane (n-C<sub>12</sub>) at 698 K and a reaction pressure (0.1 MPa ~ 15 MPa) recently, as follows

$$k_{(i)} / k_{12} = (1.89i - 12.3) \times 10^{-1}, \quad (3)$$

where  $k_{12}$  is the overall rate constant of n-C<sub>12</sub> pyrolysis at 698 K and a given pressure. This equation suggests that the carbon number dependence of the overall rate constant of n-alkane pyrolysis can be expressed by the same function for carbon number regardless of the reaction temperature and pressure (concentration).

A motivation of this study was to give a reasonable explanations for the above three correlations on the theoretical basis, and to proposed a global model for the pyrolysis of n-alkanes. In this study, we proposed the global model for pyrolysis of n-alkanes (n-C<sub>3</sub> ~ n-C<sub>32</sub>) in a wide range of reaction conditions (572 K ~ 973 K,  $6.86 \times 10^3$  M ~ 2.72 M). Next, we explain previously reported size dependence<sup>2,3,4</sup>, based on the proposed model.

## Model

The model is considered the following five elementary reaction groups: 1) initiation: a reaction of a C-C bond cleavage of n-C<sub>i</sub>, 2) isomerization: an odd electron position in an alkyl radical through intra- and intermolecular H abstraction, 3)  $\beta$ -scission: a reaction of an alkyl radical decomposition, 4) H abstraction: a reaction of an odd electron transfer between n-C<sub>i</sub> and an alkyl radical, 5) termination: a reaction of recombination of two alkyl radicals. Applying steady-state approximation for concentration of alkyl radical and considering the carbon number size dependence for the rate constants of bimolecular reactions (details in elsewhere<sup>5</sup>), the apparent first order rate constant of n-C<sub>i</sub> pyrolysis can be expressed as

$$k_{(i)} = \frac{k_{\beta(i)} k_{H(i)} \sqrt{\frac{2k_{\text{init}(i)}[n-C_i]}{k_{\text{term}0}}}}{k_{\beta(i)} + (1/i)k_{H(i)}[n-C_i]}, \quad (4)$$

where  $k_{\beta(i)}$  is the rate constant of  $\beta$ -scission of a radical ( $R_i$ ),  $k_{H(i)}$  is the rate constant of H abstraction of an alkyl radical from n-C<sub>i</sub>,  $k_{\text{init}(i)}$  is the rate constant of C-C bond cleavage of n-C<sub>i</sub>, and  $k_{\text{term}0}$  is the rate constant of recombination of two methyl radicals. In the following, the method to evaluate each elementary reaction rate constant is shown.

### 1) Initiation

In the model, initiation occurs only for mother n-alkanes (n-C<sub>i</sub>), because amount of n-C<sub>i</sub> is much more than that of the other species at a lower conversion level. We took into account of the number of C-C bond for the overall rate constant of initiation since the rate constant of C-C bond rupture of n-C<sub>i</sub> is assumed to be the same for any n-alkane. The activation energy of the rate constant of initiation with forming methyl radical ( $k_{\text{init}(M)}$ ) should be 13 kJ/mol higher than that of forming the other radicals ( $k_{\text{init}(O)}$ )<sup>6</sup>. The frequency factor is the same for  $k_{\text{init}(M)}$  and  $k_{\text{init}(O)}$  as to be  $A_{\text{init}}$ <sup>7</sup>. Therefore, the overall rate constant of initiation of n-C<sub>i</sub>,  $k_{\text{init}(i)}$ , should be as

$$k_{\text{init}(i)} = 2k_{\text{init}(M)} + (i-3)k_{\text{init}(O)} = A_{\text{init}} \exp\left(-\frac{E_{\text{init}}}{RT}\right) \left\{ 2 \exp\left(-\frac{16.7 \text{ kJ/mol}}{RT}\right) + (i-3) \right\}, \quad (5)$$

where  $A_{\text{init}}$  is  $10^{18.7} \text{ h}^{-1}$  and  $E_{\text{init}}$  is 343 kJ/mol, which is C-C bond energy between two secondary carbons for n-butane<sup>6,7</sup>.

### 2) Isomerization

Isomerization is an intramolecular H abstraction. Although this rate constant is not used in Eq. 4, this reaction is essential to determine the rate constant of  $\beta$ -scission,  $k_{\beta(i)}$ . 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. The activation energy of rate constant of intra- and inter-molecular H abstraction from primary carbon ( $k_{H(P)}$ ) is 16.7 kJ/mol higher than that from secondary carbon ( $k_{H(S)}$ )<sup>8,9</sup>, and the frequency factor of both  $k_{H(P)}$  and  $k_{H(S)}$  is the same<sup>8,9</sup>.

Isomerization of  $R_i$  produces as primary radicals,  $R_i^1$  and  $R_i^i$ , or secondary radicals,  $R_i^j$  ( $2 \leq j \leq i-1$ ). 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. Therefore, the probability of an odd electron on a primary carbon in  $R_i$  ( $R_i^1$  or  $R_i^i$ ),  $P_{(P)}$ , can be expressed as

$$P_{(P)} = \frac{6k_{H(P)}}{6k_{H(P)} + 2(i-2)k_{H(S)}} = \frac{6 \frac{k_{H(P)}}{k_{H(S)}}}{6 \frac{k_{H(P)}}{k_{H(S)}} + 2(i-2)} = \frac{6 \exp\left(\frac{-16.7 \text{ kJ/mol}}{RT}\right)}{6 \exp\left(\frac{-16.7 \text{ kJ/mol}}{RT}\right) + 2(i-2)}. \quad (6)$$

The probability of an odd electron on a secondary carbon ( $R_i^j$ ) ( $2 \leq j \leq i-1$ ),  $P_{(S)}$ , is as

$$P_{(S)} = \frac{2(i-2)k_{H(S)}}{6k_{H(P)} + 2(i-2)k_{H(S)}} = \frac{2(i-2)}{6 \frac{k_{H(P)}}{k_{H(S)}} + 2(i-2)} = \frac{2(i-2)}{6 \exp\left(\frac{-16.7 \text{ kJ/mol}}{RT}\right) + 2(i-2)}. \quad (7)$$

### 3) $\beta$ -scission

The activation energy of the rate constants of  $\beta$ -scission of forming methyl radical ( $k_{\beta(M)}$ ) is 8.4 kJ/mol higher than that for forming the other radicals ( $k_{\beta(O)}$ )<sup>9</sup> and both frequency factors of the rate constants of  $\beta$ -scission forming methyl radical ( $k_{\beta(M)}$ ) and that for forming the other alkyl radicals ( $k_{\beta(O)}$ ) are the same<sup>7</sup>. Here, we took into account of the number of C-C bond for the overall rate constant of  $\beta$ -scission.

The primary radical ( $R_i^1$  or  $R_i^i$ ), which has an odd electron on a primary carbon, has one  $\beta$ -position and produces ethylene and  $R_{i-2}$  through  $\beta$ -scission. Since the probability of the

formation of  $R_i^1$  or  $R_i^i$  through isomerization is  $P_{(i)}$ , the rate of the formation of ethylene and  $R_{i-2}$  through  $\beta$ -scission from  $R_i$  is  $P_{(i)}k_{\beta(O)}[R_i]$ . For the secondary radical that has an odd electron at 2 or  $i-1$  position in the radical ( $R_i^2$  or  $R_i^{i-1}$ ), there is one  $\beta$ -position in the molecule and the radical produces propylene and  $R_{i-3}$  through  $\beta$ -scission. The probability of  $j=2$  or  $i-1$  for  $R_i^j$  is  $2P_{(i)j}/(i-2)$  because there are two carbons corresponding to the position of  $j=2$  or  $i-1$  in  $i-2$  secondary carbons. Thus, the formation rate of propylene and  $R_{i-3}$  through  $\beta$ -scission from  $R_i$  is  $2P_{(i)j}/(i-2)k_{\beta(O)}[R_i]$ . In the case of  $R_i^3$  or  $R_i^{i-2}$ , there are two  $\beta$ -positions in the radical. From the one of the ways of  $\beta$ -scission of  $R_i^3$  or  $R_i^{i-2}$ , methyl radical and 1-alkene has  $i-1$  carbon ( $Ol_{i-1}$ ) are produced. From the another way, butylene ( $Ol_i$ ) and  $R_{i-3}$  are formed. In  $i-2$  secondary carbons, there are two position corresponding to  $j=3$  or  $i-2$ . Thus, the formation rates of methyl radical and  $Ol_{i-1}$  and that of  $Ol_i$  and  $R_{i-3}$  are  $2P_{(i)j}/(i-2)k_{\beta(O)}[R_i]$  and  $2P_{(i)j}/(i-2)k_{\beta(O)}[R_i]$ , respectively. For the case of  $4 \leq j \leq i-3$  of  $R_i^j$ , there are also two  $\beta$ -positions in the radical. The  $\beta$ -scission of  $R_i^j$  produces  $Ol_{j-1}$  and  $R_{i-(j+1)}$  from one of the two ways and  $Ol_{i-(j-2)}$  and  $R_{j-2}$  from the other. The formation rate of  $Ol_{j-1}$  and  $R_{i-(j+1)}$  or  $Ol_{i-(j-2)}$  and  $R_{j-2}$  from  $R_i^j$  through  $\beta$ -scission is thus  $2(i-j)P_{(i)j}/(i-2)k_{\beta(O)}[R_i]$  because there are  $i-j$  carbons that are  $4 \leq j \leq i-3$  in  $R_i^j$ . The overall rate constant of disappearance of  $R_i$  through  $\beta$ -scission ( $k_{\beta(O)}$ ) should be as follows since that rate is the summation of the above formation rate constant of 1-alkenes and alkyl radicals;

$$k_{\beta(O)} = P_{(M)}k_{\beta(O)} + \frac{2P_{(S)}}{i-2}k_{\beta(O)} + \frac{2P_{(S)}}{i-2}k_{\beta(M)} + \frac{2P_{(S)}}{i-2}k_{\beta(O)} + \frac{2(i-6)P_{(S)}}{i-2}k_{\beta(O)} \quad (8)$$

From Eqs. (6) and (7), Eq. (8) is as

$$k_{\beta(O)} = A_{\beta} \exp\left(-\frac{E_{\beta}}{RT}\right) \left\{ \frac{4 \exp\left(-\frac{8.4 \text{ kJ/mol}}{RT}\right)}{6 \exp\left(-\frac{16.7 \text{ kJ/mol}}{RT}\right) + 2(i-2)} + \frac{6 \exp\left(-\frac{16.7 \text{ kJ/mol}}{RT}\right) + 4(i-4)}{6 \exp\left(-\frac{16.7 \text{ kJ/mol}}{RT}\right) + 2(i-2)} \right\} \quad (9)$$

where  $A_{\beta}$  and  $E_{\beta}$  are the kinetic parameters of  $\beta$ -scission for  $R_i^1$  producing  $Ol_2$  and  $R_2$  and  $10^{15.9} \text{ h}^{-1}$  and  $100.4 \text{ kJ/mol}$ , respectively<sup>10</sup>.

#### 4) H abstraction

In this model, H abstraction occurs only for  $n-C_i$  because  $n-C_i$  is the most abundant in the system at a low conversion level. The activation energy of rate constant of H abstraction from primary carbon ( $k_{H(P)}$ ) is  $16.7 \text{ kJ/mol}$  higher than that from secondary carbon ( $k_{H(S)}$ )<sup>8,9</sup>, and the frequency factor of both  $k_{H(P)}$  and  $k_{H(S)}$  is the same. Thus,  $k_{H(O)}$  is defined as below because  $n-C_i$  has 6 primary hydrogens and  $2(i-2)$  secondary hydrogens:

$$k_{H(O)} = 6k_{H(P)} + 2(i-2)k_{H(S)} = 2A_H \exp\left(-\frac{E_H}{RT}\right) \left\{ 3 \exp\left(-\frac{16.7 \text{ kJ/mol}}{RT}\right) + (i-2) \right\} \quad (10)$$

where  $A_H$  and  $E_H$  are the kinetic parameters of H abstraction of methyl radical from a secondary carbon from  $n$ -propane and  $10^{12} \text{ M}^{-1}\text{h}^{-1}$  and  $42.5 \text{ kJ/mol}$ , respectively<sup>11</sup>. In the recent study<sup>5</sup>, we found that the rate of H abstraction for  $n-C_{16}$  by  $R_i$  can be expressed as  $(1/j)k_{H(O)}[R_i][n-C_i]$ . The radical size dependence of H abstraction is reasonable both from the collision theory and transition-state theory<sup>5</sup>. Thus, for  $n-C_i$ , the H abstraction rate for  $n-C_i$  by  $R_i$  can be described as  $1/j k_{H(O)}[R_i][n-C_i]$ .

#### 5) Termination

Since a contribution of disproportion between two alkyl radicals is negligible<sup>11</sup>, the radical reaction network of  $n-C_i$  pyrolysis is terminated by only the recombination of two radicals. With the analogy of H abstraction, the rate constant of termination between  $R_i$  and  $R_m$  is assumed to be expressed by  $(1/i)(1/m)k_{\text{term}}$ , where  $k_{\text{term}}$  is the intrinsic rate constant and  $k_{\text{term}}$  reported for two methyl radicals is employed ( $A_{\text{term}} = 10^{14.3} \text{ M}^{-1}\text{h}^{-1}$  and  $E_{\text{term}} = 0 \text{ kJ/mol}$ )<sup>11</sup>.

## Results and Discussion

### 1. Comparison between experimental results and calculated results

Figure 1 shows the parity plot between the experimental results and the model. In the case the experiments were conducted using flow type apparatus, the concentration was estimation from the reaction pressure and temperature by Peng-Robinson equation of state<sup>12</sup>. The critical constants ( $T_c$ ,  $P_c$ , and  $\omega$ ) were from the book by Reid et al.<sup>13</sup> or calculated by the ABC method<sup>14</sup>. As shown in Fig. 1, the model described the experimental results successfully over a wide range of experimental conditions ( $T = 572 \text{ K} - 973 \text{ K}$ ,  $[n-C_i] = 6.86 \times 10^{-3} \text{ M} - 2.72 \text{ M}$ , and  $i = 3-32$ ).

### 2. Correlation of the overall rate constant with carbon number of n-alkane

The rate constant of initiation (Eq. 4) can be approximated as follows because  $k_{\text{init}(M)}$  is much less than  $k_{\text{init}(O)}$ :

$$k_{\text{init}(i)} = (i-3)k_{\text{init}(O)} \quad (11)$$

From Eq. 9, the rate constant of  $\beta$ -scission at a long chain n-alkane ( $i \gg 4$ ) can be simplified to

$$k_{\beta(i)} = \frac{4(i-4)}{2(i-2)} k_{\beta(O)} = 2k_{\beta(O)} \quad (12)$$

since  $k_{\beta(M)}$  is much less than  $k_{\beta(O)}$ , and  $P_{(M)}$  is much less than  $P_{(S)}$ . The rate constant of H abstraction (Eq. 10) can be simplified as

$$k_{H(i)} \approx 2(i-2)k_{H(S)} \quad (13)$$

because the contribution of  $k_{H(O)}$  to  $k_{H0}$  is much less than that of  $k_{H(S)}$ . Thus, using the approximation of Eqs. 11 ~ 13, Eq. 4 can be approximated by

$$k_{(i)} = \frac{2k_{\beta(O)} \cdot 2(i-2)k_{H(S)}}{2k_{\beta(O)} + (1/i) \cdot 2(i-2)k_{H(S)}[n-C_i]} \sqrt{\frac{2(i-3)k_{\text{init}(O)}[n-C_i]}{k_{\text{term}0}}} \quad (14)$$

When  $i$  is much larger than 2,  $i-2/i$  is almost equal to unity. Thus, Eq. 14 becomes

$$k_{(i)} \approx \frac{2k_{\beta(O)} \cdot 2(i-2)k_{H(S)}}{2k_{\beta(O)} + k_{H(S)}[n-C_i]} \sqrt{\frac{2(i-3)k_{\text{init}(O)}[n-C_i]}{k_{\text{term}0}}} = (i-2)\sqrt{i-3} \left\{ \frac{4k_{\beta(O)}k_{H(S)}}{2k_{\beta(O)} + k_{H(S)}[n-C_i]} \sqrt{\frac{2k_{\text{init}(O)}[n-C_i]}{k_{\text{term}0}}} \right\} \quad (15)$$

Therefore, regardless to the temperature and concentration, the overall rate constant of n-alkane pyrolysis depends on  $(i-2)\sqrt{i-3}$  for carbon number of n-alkane. Normalizing the rate constant of n-alkane pyrolysis by the rate constant of n-C<sub>16</sub> pyrolysis at a given condition, Eq. 15 is as

$$\frac{k_{(i)}}{k_{(16)}} = \frac{(i-2)\sqrt{i-3}}{14\sqrt{13}} \quad (16)$$

Figure 2 shows the normalized rate by Eq. 19. Tilicheev's<sup>2</sup>, Voge and Good's<sup>3</sup>, and Yu and Eser's<sup>4</sup> correlations with Eqs. 1, 2, and 3, respectively, are also shown in these figures. As shown in Fig. 2, all the plots by Tilicheev's<sup>2</sup>, Voge and Good's<sup>3</sup>, and Yu and Eser's<sup>4</sup> correlations fall on the line calculated by Eq. 16. This analysis gives the theoretical basis to their correlations.

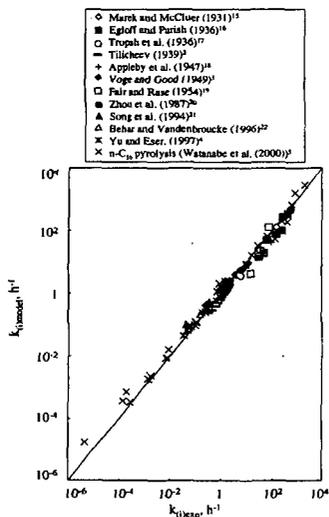
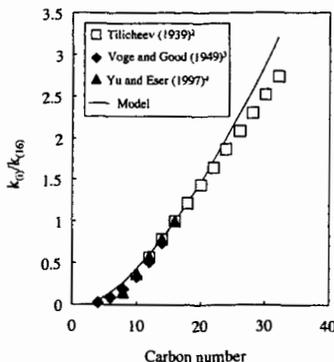


Figure 1 Parity plot of overall rate constants of n-alkanes pyrolysis

## Conclusion

We proposed a new model for overall rate constant of n-alkane pyrolysis, based on Kossiakoff and Rice theory, by taking the carbon number dependence of alkyl radical for the rate constant of bimolecular reactions into account. The model can express the experimental overall rate constant of n-alkanes ( $n\text{-C}_7 \sim n\text{-C}_{32}$ ) at wide range of temperatures (572 K ~ 973 K) and concentrations ( $6.86 \times 10^{-3} \text{ M} \sim 2.72 \text{ M}$ ), and could explain previously reported carbon number correlation of pyrolysis rate.



**Figure 2** Normalization of carbon number dependence of Voge and Good's<sup>3</sup>, Tilicheev's<sup>2</sup>, and Yu and Eser's<sup>4</sup> correlation by the overall rate constant of n-C<sub>16</sub> pyrolysis at given conditions

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