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Analysis of Reaction Path in Triangular Network Consisting of Langmuir-Hinshelwood Type Reactions

The great majority of work on kinetics of complex reaction system has dealt with the reaction expressed by an integer-power kinetic equation such as a zero-, first-, or second-order reaction. On the heterogeneous catalytic reaction, however, the kinetics follows, in general, a more complex expression, as represented for example, by the Langmuir-Hinshelwood type of rate equation. And very little attention has been paid to analyzing the complex reaction system consisting of those Langmuir-Hinshelwood type reactions, probably as a result of mathematical difficulty.

The case is different in which the time variable is eliminated and only the dependences between the concentrations of the reaction components are analyzed.

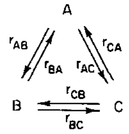
Wei and Prater (*1*) have shown that if certain conditions are fulfilled,[1] heterogeneous catalytic reactions will be pseudo-monomolecular and the reaction path[2] exhibited by a pseudo-monomolecular system will be identical with the reaction path of a monomolecular system. Examples of such pseudo-monomolecular systems are the isomerization of *n*-butenes and the isomerization of xylenes.

On the other hand, Haag and Pines (*2*) have proposed a method to estimate the relative values of six rate constants for the interconversion of 1-butene, *cis*-2-butene, and *trans*-2-butene, and shown that the reaction path can be calculated from the first-order rate equation by using the relative values of rate constants. Although not so precise in comparison with the Wei and Prater method, the Haag and Pines method has been widely used by catalytic chemists [e.g. (*3*)] for reasons of simplicity and convenience.

The purpose of present study was to clarify the factors determining a reaction path for the Langmuir-Hinshelwood type monomolecular system, and the kinetic meaning of the rate constants obtained from the analysis of a reaction path.

Calculation of Reaction Path by First-Order Rate Equation

In the present paper, we deal with a problem of the reaction path in the triangular network expressed by Eq. (1), in which each component reaction follows the rate equation of Langmuir-Hinshelwood type expressed by Eq. (2),



(1)

$$r_{ij} = \frac{k_{ij}K_iP_i}{1 + K_AP_A + K_BP_B + K_CP_C + K_IP_I}, \tag{2}$$

where A, B, and C are reaction components, I the inert component, r_{ij} the reaction rate of transformation of the ith component to the jth one, k_{ij} the surface reaction rate constant, K_i the adsorption equilibrium constant of the ith component, and P_i the partial pressure.

Since there is no change in the total number of mole with extent of reaction, the overall reaction rates can be expressed as

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[1] These conditions are nearly equivalent to the assumption that the reaction is of the Langmuir-Hinshelwood type monomolecular.

[2] The reaction path means the trajectory in the composition space.

$$\frac{1}{RT}\frac{dP_A}{dt}=\frac{1}{1+\Sigma K_iP_i}\{-(k_{AB}+k_{AC})K_AP_A+k_{BA}K_BP_B+k_{CA}K_CP_C\}, \tag{3a}$$

$$\frac{1}{RT}\frac{dP_B}{dt}=\frac{1}{1+\Sigma K_iP_i}\{k_{AB}K_AP_A-(k_{BA}+k_{BC})K_BP_B+k_{CB}K_CP_C\}, \tag{3b}$$

$$\frac{1}{RT}\frac{dP_C}{dt}=\frac{1}{1+\Sigma K_iP_i}\{k_{AC}K_AP_A+k_{BC}K_BP_B-(k_{CA}+k_{CB})K_CP_C\}, \tag{3c}$$

if we deal with a mixture of ideal gases.

Let x_A, x_B, and x_C be the mole fractions among three reactants, that is $x_A+x_B+x_C=1$, and let π be the sum of the partial pressures of three reactants. It then follows that $P_i=x_i\pi$.

Division of Eq. (3a) by Eq. (3b) gives us

$$\frac{dx_A}{dx_B}=\frac{-(k'_{AB}+k'_{AC})x_A+k'_{BA}x_B+k'_{CA}x_C}{k'_{AB}x_A-(k'_{BA}+k'_{BC})x_B+k'_{CB}x_C}, \tag{4}$$

where k'_{ij} is the apparent rate constant given by $k'_{ij}=k_{ij}K_i$.

A problem of the reaction path in this system is reduced to a problem of the solution curves of Eq. (4). Eliminating x_C from Eq. (4) by the relation of $x_C=1-x_A-x_B$, and reducing it to a homogeneous equation, we can get the solution of Eq. (4) directly. In the present paper, however, in order to compare with a first-order rate equation, let us derive the solution curve by another convenient method.

The solution curve of Eq. (4) should satisfy the mutual relationship of x_A, x_B, and x_C, which are given by the simultaneous ordinary differential equations

$$\frac{dx_A}{d\theta}=-(k'_{AB}+k'_{AC})x_A+k'_{BA}x_B+k'_{CA}x_A, \tag{5a}$$

$$\frac{dx_B}{d\theta}=k'_{AB}x_A-(k'_{BA}+k'_{BC})x_B+k'_{CB}x_C, \tag{5b}$$

$$\frac{dx_C}{d\theta}=k'_{AC}x_A+k'_{BC}x_B-(k'_{CA}+k'_{CB})x_C, \tag{5c}$$

where θ is a parameter introduced for convenience.

Therefore, the reaction path is identical with one determined by Eqs. (5), which are equal to the rate equations for a system of first-order reactions involving three components if we regard k'_{ij} as a reaction rate constant, and θ as a reaction time.

The particular solution of Eqs. (5) satisfying the conditions of initial composition x_i^0 at $\theta=0$ and equilibrium composition x_i^e at $\theta=\infty$ is

$$\begin{aligned}x_A=x_A{}^e+[&\{(x_A{}^0-x_A{}^e)+u_1(x_B{}^0-x_B{}^e)\}u_2\exp(-\lambda_1\theta)\\&-\{x_A{}^0-x_A{}^e)+u_2(x_B{}^0-x_B{}^e)\}u_1\exp(-\lambda_2\theta)]/(u_2-u_1),\end{aligned} \tag{6a}$$

$$\begin{aligned}x_B=x_B{}^e+[&\{(x_A{}^0-x_A{}^e)+u_1(x_B{}^0-x_B{}^e)\}\exp(-\lambda_1\theta)\\&+\{(x_A{}^0-x_A{}^e)+u_2(x_B{}^0-x_B{}^e)\}\exp(-\lambda_2\theta)]/(u_2-u_1),\end{aligned} \tag{6b}$$

$$x_C=1-x_A-x_B, \tag{6c}$$

where $\lambda_1=(k_a+k_b+\Delta^{1/2})/2$, $\lambda_2=(k_a+k_b-\Delta^{1/2})/2$, $u_1=(k_a-k_b-\Delta^{1/2})/2k_c$, $u_2=(k_a-k_b+\Delta^{1/2})/2k_c$, $\Delta=(k_a-k_b)^2+4k_ck_d$, $k_a=k_{CA}+k_{AC}+k_{AB}$, $k_b=k_{BC}+k_{CB}+k_{BA}$, $k_c=k_{AB}-k_{CB}$, $k_d=k_{BA}-k_{CA}$.

If k'_{ij}, x_i^0, and x_i^e are given, the values of x_A, x_B, and x_C corresponding to arbitrary values for θ are calculated by Eqs. (6), respectively, and then a plot of x_A against x_B or x_C gives us the solution curve, that is the reaction path. It is a matter of course that, in the case of the Langmuir-Hinshelwood type reaction, in general, θ does not stand for a reaction time, but is a parameter for calculating the reaction path. As shown in Eqs. (3), only under the condition where three adsorption equilibrium constants are equivalent, θ stands for a reaction time and the equation of first-order reaction holds truly.

FACTORS DETERMINING A REACTION PATH

Equation (4) shows that the reaction path depends on the relative values of six apparent rate constants which are the product of the reaction rate constant and the adsorption equilibrium constant.

In conformity with the principle of detailed balancing, the rate constants are related to the equilibrium composition by the equations

$$\frac{x_A{}^e}{x_B{}^e} = \frac{k_{BA}K_B}{k_{AB}K_A} = \frac{k'_{BA}}{k'_{AB}},\quad \frac{x_B{}^e}{x_C{}^e} = \frac{k_{CB}K_C}{k_{BC}K_B} = \frac{k'_{CB}}{k'_{BC}},\quad \frac{x_C{}^e}{x_A{}^e} = \frac{k_{AC}K_A}{k_{CA}K_C} = \frac{k'_{AC}}{k'_{CA}} \qquad (7)$$

and hence

$$\left(\frac{k_{AC}}{k_{AB}}\right)\left(\frac{k_{BA}}{k_{BC}}\right)\left(\frac{k_{CB}}{k_{CA}}\right) = 1. \qquad (8)$$

For known equilibrium, the six apparent rate constants reduce to three independent parameters. These parameters are selected to be a single rate constant and two ratios of rate constants among three ratios in Eq. (8), for example, k_{AC}, k_{AC}/k_{AB}, and k_{CB}/k_{CA}. Using these parameters, the relative values of six apparent rate constants can be expressed as

$$k'_{AB}:k'_{BA}:k'_{BC}:k'_{CB}:k'_{CA}:k'_{AC} = \left(\frac{k_{AB}}{k_{AC}}\right) : \left(\frac{x_A{}^e}{x_B{}^e}\right)\left(\frac{k_{AB}}{k_{AC}}\right) : \left(\frac{x_A{}^e}{x_B{}^e}\right)\left(\frac{k_{CB}}{k_{CA}}\right) : \left(\frac{x_A{}^e}{x_C{}^e}\right)\left(\frac{k_{CB}}{k_{CA}}\right) : \left(\frac{x_A{}^e}{x_C{}^e}\right) : 1. \qquad (9)$$

Therefore, the reaction path in this reaction system does not depend on the adsorption equilibrium constant and the total pressure, but only on the two ratios of surface reaction rate constants (or two ratios of apparent rate constants).

EXPERIMENTAL DETERMINATION OF APPARENT RATE CONSTANTS

If the two ratios of the reaction rate constants are given, the relative values of the apparent rate constants will be determined by Eq. (9) and then the reaction path by Eq. (6). The inverse process of determining the ratio of rate constants from the experimentally observed time course of the reaction is done as follows.

From Eq. (3), the initial rates of the reaction with pure C, that is $x_C{}^0 = 1$, are

$$\lim_{t\to 0}\left(\frac{dx_A}{dt}\right) = \frac{k_{CA}K_C}{1 + K_C P_C{}^0 + K_I P_I}, \qquad (10a)$$

$$\lim_{t\to 0}\left(\frac{dx_B}{dt}\right) = \frac{k_{CB}K_C}{1 + K_C P_C{}^0 + K_I P_I}. \qquad (10b)$$

Hence

$$\lim_{t\to 0}\,(x_B/x_A)_t = k_{CB}/k_{CA}, \qquad (11)$$

where $(x_B/x_A)_t$ is the ratio x_B/x_A at the time t. Thus, determining the ratio x_B/x_A at low conversion and extrapolating back to zero time gives the ratio k_{CB}/k_{CA} (or k'_{CB}/k'_{CA}). Similarly, the ratio k_{AB}/k_{AC} can be determined from the reaction with pure A.

The practice is identical with the method proposed by Haag and Pines for analyzing the isomerization of *n*-butenes. From above discussions, the Haag and Pines method is certified as correct for the Langmuir-Hinshelwood type monomolecular reaction system. It has been shown by Forni and co-workers (*4*) that 1-butene isomerization follows the rate equation of the Langmuir-Hinshelwood type. Therefore, the Haag and Pines method should be applicable to this reaction system.

However, it should be emphasized that the relative values of the apparent rate constants determined from a reaction path are the relative values of the product of the reaction rate constant and the adsorption equilibrium constant, not excepting the relative values of the apparent rate constants determined by the Wei and Prater method or the extended Wei and Prater method (5).

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SHUICHI KAGAWA

Department of Industrial Chemistry
Faculty of Engineering
Nagasaki University
Nagasaki 852, Japan

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