JOURNAL OF CATALYSIS 14, 273-280 (1969)

## NOTES

# Reaction Rate Modeling near Chemical Equilibria

In developing a rate equation for a heterogeneous catalytic reaction, it is common practice to postulate plausible consecutive chemical steps and to formulate the rate expression with the tacit assumption that there exist rate-determining steps. The concept of rate-determining step is well documented and extensively discussed elsewhere (*1, 2*). In general, the utilization of the concept greatly simplifies the derivation of rate expression. For some reaction systems, however, rate equations which involve more than one rate-controlling step need be considered in obtaining an adequate representation of experimental data (*3–5*). These rate equations may be of particular value for the analysis of reaction data which are obtained in the vicinity of chemical equilibria. Usually the rate of chemical reaction decreases as degree of conversion increases. In addition, the nearer the equilibrium state becomes, the poorer the assumption of *existence of a rate-determining step* becomes. This is especially true when two or more successive chemical reactions take place on a catalyst surface. The assumption which is satisfied for some elementary steps for a reaction condition—most likely a condition which is far away from the thermodynamic equilibrium—may completely break down as the experimental condition approaches equilibrium.

It is the purpose of this note to present a generalized rate expression which may be applicable for an entire spectrum of reaction condition. The importance of reaction modeling near chemical equilibria is also discussed in detail.

### *Nomenclature*

| | |
|---|---|
| $C_{A1}$, $C_{B1}$, $C_1$ | The fraction of surface sites covered by A and B and the fraction of empty surface sites, respectively |
| $k_{+i}$, $k_{-i}$ | The rate constants of the forward and of the reverse reactions |
| $K$ | The thermodynamic equilibrium constant |
| $K_i$ | The adsorption equilibrium constant of the $i$ component |
| $p_A$, $p_B$, $p_C$ | The partial pressures of A, B, and C |
| $R$ | Universal gas constant |
| $T$ | Reaction temperature |
| $v_{+i}$, $v_{-i}$ | The rate of $i$th forward and the rate of $i$th reverse reaction |
| $V_f$, $V_r$ | The forward and reverse rate of overall reaction |
| $\Delta g_i$ | Gibbs free energy change for the $i$th step |
| $\Delta G$ | Gibbs free energy change for overall reaction |
| $\nu_i$ | Stoichiometric number of $i$th step |

### *Formulation of Rate Expressions*

In order to demonstrate the formulation of the rate expressions, let us consider a hypothetical chemical system in which the overall reaction on a catalyst is

$$A \rightleftarrows B + C \qquad (1)$$

The formulation is limited to a relatively simple system; however the methods are more generally applicable. For this system the following rate model is tentatively entertained. The chemical species C is assumed to be reactively adsorbed on sites which are already occupied by B.

$$
\begin{aligned}
&1. \quad \mathrm{A} + \mathrm{l} \underset{v_{-1}}{\overset{v_{+1}}{\rightleftarrows}} \mathrm{Al} \\
&2. \quad \mathrm{Al} \underset{v_{-2}}{\overset{v_{+2}}{\rightleftarrows}} \mathrm{Bl} + \mathrm{C} \\
&3. \quad \mathrm{Bl} \underset{v_{-3}}{\overset{v_{+3}}{\rightleftarrows}} \mathrm{B} + \mathrm{l}
\end{aligned}
\tag{2}
$$

where l represents sites on the catalyst surface at which adsorption occurs. The rates $v_{+i}$ denote those for individual elementary steps. The conventional mass action law gives

$$
\begin{aligned}
v_{+1} &= k_{+1}p_{\mathrm{A}}C_{\mathrm{l}} & v_{-1} &= k_{-1}C_{\mathrm{Al}} \\
v_{+2} &= k_{+2}C_{\mathrm{Al}} & v_{-2} &= k_{-2}p_{\mathrm{C}}C_{\mathrm{Bl}} \\
v_{+3} &= k_{+3}C_{\mathrm{Bl}} & v_{-3} &= k_{-3}p_{\mathrm{B}}C_{\mathrm{l}}
\end{aligned}
\tag{3}
$$

where $p_{\mathrm{A}}$, $p_{\mathrm{B}}$, and $p_{\mathrm{C}}$ refer to the partial pressures of A, B, and C and $C_{\mathrm{l}}$, $C_{\mathrm{Al}}$, and $C_{\mathrm{Bl}}$ refer to the fractions of surface sites which are empty and occupied by chemisorbed A and B, respectively. Thus

$$C_{\mathrm{Al}} + C_{\mathrm{Bl}} + C_{\mathrm{l}} = 1 \tag{4}$$

According to Temkin's method (*6*), under steady state conditions the forward and reverse reaction rates of this reaction system may be presented in the following way:

$$V_{\mathrm{f}} = \frac{v_{+1}v_{+2}v_{+3}}{v_{+2}v_{+3} + v_{-1}v_{+3} + v_{-1}v_{-2}} \tag{5}$$

and

$$V_{\mathrm{r}} = \frac{v_{-1}v_{-2}v_{-3}}{v_{+2}v_{+3} + v_{-1}v_{+3} + v_{-1}v_{-2}} \tag{6}$$

where $V_{\mathrm{f}}$ and $V_{\mathrm{r}}$ denote, respectively, the forward and reverse reaction rates. The overall Gibbs free energy for the complete reaction is the sum of free energies for all elementary steps multiplied by the stoichiometric number of the corresponding step. Thus

$$\Delta G = \nu_1\Delta g_1 + \nu_2\Delta g_2 + \nu_3\Delta g_3 \tag{7}$$

The forward and back reaction rates for each of the three steps involved are related by

$$\Delta g_i = -RT \ln \frac{v_{+i}}{v_{-i}} \tag{8}$$

The relationship of Eq. (8) was developed by Horiuti (*7, 8*) on the basis of statistical mechanical transition state theory. If the reaction of Eq. (1) follows the path shown by Eq. (2), then the stoichiometric number of each of the steps is unity. For a catalyst with uniform and nonreacting sites, the combination of Eq. (3) through (8) yields

$$V = \frac{k_{+1}k_{+2}k_{+3}}{k_{+2}k_{+3} + k_{+3}k_{-1} + k_{-1}k_{-2}p_{\mathrm{C}}} C_{\mathrm{l}}\left[p_{\mathrm{A}} - \frac{p_{\mathrm{B}}p_{\mathrm{C}}}{K}\right] \tag{9}$$

where $K$ is the thermodynamic equilibrium constant for the overall reaction and

$$C_{\mathrm{l}} = \frac{k_{-1}k_{-2}p_{\mathrm{C}} + k_{-1}k_{+3} + k_{+2}k_{+3}}{1 + k_{+1}(k_{-2}p_{\mathrm{C}} + k_{+2} + k_{+3})p_{\mathrm{A}} + k_{-3}(k_{-1} + k_{+2} + k_{-2}p_{\mathrm{C}})p_{\mathrm{B}}} \tag{10}$$

From Eqs. (9) and (10) we can obtain a number of mechanistic rate equations depending upon the rate controlling step. If we assume that the adsorption rate of B is fast and assume that $k_{+3} \gg k_{+1}p_{\mathrm{A}}$, $k_{-1}$, $k_{+2}$, $k_{-2}p_{\mathrm{C}}$ for example, then we will have

$$V = \frac{K_1k_{+2}[p_{\mathrm{A}} - (p_{\mathrm{B}}p_{\mathrm{C}}/K)]}{1 + \dfrac{k_{+2}}{k_{-1}} + K_1p_{\mathrm{A}} + \dfrac{1}{K_3}\left(1 + \dfrac{k_{+2}}{k_{-1}} + \dfrac{k_{-2}}{k_{-1}}p_{\mathrm{C}}\right)p_{\mathrm{B}}} \tag{11}$$

where

$$K_1 = k_{+1}/k_{-1} \qquad K_3 = k_{+3}/k_{-3}$$

Eq. (11) presents a rate model in which the net adsorption rate of A and the surface reaction rate are comparable. If the surface reaction is only controlling, we have $k_{+2}$, $k_{-2}p_{\mathrm{C}} \ll k_{+1}p_{\mathrm{A}}$, $k_{-1}$, $k_{+3}$, $k_{-3}p_{\mathrm{B}}$ and Eq. (11) is reduced to

$$V = \frac{K_1 k_{+2}[p_A - (p_B p_C/K)]}{1 + K_1 p_A + (p_C/K_3)} \qquad (12)$$

Note that Temkin's method outlined in this paper is not directly applicable to the systems in which rate-determining steps occur separately on two or more branched paths of reaction. Equations (5) and (6) can be derived only when all rate-determining steps are consecutive in the same path. The limitation of Temkin's method is extensively discussed elsewhere (*4*).

## Discussion

An adequate rate model obtained from experimental study of an extreme condition may provide only limited information. Such a model offers little insight into the true nature of the entire system. For example, an adequate model built on the basis of forward reaction data is never likely to be an adequate model for the reverse reaction of the system studied. In accordance with the principle of microscopic reversibility (*9, 10*), the pathway of a forward reaction and that of the backward reaction must be precisely the same. This is especially true under the circumstances wherein the state of the surface remains unchanged for the entire range of reaction conditions. For the system illustrated in this paper, the catalytic decomposition of A and the catalytic synthesis of A must be given by the same elementary steps. In this light, with a kinetic study near equilibrium it would be possible to establish a mechanistic model which possesses an adequate representation of both forward and backward rates if reaction mechanism remains invariant.

It should be noted, however, that there are disadvantages in using the equations proposed and modeling rates due to equilibrium. First, as described previously, the forward and backward reaction rates are slow in the vicinity of equilibrium. Thus the experimental measurements of these rates are not always easy. Second, as can be seen from the rate equations developed in the previous section, the equations tend to be more complicated, containing many nonlinear parameters. Furthermore the rate equations derived assuming the existence of two or more rate-determining steps contain more highly correlated rate parameters. The rate parameters $k_{-1}$, $k_{+2}$, and $k_{-2}$ of Eq. (11) are found in the form of ratios. In this situation precise determination of these ratios may not be difficult, but the estimations of individual parameters would be rather difficult. In fact there exists an infinite set of parameters which gives the same value of parameter ratio. A way to obtain the precise point estimates of parameters would be to gather low conversion rate data with pure reactant feed.

The rates of individual elementary steps are dependent upon reaction temperature and the partial pressures of both reactants and products. Thus, as pointed out by Boudart (*11*), a shift in rate-determining steps may take place with the change of temperature and partial pressures. In the development of Eqs. (9) and (10) we are not limited to situations involving a single rate-determining step which is subject to change with experimental conditions. This offers a great flexibility in utilizing the rate equations since they can readily furnish several mechanistic rate expressions by considering the relative magnitudes of the forward and backward rates of plausible individual rate steps. As described previously, the inclusion of more general kinetic situations results in mathematical rate expressions of some complexity. Recent progress in digital computation techniques, however, enables one to handle these more elaborate mechanistic rate models.

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*Received October 1, 1968;*
*revised January 21, 1969*

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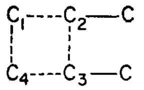
# Four-Center Mechanism for Olefin Reactions

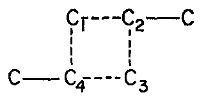
The occurrence of disproportionation, polymerization, and isomerization of olefins over similar catalysts or simultaneously over the same catalyst suggests a similarity of mechanisms for these reactions. However, this is not to say that one can predict a given catalyst will promote one or more of these reactions or that a given catalyst known to promote one of these reactions also will promote another. Reaction schemes involving a four-center, cyclobutane intermediate such as proposed by Schoepfle and Ryan (*1*) for the dimerization of diphenylethylene also have been postulated for the disproportionation of olefins (*2*) and the dimerization of propylene (*3*). This note discusses a mechanistic relationship of olefin reactions occurring via the four-center intermediate.

Olefins disproportionate over a number of heterogeneous catalysts such as hexacarbonyls and oxides of molybdenum and tungsten supported on alumina or silica (*4*, *5*, *6*). Bradshaw, Howman, and Turner (*2*) suggested a four-center or quasi-cyclobutane mechanism for this reaction. Isotope studies by Clark (*7*) and by Mol, Moulijn, and Boelhouwer (*8*) support the four-center mechanism for olefin disproportionation. Calderon and associates (*9*) arrived at this mechanism for olefin disproportionation from studies with soluble tungsten complexes as catalyst.

The four-center intermediates postulated with propylene are



(I)



(II)

Dissociation of (I) by breaking of the opposite $C_1$–$C_2$ and $C_3$–$C_4$ ring bonds forms the observed disproportionation products, ethylene and 2-butene (*4*). Breaking of the other opposite pair of ring bonds in (I) or of either pair of opposite ring bonds in (II) results in the starting material. A hydrogen shift (intramolecular hydrogen transfer) between carbon atoms is not needed for disproportionation.

In our early disproportionation studies we contacted ethylene with a series of catalysts prepared by supporting Group VI

| Catalyst: alumina impregnated with— | Products |
|---|---|
| $W(CO)_6$ | 21% Propylene, 71% 1-butene, 8% 2-butene |
| $Mo(CO)_6$ | 8% Cyclopropane, 12% methylcyclopropane, 28% propylene, 26% 1-butene, 26% 2-butene |
| $Cr(CO)_6$ | 3% Butenes, 97% solid polyethylene |