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## NOTES

# Discrimination of Alternative Kinetic Equations for Heterogeneous Catalytic Reactions by Competitive Experiments

Rate equations for heterogeneous catalytic reactions of the type shown by Eq. (1)

$$A + B \rightarrow C + D \qquad (1)$$

very often have the form of Eqs. (2) or (3) (for the irreversible case and nonadsorbing products or for initial conditions),

$$r = k(K_Ap_A)^a(K_Bp_B)^b/[1 + (K_Ap_A)^c + (K_Bp_B)^d]^e, \qquad (2)$$

$$r = k_Ik_{II}p_A{}^ap_B{}^b/(k_Ip_A{}^a + k_{II}p_B{}^b), \qquad (3)$$

where $r$ denotes reaction rate; $k$, $k_I$, and $k_{II}$ rate constants; $K_A$ and $K_B$ adsorption coefficients; and $p_A$ and $p_B$ partial pressures of reactants. The well-known Langmuir-Hinshelwood equation of type (2) is based on the assumption of equilibrium adsorption and rate-determining surface reactions (*1*). Equation (3), which has frequently been found suitable for oxidation reactions, expresses a two-step reaction model with equal rates of the steps in steady state (e.g., *2–4*). Usually, the set of rate data is treated by a series of rate equations using some regression method, and the best-fitting equations are found on the basis of a suitable statistical criterion (e.g., *5*). However, quite often several equations are selected because they fit the data in an indistinguishable manner at a given significance level. There are some possibilities of discriminating between alternative equations by additional experiments (e.g., *6*). In some cases, the "best" equations differ by the values of the exponents $a$ and $b$ in the numerator (*7, 8*). The purpose of this note is to show that, in this case, simple competitive experiments with two related reactants may also be useful for discrimination between alternative equations. The structural relationship of the two reactants must be very close; otherwise, the validity of the same rate equation for both compounds cannot be safely assumed.

Determination of the reaction order by means of competitive experiments is well known in homogeneous kinetics, and the advantages of this method have been stressed by Jungers *et al.* (*9*). Although Eqs. (2) and (3) are more complicated than the rate expressions for homogeneous transformations, it is possible to derive the same relations for conversions of competing reactants in heterogeneous reactions as from power-law rate equations for homogeneous reactions.

Let us assume that reactants $A_1$ and $A_2$ compete for the common reagent B and for the same active sites. In the case of the Langmuir-Hinshelwood type equation (2) for $A_1$, the denominator must be expanded by the adsorption term of the reactant $A_2$ (or vice versa) and of all products. Thus, we obtain for the two reactions (if, for simplicity, adsorption terms for the products are omitted):

$$r_1 = \frac{k_1(K_{A_1}p_{A_1})^a(K_Bp_B)^b}{[1 + (K_{A_1}p_{A_1})^c + (K_{A_2}p_{A_2})^c + (K_Bp_B)^d]^e}, \qquad (4)$$

$$r_2 = \frac{k_2(K_{A_2}p_{A_2})^a(K_Bp_B)^b}{[1 + (K_{A_1}p_{A_1})^c + (K_{A_2}p_{A_4})^c + (K_Bp_B)^d]^e}. \tag{5}$$

Similarly, for Eq. (3), the expanded forms are

$$r_1 = \frac{k_{I,1}k_{II,1}k_{II,2}p_{A_1}{}^a p_B{}^b}{k_{II,1}k_{II,2}p_B{}^b + k_{I,1}k_{II,2}p_{A_1}{}^a + k_{I,2}k_{II,1}p_{A_2}{}^a}, \tag{6}$$

$$r_2 = \frac{k_{I,2}k_{II,1}k_{II,2}p_{A_2}{}^a p_B{}^b}{k_{II,1}k_{II,2}p_B{}^b + k_{I,1}k_{II,2}p_{A_1}{}^a + k_{I,2}k_{II,1}p_{A_2}{}^a}. \tag{7}$$

By dividing the pairs of corresponding equations the relation

$$r_1/r_2 = R(p_{A_1}/p_{A_2})^a \tag{8}$$

results, where for Eq. (2) $R = (k_1/k_2)(K_{A_1}/K_{A_2})^a$ and for Eq. (3) $R = (k_{I,1}/k_{I,2})$. It is of course possible to find out the value of $a$ using Eq. (8) and initial rate data, but the following procedure has some advantages, being less sensitive to experimental error. Introducing conversions $x_1$ and $x_2$, initial partial pressures $p°_{A_1}$, $p°_{A_2}$ (i.e., $p_A = p°_A(1 - x)$) and ratio of the initial partial pressures of reactants $\alpha = p°_{A_1}/p°_{A_2}$, we obtain

$$\frac{dx_1}{dx_2} = R\alpha^{a-1}\left(\frac{1 - x_1}{1 - x_2}\right)^a. \tag{9}$$

For the most frequent values of $a$ the integration yields:

$$a = 0{,}5 \quad x_1 = (2R/\alpha^{1/2})[1 - (1 - x_2)^{1/2}] + (R^2/\alpha)[2(1 - x_2)^{1/2} + x_2 - 2], \tag{10}$$

$$a = 1 \quad x_1 = 1 - (1 - x_2)^R, \tag{11}$$

$$a = 2 \quad x_1 = \alpha R x_2/(1 + \alpha R x_2 - x_2). \tag{12}$$

Equation (11) has been derived and applied many times for calculation of relative reactivities $R$ (*10–14*).

It is important to vary $\alpha$ over a wide range for discrimination among cases (10–12). The result is more valuable if the range of conversions has been large, because the selected equation has been thus proved also in the presence of reaction products. The advantage of this procedure is that expressions (10–12) do not contain parameters such as weight of catalyst, actual activity of catalysts, feed rate, and absolute values of partial pressures, which are sources of experimental error. The competitive method is less sensitive to temperature fluctuations since related reactants react with similar activation energies.

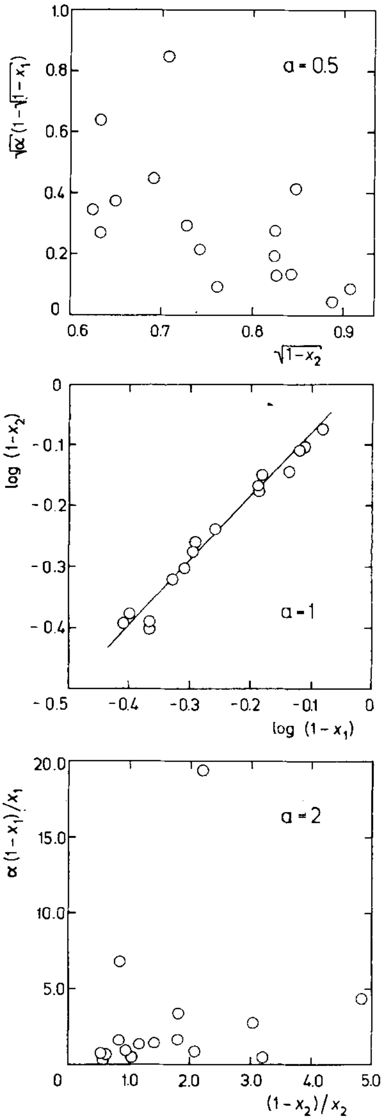

FIG. 1. Results of competitive hydrogenolysis of butyl acetate ($A_1$) and propyl butyrate ($A_2$) on rhodium at 300°C, plotted according to linearized forms of Eqs. (10–12). Parameters $\alpha$ and ($p°_{A_1} + p°_{A_2}$) were varied in the range 0.125–8.0 and 0.2–0.8 atm, respectively.

By competitive experiments it is thus possible to determine the value of the exponent $a$ without the knowledge of the actual form of the rate equation, because almost all types of equations yield Eq. (8), of course with different meanings of the constant R. As Eq. (8) can be obtained from different rate equations with the same value of $a$, the discrimination of alternative equations by using Eqs. (10–12) gives no evidence of the validity of the whole model. However, information about the value of $a$ seems to be unambiguous and may be used in proposing the mechanism.

The method described above has been used in a study of the hydrogenolysis of aliphatic esters on rhodium at 300°C (*8*). Statistical treatment of initial rate data and use of the Beale criterion (*5*) yielded at 95% significance level two indistinguishable equations (13) and (14) for the initial reaction rate $r^0$.

$$r^0 = \frac{k(K_A p^\circ{}_A)^{0,5} K_B p^\circ{}_B}{[1 + (K_A p^\circ{}_A)^{0,5} + K_B p^\circ{}_B]^3}, \quad (13)$$

$$r^0 = \frac{k K_A p^\circ{}_A K_B p^\circ{}_B}{[1 + (K_A p^\circ{}_A)^{0,5} + K_B p^\circ{}_B]^4}. \quad (14)$$

Subscript A denotes here the ester, B hydrogen. Competitive experiments with several pairs of esters were carried out and the results were confronted with linearized forms of Eqs. (10–12). Good straight lines were obtained for all pairs only in the coordinates of Eq. (11), as shown in Fig. 1 for the pair butyl acetate–propyl butyrate. This shows that the exponent for the partial pressure of the ester in the numerator equals unity, i.e., Eq. (13) could be eliminated.

It should be noted that this procedure is not limited to competitive reaction of members of homologous series but isotopically labelled substances may be used as well.

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