JOURNAL OF CATALYSIS 22, 266–268 (1971)

Surface Reactions with Nonequilibrium Adsorption

PETER HARRIOTT

School of Chemical Engineering, Cornell University, Ithaca, New York

Received November 10, 1970

The kinetics of competitive adsorption plus a bimolecular surface reaction are investigated for the case where Reactant A is far from adsorption–desorption equilibrium. The overall rate goes through a sharper than normal maximum with reactant pressure, giving a very large negative order to A in the region past the maximum.

In formulating models for catalytic reactions, it is usually assumed that one step controls and that the other steps occur at nearly equilibrium conditions. If the slow step is the reaction between molecules of A and B which, together with Product C, are adsorbed on the same type of sites, the rate equation is

$$r = k\theta_A\theta_B = \frac{kK_AK_BP_AP_B}{(1 + K_AP_A + K_BP_B + K_CP_C)^2}. \quad (1)$$

If the slow step is the rate of adsorption of A, with equilibrium adsorption of B and C, the equation becomes

$$r = kP_A(1 - \theta) = \frac{kP_A}{(1 + K_BP_B + K_CP_C)}. \quad (2)$$

These equations are similar in that they both allow for retardation by the product and the possibility of a negative reaction order for B. If A were weakly adsorbed and B strongly adsorbed, the data might be fitted to either equation. Because of the similarity, it might seem that if two such steps influence the overall rate, the apparent reaction orders would always fall between values predicted from the limiting cases. However this is not a correct generalization, as will be shown by the following example for reaction with nonequilibrium adsorption.

Consider the case where both reactants compete for sites on the catalyst surface and where, to simplify the problem, hardly any of the surface is covered by the product.

$$A_g + s \underset{2}{\overset{1}{\rightleftharpoons}} A_s. \quad (3)$$

$$B_g + s \underset{4}{\overset{3}{\rightleftharpoons}} B_s. \quad (4)$$

$$A_s + B_s \xrightarrow{5} C_s \xrightarrow{\text{fast}} C_g. \quad (5)$$

The net rate of adsorption for A and B is set equal to the surface reaction rate.

$$r = k_1P_A(1 - \theta_A - \theta_B) - k_2\theta_A. \quad (6)$$

$$r = k_3P_B(1 - \theta_A - \theta_B) - k_4\theta_B. \quad (7)$$

$$r = k_5\theta_A\theta_B. \quad (8)$$

Equations (6), (7), and (8) were solved for a number of cases in which the rate of desorption of A was about the same or much smaller than the rate of removal of A by reaction. This means that θ_A, the fraction of surface covered by A during the reaction, is quite a bit smaller than the equilibrium value for adsorption without reaction. This is likely to be the case for many reactions involving hydrogen, nitrogen, or oxygen, which are strongly chemisorbed on metal catalysts and have very low desorption rates at typical reaction temperatures. The adsorption and desorption rate constants for B were made quite large to give nearly equilibrium coverage of B on the portion of the surface not occupied by A.

Figure 1 shows how the rate varies with pressure of A for surface reaction constants of 1 to 100 times the desorption rate constant for A. The reaction is first order to A at low pressures, goes through a maximum, and is approximately -1 order at high pressures. At low pressures the rate is less than that based on equilibrium adsorption (Eq. 1), because the rate of adsorption of A becomes limiting, and at very high pressures, the finite rate of adsorption of B makes the rate slightly less than that based on equilibrium adsorption. The most interesting effect is the shift of the maximum to higher pressures and the fact that the rates can be higher than that predicted by Eq. (1). This effect is more pronounced for higher surface-rate constants or when the desorption of A is almost negligible, as for the cases shown in Fig. 2. Here the peak becomes quite narrow, and the reaction order for A is -2 to -6 in the steepest portions of the curves.

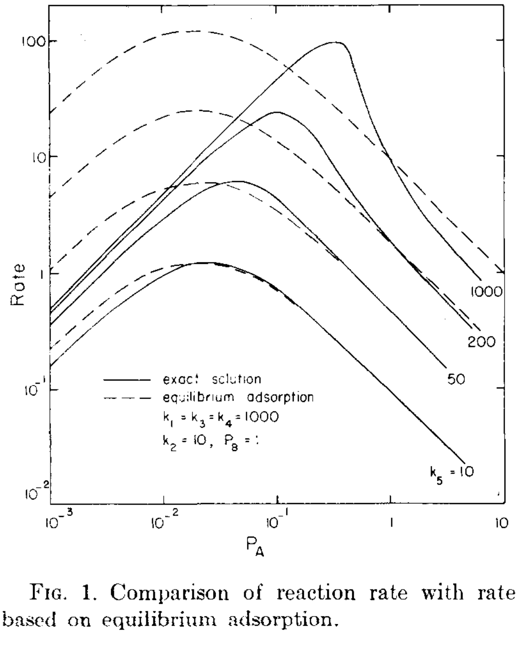

FIG. 1. Comparison of reaction rate with rate based on equilibrium adsorption.

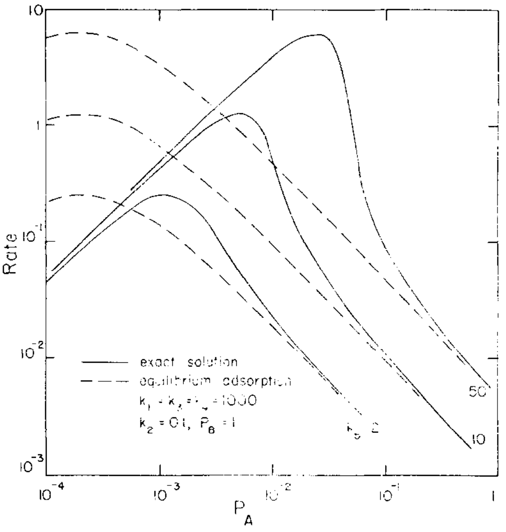

FIG. 2. Comparison of reaction rate with rate based on equilibrium adsorption.

The strong negative effect of P_A on the rate is explained by a rapid decrease in θ_B when the surface is nearly covered by A. To show this more clearly, the equations for adsorption, reaction and desorption of A are presented in Fig. 3 for arbitrary rate constants. To simplify the problem, B was assumed to be in adsorption–desorption equilibrium with the surface not covered by A, which was practically true for most of the cases in Figs. 1 and 2. For a constant P_B, θ_B is then a certain fraction of $(1 - \theta_A)$, which makes the surface reaction a quadratic function of θ_A, and the rate of adsorption of A a linear function of θ_A.

$$r = k_5\theta_A\theta_B = k_5\theta_A \frac{K_BP_B(1 - \theta_A)}{(1 + K_BP_B)}. \tag{9}$$

$$\begin{aligned} r_{\text{ads}} &= k_1P_A(1 - \theta_A - \theta_B) \\ &= k_1P_A(1 - \alpha)(1 - \theta_A). \end{aligned} \tag{10}$$

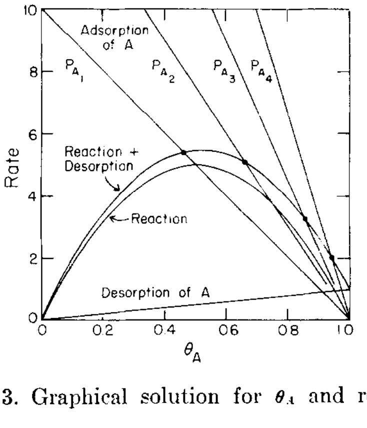

FIG. 3. Graphical solution for θ_A and reaction rate.

The actual value of θ_A is determined by the intersection of the adsorption line with that for reaction plus desorption. The adsorption lines in Fig. 3 are for pressures that change by a factor of 1.5 between cases. This increase in P_A in the region past the maximum produces a large decrease in the reaction rate, corresponding to a reaction order of about —2. If there were no desorption of A, the rate would decrease even more rapidly with P_A and would be zero at or above a critical pressure where the adsorption line no longer intersected the reaction curve. The surface would be completely covered with A at this point.

Negative reaction orders for hydrogen ranging from —1 to —3 have been found in several studies of the hydrogenolysis of ethane or propane (*1*).

These orders are not in accord with the usual Langmuir–Hinshelwood equation, and an equilibrium dissociation of the hydrocarbons on the surface has been suggested. However the dissociation would have to produce a hydrogen-free species to explain an order of —2 for ethane, which seems unlikely, and stronger negative effects would not be possible. The postulate of reaction with nonequilibrium adsorption offers an alternate explanation for these results. As shown in Figs. 1 and 2, the order would not be constant, though over a three to four-fold range in pressure, the change might not be apparent. Figure 4 shows some of the data of Taylor, Sinfelt, and Yates for ethane hydrogenolysis over nickel catalysts (*2*). In most cases, the apparent order to hydrogen becomes more negative at high pressures, which fits the theory of nonequilibrium adsorption better than the postulate of dissociation on the surface.

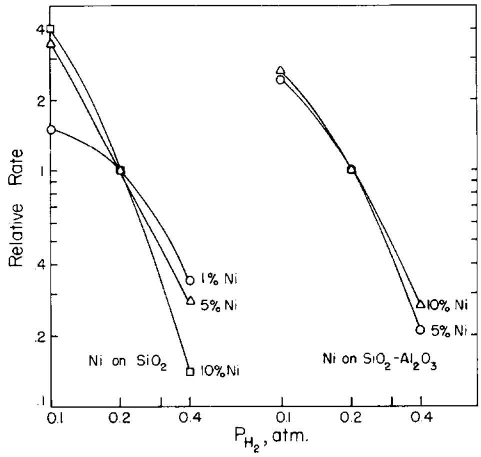

FIG. 4. Data of Taylor, Sinfelt, and Yates for ethane hydrogenolysis.

REFERENCES

1. BOND, G. C., "Catalysis by Metals," p. 396. Academic Press, New York, 1962.
2. TAYLOR, W. F., SINFELT, J. H., AND YATES, D. J. C., *J. Phys. Chem.* **69**, 3857 (1965).