COMMUNICATIONS TO THE EDITOR

On Noncompetitive Adsorption in Catalytic Hydrogenation

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In a recent paper Rogers, Lih, and Hougen (*1*) analyzed the kinetics of the catalytic hydrogenation of propylene and *i*-butylene over supported platinum. They employed a rate equation derived from a model postulating "mixed" modes of hydrogen chemisorption on the surface. Such behavior may occur in the case of surface reactions between large and small molecules in which steric hindrance or related effects can dictate a monolayer coverage by large molecules before all the adsorption sites on the surface have been used. These remaining sites are then available, on a noncompetitive basis, for the chemisorption of the smaller reactant molecules, and the overall rate equation consists of contributions from both competitively and noncompetitively chemisorbed reactants. Detailed discussions of this are given by Rogers et al. and by Bond and Turkevich (*2*) in their original consideration of such effects.

The overall rate equation of hydrogenation is written on this basis as

$$r = r_1 + r_2 = \alpha\theta_1'\theta_2' + \beta\theta_1''\theta_2' \tag{1}$$

in which the nomenclature is that of reference *1*. Although Rogers et al. pointed out that the actual reaction mechanism is more complex than such a model, they were able to fit their rate data quite well using Langmuir isotherms for the surface coverages of olefin and competitively and noncompetitively adsorbed hydrogen.

We feel, however, that there are some serious problems associated with the use of this model which are well illustrated by a comparison of the extensive $C_3^=$ and i—$C_4^=$ data of Rogers et al. and which are not apparent in the earlier work of Bond and Turkevich. It is easily shown that the two constants α and β are given in terms of the rate constants for the surface reaction and f, the fraction of sites available only for noncompetitive adsorption. To the extent of the detail that it is reasonable to incorporate in the model, the rate constants in r_1 and r_2 are the same, and thus

$$\begin{aligned} \alpha &= k_r\ n_s^2 \\ \beta &= k_r\ n_s^2 f \\ (\beta/\alpha) &= f \end{aligned} \tag{2}$$

where k_r is the rate constant and n_s the total number of sites per unit area. It should be noted that $(\beta/\alpha) = f/1 - f$ when f is not $<< 1$. The values of the fraction of sites available only for noncompetitive adsorption as computed from both $C_3^=$ and i—$C_4^=$ hydrogenation data are plotted on Figure 1. Clearly, this fraction *decreases* with increasing temperature for propylene but *increases* with increasing

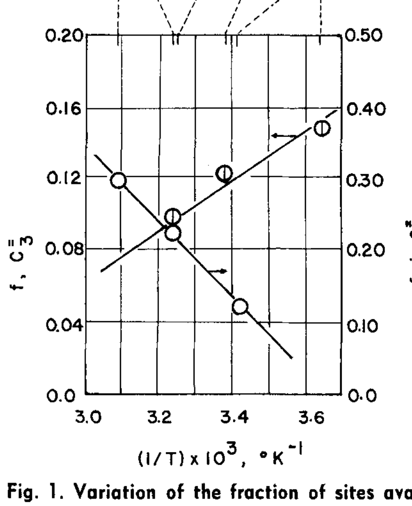

Fig. 1. Variation of the fraction of sites available for noncompetitive adsorption with temperature; $C_3^=$ and i-$C_4^=$ hydrogenation.

temperature for *i*-butylene. It is not possible to predict *a priori* whether f should increase or decrease with temperature increase, since a number of unknown factors such as changing mobility of the chemisorbed layers may be involved; nonetheless, there is no reason why one should not expect the variation in f with temperature to be in the same direction, given the similarity of reactants, catalyst, and reaction conditions. Further, the fraction of total sites available for noncompetitive hydrogen adsorption ranges up to 0.4 in the case of $i{-}C_4^=$ at higher temperatures. For molecules no larger or more complex than $C_3^=$ or $i{-}C_4^=$ this figure seems unreasonably large if the dual site associative mechanism for olefin chemisorption (*2*) is correct, while estimated values for heats of chemisorption (1 to 5 Kcal./mole for hydrogen, for example) are unreasonably low in view of estimates ($\sim$ 20 Kcal./mole for H_2) for these reactants on platinum surfaces (*3*); indeed, the magnitudes reported are on the order of heats of physisorption.

Although no viable model can hope to be correct in microscopic detail, we conclude that the competitive-noncompetitive adsorption postulate possesses some severe limitations. It would appear that the physical reasonableness of such a model can be evaluated only after further information is available concerning the details of chemisortion of olefins such as $i{-}C_4^=$ on platinum.

LITERATURE CITED

1. Rogers, G. B., M. M. Lih, and O. A. Hougen, *AIChE J.*, **12,** 369 (1966).
2. Bond, G. C., and J. Turkevich, *Trans. Faraday Soc.*, **49,** 281 (1953).
3. Hayward, D. O., and B. M. W. Trapnell, "Chemisorption," Butterworth, Inc., Washington (1964).

In the paper by G. B. Rogers, M. H. Lih, and O. A. Hougen entitled "Catalytic Hydrogenation of Propylene and Isobutylene over Platinum: Effect of Noncompetitive Adsorption" [*AIChE Journal,* 12, 369 (1966)], the following mathematical model was presented for expressing the overall reaction rate:

$$r = r_1 + r_2 = \frac{\alpha K_1 K_2 p_1 p_2}{(1 + K_1 p_1 + K_2 p_2)^2} + \frac{\beta K_1 p_1 K_2 p_2}{(1 + K_1 p_1)(1 + K_1 p_1 + K_2 p_2)}$$

This model and its four constants, α, β, K_1, and K_2 were obtained directly from experimental data without regard to any mathematical interpretation of surface coverage. Kehoe and Butt have stated since that the terms α and β are related to surface coverage by the following:

$$\beta = k\, f(1-f)$$

$$\alpha = k(1-f)^2$$

or

$$\frac{\beta}{\alpha} = \frac{f}{1-f}$$

where f is the fraction of total catalyst sites available for the noncompetitive adsorption of hydrogen. From this relation they calculated the values of f at different temperatures for the hydrogenation of both propylene and isobutylene, shown as a function of temperature in their Figure 1.

The disturbing part of this correlation is that the temperature trends of f for the two olefins run in opposite directions. The value of f for propylene increases with the reciprocal of absolute temperature and decreases for isobutylene. However, this anomalous behavior is based upon our experimental data and has no bearing upon our own interpretation of surface coverage. In explaining this difference in the behavior of the two hydrocarbons we assumed that different surface velocity constants for the same olefins are involved for competitive and noncompetitive adsorption. With this interpretation

$$\frac{f}{1-f} = \frac{k_1}{k_2}\,\frac{\beta}{\alpha}$$

where k_1 is related to the surface velocity constant for competitive adsorption and k_2 for noncompetitive adsorption of hydrogen.

This controversy perhaps could have been avoided if we had omitted Equation (1), which we did not use, from our original paper or had primed the constants α and β to distinguish them from the values used in our mathematical model, thus

$$r = r_1 + r_2 = \alpha'\theta_1\theta_2' + \beta'\theta_1'\theta_2'$$

Whether the inconsistency in the effect of temperature on values of f for different olefins is real or not should be established by additional experimental data, especially on other olefins. Many published experimental data are available to permit this study.

Incidentally, evidence of noncompetitive and competitive adsorption was reported in 1957 by B. D. Babcock, G. T. Mejdell, and myself in a paper on the hydrogenation of alpha-methyl-styrene by a supported palladium catalyst in a trickling bed reactor [*AIChE Journal,* 3, 366-370 (1957)].

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