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Modification of a Reaction Rate Model Involving Competitive–Noncompetitive Adsorption

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The dissociative adsorption of hydrogen was considered for the competitive–noncompetitive adsorption model of olefin hydrogenation. The parameters of the model developed were estimated by utilizing the existing hydrogenation data of propylene and isobutylene. The resulting parameter estimates were compared with those of a model which does not include the dissociative adsorption term for hydrogen. The hydrogenation condition in which the competitive reaction predominates was discussed.

INTRODUCTION

Since the separate research activities of G. B. Rogers (*1*) and M. M. Lih (*2*), resulting 5 years later in a paper entitled "Catalytic Hydrogenation of Propylene and Isobutylene over Platinum; Effect of Noncompetitive Adsorption" (*3*), great progress has been made in computer programming and in statistical analysis of data, justifying an improvement in the mathematical model presented in their joint paper. This revised model also results in a consistent temperature effect for the two olefins in contrast to the previous correlation. In the original paper dissociation of hydrogen upon adsorption was neglected on the assumption that accuracy of data did not permit such discrimination. For purposes of engineering design either model is satisfactory. From a scientific basis the dissociation of hydrogen when adsorbed by platinum where adjoining vacant active catalyst sites are present has been well established and should be included in the rate equation. Recent progress in computer programming permitted a rapid selection of the most satisfactory model and permitted treatment of temperature as a simultaneous variable in evaluating the parameters in the evolving equations. By improved statistical procedures of weighting, reliability and accuracy of values were established for each parameter.

NOMENCLATURE

A_1, A_2	Constants [g moles/g hr]
A'_H, A'_H, A_U	Constants (atm^{-1})
f	Fraction of sites available for noncompetitive adsorption
$\Delta H_1^‡$, $\Delta H_2^‡$	Energy of activation (kcal/g-mole)
ΔH_H, $\Delta H'_H$, ΔH_U	Heat of adsorption (kcal/g-mole)
K_H	Dissociative adsorption constant for hydrogen (atm^{-1})
K'_H	Molecular adsorption constant for hydrogen (atm^{-1})
K_U	Adsorption constant for olefin (atm^{-1})
p_H	Partial pressure of hydrogen (atm)
p_U	Partial pressure of olefin (atm)
r	Reaction rate (g-moles/hr)
r_1	Competitive reaction rate (g-moles/g hr)
r_2	Noncompetitive reaction rate (g-moles/g hr)
R	Gas constant (cal/g-moles) (°K)
T	Reaction temperature (°K)

α	Rate constant (g-moles/g hr)
β	Rate constant, (g-moles/g hr)

RESULTS AND DISCUSSION

A surface reaction rate model involving simultaneous competitive and noncompetitive adsorption of hydrogen [Eq. (1)] was proposed by Rogers, Lih, and Hougen (*3*) for the hydrogenation of propylene and of isobutylene catalyzed by platinum supported on alumina.

$$r = r_1 + r_2 = \underset{\text{(Competitive adsorption)}}{\frac{\alpha K_{\mathrm{H}} K_{\mathrm{U}} p_{\mathrm{H}} p_{\mathrm{U}}}{(1 + K_{\mathrm{H}} p_{\mathrm{H}} + K_{\mathrm{U}} p_{\mathrm{U}})^2}} + \underset{\text{(Noncompetitive adsorption of hydrogen)}}{\frac{\beta K_{\mathrm{H}} K_{\mathrm{U}} p_{\mathrm{H}} p_{\mathrm{U}}}{(1 + K_{\mathrm{H}} p_{\mathrm{H}})(1 + K_{\mathrm{H}} p_{\mathrm{H}} + K_{\mathrm{U}} p_{\mathrm{U}})}} \qquad (1)$$

A similar model was previously proposed by Bond and Turkevich (*4*) for the deuteration of propylene. In formulating Eq. (1), it was assumed that all vacant active sites were available for the adsorption of molecular hydrogen but that the fraction of surface coverage of chemisorbed olefin is limited by steric hindrance because of large molecular size. It was assumed that this steric hindrance did not limit surface coverage by adsorption of molecular hydrogen.

In Eq. (1) the terms α and β may be the subject of discussion. Kehoe and Butt (*5*) showed that (β/α) is simply equal to the fractions of the sites available only for noncompetitive adsorption, assuming that the rate constants in r_1 and r_2 are the same. However, it may be conceivable also that the terms α and β are empirical constants of a complex nature including surface reaction velocity constants k_1 and k_2 corresponding to rates r_1 and r_2, respectively, as well as the number of active sites per unit mass of catalyst and their manner of distribution over the surface of the catalyst. Surface reaction velocity constants are known to be highly temperature-dependent following the Arrhenius relation, whereas the number of active sites and their distribution are not known to be highly temperature-dependent except as adsorbed gases are influenced by surface diffusion.

In the chemisorption of hydrogen on platinum, it is well known that dissociation of molecular hydrogen occurs (*6–8*). This dissociation was neglected in the formulation of Eq. (1) partly because of the difficulty in computer programming at the time the investigations were made. Where adsorption of hydrogen is restricted to single sites with no adjoining vacant sites, it is assumed that no dissociation of hydrogen takes place. Eq. (1) was modified to show both the effects of hydrogen dissociation and adsorption on single sites. In the resultant rate equation two equilibrium adsorption constants for hydrogen thus appear, K_{H} for adsorption of hydrogen with dissociation and K'_{H} for the adsorption of molecular hydrogen without dissociation.

With these modifications Eq. (1) reduces to

$$r = r_1 + r_2 = \underset{\text{(Competitive adsorption with dissociation of } H_2\text{)}}{\frac{\alpha K_{\mathrm{H}} K_{\mathrm{U}} p_{\mathrm{H}} p_{\mathrm{U}}}{[1 + (K_{\mathrm{H}} p_{\mathrm{H}})^{1/2} + K_{\mathrm{U}} p_{\mathrm{U}}]^3}} + \underset{\text{(Noncompetitive adsorption of hydrogen with no dissociation of hydrogen on single sites)}}{\frac{\beta K'_{\mathrm{H}} K_{\mathrm{U}} p_{\mathrm{H}} p_{\mathrm{U}}}{(1 + K'_{\mathrm{H}} p_{\mathrm{H}})[1 + (K_{\mathrm{H}} p_{\mathrm{H}})^{1/2} + K_{\mathrm{U}} p_{\mathrm{U}}]}} \qquad (2)$$

Both Eqs. (1) and (2) apply to the surface chemical reaction and do not include effects due to mass and heat transfers in the ambient stream or inside the catalyst pellets, nor do they include resistances imposed by adsorption of reactants or desorption of products.

The data of Rogers (*1*) on the hydrogenation of propylene and of Lih (*2*) on the hydrogenation of isobutylene were reevaluated in terms of Eq. (2). A comparison of properties calculated by the two equations is given in Tables 1 and 2.

In the values of residual mean square, some differences are noticeable between the results from Eq. (1) and those from Eq. (2) for both propylene and isobutylene. However, no attempt was made to test the

TABLE 1

For the Hydrogenation of Propylene

	By Eq. (2)	By Eq. (1)
$\alpha = A_1 \exp(-\Delta H_1^{\pm}/RT)$	$A_1 = 9.735 \times 10^{13}$ $\Delta H_1^{\pm} = +17.230$	$A_1 = 0.922 \times 10^{12}$ $\Delta H_1^{\pm} = +15.629$
$\beta = A_2 \exp(-\Delta H_2^{\pm}/RT)$	$A_2 = 1.133 \times 10^{10}$ $\Delta H_2^{\pm} = +13.890$	$A_2 = 1.671 \times 10^{9}$ $\Delta H_2^{\pm} = +13.144$
$K_H = A_H \exp(-\Delta H_H/RT)$	$A_H = 9.400 \times 10^{-6}$ $\Delta H_H = -5.690$	$A_H = 2.997 \times 10^{-4}$ $\Delta H_H = -4.208$
$K'_H = A'_H \exp(-\Delta H'_H/RT)$	$A'_H = 1.164 \times 10^{-4}$ $\Delta H'_H = -4.820$	$K'_H = K_H$
$K_U = A_U \exp(-\Delta H_U/RT)$	$A_U = 4.252 \times 10^{-5}$ $\Delta H_U = -7.350$	$A_U = 8.634 \times 10^{-6}$ $\Delta H_U = -9.022$
Residual mean square of overall rates	4.3×10^{-5}	$30. \times 10^{-5}$

TABLE 2

For the Hydrogenation of Isobutylene

	By Eq. (2)	By Eq. (1)
$\alpha = A_1 \exp(-\Delta H_1^{\pm}/RT)$	$A_1 = 2.151 \times 10^{13}$ $\Delta H_1^{\pm} = +17.880$	$A_1 = 2.340 \times 10^{5}$ $\Delta H_1^{\pm} = +7.150$
$\beta = A_2 \exp(-\Delta H_2^{\pm}/RT)$	$A_2 = 1.8784 \times 10^{10}$ $\Delta H_2^{\pm} = +14.990$	$A_2 = 1.600 \times 10^{10}$ $\Delta H_2^{\pm} = +14.840$
$K_H = A_H \exp(-\Delta H_H/RT)$	$A_H = 1.554 \times 10^{-5}$ $\Delta H_H = -7.020$	$A_H = 0.0680$ $\Delta H_H = -1.283$
$K'_H = A'_H \exp(-\Delta H'_H/RT)$	$A'_H = 1.079 \times 10^{-2}$ $\Delta H'_H = -3.280$	$K'_H = K_H$
$K_U = A_U \exp(-\Delta H_U/RT)$	$A_U = 1.554 \times 10^{-5}$ $\Delta H_U = -8.880$	$A_U = 6.420 \times 10^{-4}$ $\Delta H_U = -7.083$
Residual mean square of overall rates	6.9×10^{-4}	11.0×10^{-4}

adequacy of these two hydrogenation models, because replicated runs which would give an estimate of experimental errors, were not available. For the hydrogenation of propylene, in the light of the value of the residual sum square, it may be concluded that the model described by Eq. (2) is significantly better than the one of Eq. (1). For isobutylene, however, the difference between these two models may be negligible.

For the hydrogenation of the two olefins it will be observed that the values for adsorption equilibrium constants are evidence of selective chemisorption and that the temperature effects on α, β, K_H, K'_H, and K_U are consistent with the endothermic nature of activation energies and the exothermic nature of adsorption. In this paper the physical-chemical significance of the point estimates tabulated in Table 1 and Table 2 is not fully interpreted. It is a general observation that the heat of adsorption obtained from kinetic experiments is different from the value obtained from adsorption experiments. The heat of adsorption of molecular hydrogen, for example, is reported to be 30 kcal/mole at low coverage (*8*, *9*). Hence the heats of adsorp-

TABLE 3

THE APPROXIMATE 95% CONFIDENCE REGIONS FOR THE ESTIMATES OF THE HEAT OF ADSORPTION OF HYDROGEN

	Point estimate, ΔH (with dissociation)	Confidence region	Point estimate. $\Delta H'$ (without dissociation)	Confidence region
Propylene	−5690	−4100∼−6150	−4820	+260∼−11 300
Isobutylene	−7020	−6800∼−8000	−3280	+1120∼−10 500

tion of molecular hydrogen estimated in this paper are quite low. To find a definite correlation between these independently obtained heats, needless to say, more information would be needed on surface coverage, the physical and chemical properties of the metals, the effect of the presence of foreign gases, and the interaction of adsorbed gas molecules.

Due to the contribution of dissociation energy, the heat of dissociative adsorption of hydrogen is predicted to be lower than the heat of adsorption of molecular hydrogen. The point estimates of the heats of adsorption, however, resulted in the exact reverse. Accordingly the approximate 95% confidence regions of ΔH_H and $\Delta H'_H$ for both propylene and isobutylene were examined. They were shown in Table 3. As can be seen from the table, the confidence regions of the heats of adsorption of hydrogen without dissociation are rather large for both propylene and isobutylene. In order to obtain more precise estimates of these heats, a sequential design technique developed by Box (*10*) should be employed. Because of the values of these confidence regions, there may exist a case in which the heat of adsorption of hydrogen without dissociation becomes larger than the heat of adsorption of hydrogen with dissociation.

The revised formulation gives a consistent effect of temperature for the ratio of β/α, as shown in Fig. 1, and in the ratio of

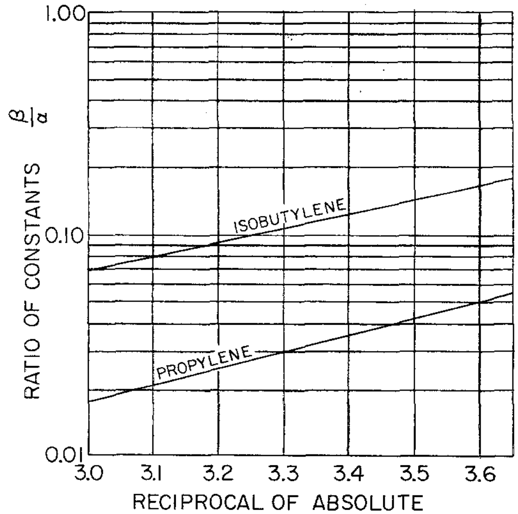

FIG. 1. The ratio of noncompetitive to competitive rate constant and reaction temperature.

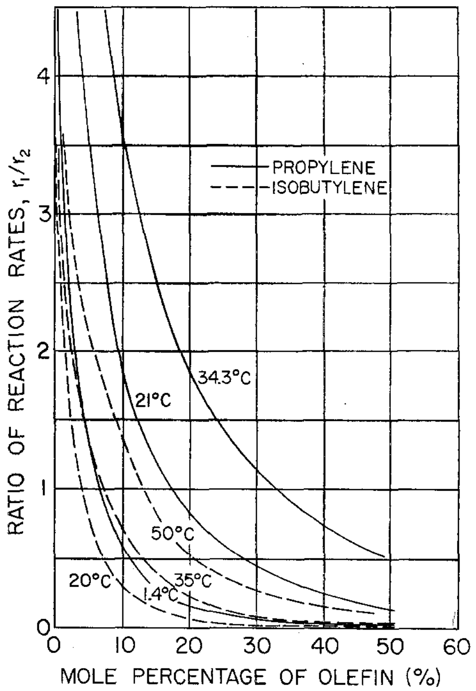

FIG. 2. Ratio of reaction rates involving competitive and noncompetitive adsorption in the catalytic hydrogenation of propylene and isobutylene (at 1.1 atm total pressure and different temperatures).

the reaction rates r_1/r_2 as shown in Fig. 2 for the two olefins, contrary to the inconsistency in the original formulation, where dissociation of hydrogen was neglected. From Fig. 2, which shows the variation of the ratio r_1/r_2 with the percentage mole fraction of olefin, it will be observed that reaction rate r_1 predominates at low concentrations and that this effect is more pronounced with isobutylene than with propylene, as is to be expected. This indicates that high surface coverage of active sites is established even at low olefin concentrations and that such coverage is greater with isobutylene than with propylene. The temperature effect indicates that with either olefin, surface coverage decreases with increase in temperature. The temperature dependency of r_1/r_2 would also be of interest. At a given mole percentage of olefin the mobility of adsorbed olefin may be increased with increase in reaction temperature. Furthermore surface coverage by olefin molecules, as discussed above, decreases with increase in temperature. Combining these two effects of temperature on adsorbed olefin, it would be conceivable that the competitive reaction is more predominant over the noncompetitive reaction at higher temperature.

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References

1. Rogers, R. B., Ph.D. Thesis, University of Wisconsin, Madison, Wisconsin, 1961.
2. Lih, M. M., Ph.D. Thesis, University of Wisconsin, Madison, Wisconsin, 1962.
3. Rogers, G. B., Lih, M. M., and Hougen, O. A., *AIChE J.* **12**, 369–372 (1966).
4. Bond, G. C., and Turkevich, J., *Trans. Faraday Soc.* **49**, 281 (1953).
5. Kehoe, P., and Butt, J. B., *AIChE J.* **13**, 1018 (1967).
6. Bond, G. C., "Catalysis by Metals." Academic Press, New York, 1962.
7. Pliskin, W. A., and Eischens, R. P., *Z. Phys. Chem.* **24**, 11 (1960).
8. Hayward, D. O., and Trapnell, B. M. W., "Chemisorption." Butterworth's, Washington, D. C., 1964.
9. Ashmore, P. G., "Catalysis and Inhibition of Chemical Reactions." Butterworths, London, 1963.
10. Box, G. E. P., and Hunter, W. G., Proceedings IBM Scientific Computing Symposium, Statistics, p. 113 (1965).