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Kinetics of Olefin Hydrogenation Over a Platinum Catalyst with More Than One Set of Active Sites

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It is shown that published data on hydrogenation of propylene and isobutylene over a platinum catalyst, which have previously been explained on basis of a reaction model involving competitive–noncompetitive adsorption, can be more satisfactorily explained on the basis of the dissociative model for olefin hydrogenation when the possible, and probable, existence of more than one set of active sites on a catalyst is taken into account. Accordance between measured and calculated hydrogenation rates are obtained when two sets of sites are assumed.

The rate equation is,

$$r = \sum_{j=1}^{j=2} \frac{k_j K_{A,j} p_A (K_{\mathrm{H},j} p_{\mathrm{H}})^{1/2}}{[1 + K_{A,j} p_A/(K_{\mathrm{H},j} p_{\mathrm{H}})^{1/2} + (K_{\mathrm{H},j} p_{\mathrm{H}})^{1/2}]^3}.$$

The same set of parameters associated with hydrogen adsorption can be used for both the propylene and isobutylene hydrogenation. The estimates which have been obtained for the adsorption enthalpies and adsorption entropies when fitting the kinetic expression to the data are all small, as is to be expected for a dissociative reaction scheme. The mean deviation between calculated and observed reaction rates for both the propylene and isobutylene data are less than 3%.

Kinetic equations based on the associative model have also been investigated, but the equations investigated so far are not fully consistent with the experimental data.

INTRODUCTION

Rogers *et al.* (*1*) carried out an investigation of the kinetics of hydrogenation of propylene and isobutylene over an alumina–supported platinum catalyst. They found that none of the classical Hougen–Watson equations (*2*) could be fitted to the observed results, which were known to be accurate within a few percent. The authors found, however, that a model leading to the following kinetic equation,

$$r = \frac{k_1 K_A K_{\mathrm{H}} p_A p_{\mathrm{H}}}{(1 + K_A p_A + K_{\mathrm{H}} p_{\mathrm{H}})^2} + \frac{k_2 K_A K_{\mathrm{H}} p_A p_{\mathrm{H}}}{(1 + K_A p_A + K_{\mathrm{H}} p_{\mathrm{H}})(1 + K_{\mathrm{H}} p_{\mathrm{H}})}, \quad (1)$$

was essentially consistent with the observed rates.

The model which leads to Eq. (1) assumes two parallel reactions on the catalyst surface. Both reactions are surface reactions controlled with no dissociation. The first term corresponds to a competitive adsorption of the reactants, and the second term arises from noncompetitive adsorption.

Recently, Mezaki (*3*) has published the results of a refinement of the model proposed by Rogers *et al.* (*1*). This refinement still rests on the basic assumption of a competitive–noncompetitive adsorption, but the well-known fact that dissociation of hydrogen occurs when adsorbed on platinum was incorporated into the model. The resulting rate equation was

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$$r = r_1 + r_2 = \frac{k_1 K_\mathrm{H} K_A p_\mathrm{H} p_A}{(1 + (K_\mathrm{H} p_\mathrm{H})^{1/2} + K_A p_A)^3} + \frac{k_2 K'_\mathrm{H} K_A p_\mathrm{H} p_A}{(1 + K'_\mathrm{H} p_\mathrm{H})(1 + (K_\mathrm{H} p_\mathrm{H})^{1/2} + K_A p_A)}. \qquad (2)$$

The distinction between dissociative and nondissociative hydrogen adsorption leads to the introduction of an extra parameter (2 parameters if nonisothermal data are considered).

The outcome of this refinement was that better agreement between calculated and observed rates was obtained. But neither the model proposed by Rogers *et al.* (*1*) nor the more refined model used by Mezaki (*3*) can be considered to be adequate models for olefin hydrogenation on metals, because they cannot explain that there is an isotopic exchange of hydrogen atoms in the olefin molecules taking place parallel to the hydrogenation reaction (see below for literature references). When a fairly accurate mathematical description of the reaction rate as a function of temperature and concentration, e.g., for engineering design purposes, is all that is wanted, both models are satisfactory. However, from a scientific point of view, the fit must be fortuitous because the models are only in partial agreement with what is known about olefin hydrogenation. Possibly, a model involving competitive–noncompetitive adsorption can be extended and refined to be consistent with all that is known about olefin hydrogenation. The purpose of the present article, however, is to show that a rather different model can be found, which is consistent with the results obtained by Rogers *et al.* (*1*) and with the general knowledge available about hydrogen exchange under hydrogenation conditions.

Nomenclature

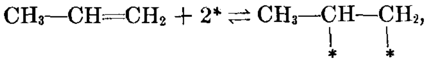
E	activation energy (cal/mole) see k
ΔH_A	adsorption enthalpy (cal/mole) see K_A
ΔH_{EQ}	enthalpy change (cal/mole) see K_{EQ}
ΔH_H	adsorption enthalpy (cal/mole) see K_H
k	$\exp(\mathcal{H} - E/RT)$ = rate constant
K_A	$\exp(\Delta S_A/R - \Delta H_A/RT)$ = adsorption constant for olefin
K_{EQ}	$\exp(\Delta S_{EQ}/R - \Delta H_{EQ}/RT)$ = equilibrium constant for reaction leading to half hydrogenated state
K_H	$\exp(\Delta S_H/R - \Delta H_H/RT)$ = adsorption constant for hydrogen
N	number of sets of active sites
p_A	olefin pressure
p_H	hydrogen pressure
r	reaction rate [moles/(unit time) (unit wt of catalyst)]
r_j	reaction rate on jth set of sites
R	gas constant
ΔS_A,ΔS_{EQ},ΔS_H	entropy change of reaction (cal/mole) see K_A, K_{EQ}, and K_H
T	absolute temperature
$\mathcal{H}$	natural logarithm of pre-exponential factor in the rate constant k
*	active center

A Survey of the Hydrogenation Reaction of Olefins Over Metal Catalysts

Much effort has been devoted to the study of the hydrogenation reaction of olefins over metal catalysts, and many mechanisms have been proposed for the hydrogenation (and isotopic exchange) reactions. The field is well covered by review articles (*4–9*), and only the main points will be given here.

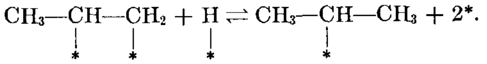
The many models which have been proposed for olefin hydrogenation and isotopic exchange may be divided in two main groups, namely, the associative model first proposed by Horiuti and Polanyi (*10*) and the dissociative model proposed by Farkas (*11*). For an extensive discussion of both models, see Ref. (*4*).

Horiuti's associative model may be formulated as follows:



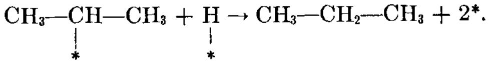
$$\mathrm{CH_3{-}CH{=}CH_2} + 2^* \rightleftharpoons \mathrm{CH_3{-}\underset{*}{\underset{|}{CH}}{-}\underset{*}{\underset{|}{CH_2}}}, \quad (2)$$

followed by addition of a chemisorbed hydrogen (deuterium) atom to give a half-hydrogenated state:



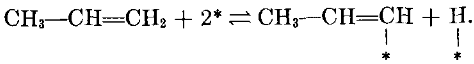
$$\mathrm{CH_3{-}\underset{*}{\underset{|}{CH}}{-}\underset{*}{\underset{|}{CH_2}}} + \underset{*}{\underset{|}{\mathrm{H}}} \rightleftharpoons \mathrm{CH_3{-}\underset{*}{\underset{|}{CH}}{-}CH_3} + 2^*. \quad (3)$$

Exchange results when reactions (2) and (3) are reversed, and hydrogenation results when a further hydrogen (deuterium) atom is added:



$$\mathrm{CH_3{-}\underset{*}{\underset{|}{CH}}{-}CH_3} + \underset{*}{\underset{|}{\mathrm{H}}} \rightarrow \mathrm{CH_3{-}CH_2{-}CH_3} + 2^*. \quad (3b)$$

The dissociative model assumes the adsorption leading to isotopic exchange, double bond shift, etc., to proceed as follows:*



$$\mathrm{CH_3{-}CH{=}CH_2} + 2^* \rightleftharpoons \mathrm{CH_3{-}CH{=}\underset{*}{\underset{|}{CH}}} + \underset{*}{\underset{|}{\mathrm{H}}}. \quad (4)$$

Concerning the hydrogenation reaction, Farkas' view on the nature of the adsorbed olefin is not very clear (*4*, *5*, *11*), but a main point is that the addition of hydrogen is thought to consist of the simultaneous addition of two hydrogen atoms.

In spite of an impressive amount of work having been devoted to studies of various aspects of the problem, it has not been possible to decide unequivocally for either of the two main classes of reaction models.

RESULTS AND DISCUSSION

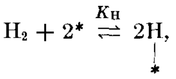
Following the general reasoning of Hougen and Watson (*2*), kinetic equations can be established for the associative model as well as for the dissociative model. One of the main assumptions of the Langmuir–Hinshelwood–Hougen–Watson model is that the active sites of a catalyst can all be taken to be identical. This author has recently stressed the point that this assumption may be too restrictive (*12*), and experimental results obtained on the system zinc oxide/isopropyl alcohol have provided evidence that, for that system, the existence of several distinct sets of active sites must be taken into account (*13–15*). A similar conclusion was reached by Schrage and Burwell (*16*) who found that there were at least five distinguishable processes in isotopic exchange between cyclopentane and deuterium on palladium-on-alumina catalysts.

The purpose of the present study was to investigate if any of the kinetic equations, which can be deduced from the dissociative or associative reaction mechanisms, are consistent with the hydrogenation rate measurements, when the oversimplification of only one set of active sites is discarded. As it turns out, the dissociative mechanism leads to a kinetic equation which is fully consistent with the rate measurements of Rogers *et al.* (*1*), but the associative mechanism appears to be less satisfactory in this respect.

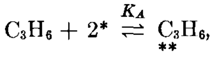
KINETIC EQUATIONS

The Associative Model

This model as proposed by Horiuti and Polanyi (*10*) proceeds via the steps (propylene is taken as an example):

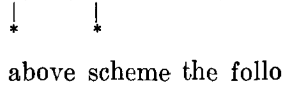


$$\mathrm{H_2} + 2^* \overset{K_H}{\rightleftharpoons} 2\underset{*}{\underset{|}{\mathrm{H}}}, \quad (5)$$



$$\mathrm{C_3H_6} + 2^* \overset{K_A}{\rightleftharpoons} \underset{**}{\mathrm{C_3H_6}}, \quad (6)$$

$$\underset{**}{\mathrm{C_3H_6}} + \underset{*}{\underset{|}{\mathrm{H}}} \overset{K_{EQ}}{\rightleftharpoons} \underset{*}{\underset{|}{\mathrm{C_3H_7}}} + 2^*, \quad (7)$$



$$\underset{*}{\underset{|}{\mathrm{C_3H_7}}} + \underset{*}{\underset{|}{\mathrm{H}}} \overset{k}{\rightarrow} \mathrm{C_3H_8} + 2^*. \quad (8)$$

From the above scheme the following rate equation is obtained (see Appendix):

$$r_j = \frac{k_j K_{EQ,j} K_{\mathrm{H},j} p_{\mathrm{H}}}{4K_{A,j} p_A} [(Q_j^2 + 4K_{A,j} p_A)^{1/2} - Q_j]^2, \quad (9)$$

where

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* The structure of the adsorbed olefin may well be different, e.g., double bond shift is more obviously possible if a π-allylic structure is assumed (*9*), but this point has no bearing on the kinetic equation and the arguments to be presented.

$$Q_j = [1 + (K_{\mathrm{H},j}p_{\mathrm{H}})^{1/2} + K_{EQ,j}K_{A,j}p_A(K_{\mathrm{H},j}p_{\mathrm{H}})^{1/2}]$$

for the jth set of active sites. When there are N sets of active sites, the total rate according to this model is

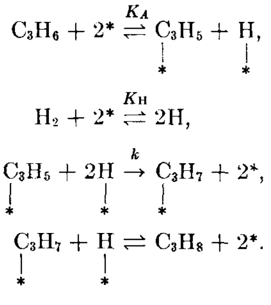
$$r = \sum_{j}^{N} r_j. \tag{10}$$

When Eqs. (9) and (10) are to be applied to arbitrary temperatures, the proper temperature dependence of k, K_{EQ}, K_{H}, K_A must be introduced.

Various modified models for the associative mechanism have been published. They will not be treated here; but for a literature review, see Ref. (*4*) and Bond *et al.* (*17*, *18*).

The Dissociative Model

It was stated above that the dissociative model, as advanced by Farkas, is vague regarding the nature of the adsorbed olefin in the hydrogenation reaction. The present treatment assumes that there is only one species of olefin molecules on the surface; this species may give rise to isotopic exchange or hydrogenation as the case may be. The following reaction scheme is then proposed (propylene is taken as an example).



$$C_3H_6 + 2^* \overset{K_A}{\rightleftarrows} \underset{\overset{|}{*}}{C_3H_5} + \underset{\overset{|}{*}}{H}, \tag{11}$$

$$H_2 + 2^* \overset{K_{\mathrm{H}}}{\rightleftarrows} 2\underset{}{H}, \tag{12}$$

$$\underset{\overset{|}{*}}{C_3H_5} + 2\underset{\overset{|}{*}}{H} \overset{k}{\rightarrow} \underset{\overset{|}{*}}{C_3H_7} + 2^*, \tag{13}$$

$$\underset{\overset{|}{*}}{C_3H_7} + \underset{\overset{|}{*}}{H} \rightleftarrows C_3H_8 + 2^*. \tag{14}$$

Isotopic exchange of the olefin molecule takes place because of the reversibility of reaction (11). Reaction (13) constitutes the hydrogenation step and, in agreement with Farkas' view, it is assumed that there is simultaneous addition of two hydrogen atoms. Reaction (13) is considered the rate determining step of the hydrogenation reaction. The forward rate in Eq. (14) is presumably fast, so the surface concentration of alkyl radicals is low and can be neglected. It is known that an alkane is adsorbed from the gas phase to a very small extent only (*4*–*9*).

Following the general lines of thought of Hougen and Watson one obtains (see Appendix):

$$r_j = \frac{k_jK_{A,j}p_A(K_{\mathrm{H},j}p_{\mathrm{H}})^{1/2}}{[1 + K_{A,j}p_A/(K_{\mathrm{H},j}p_{\mathrm{H}})^{1/2} + (K_{\mathrm{H},j}p_{\mathrm{H}})^{1/2}]^3}, \tag{15}$$

for the jth set of sites, and

$$r = \sum_{j}^{N} r_j, \tag{16}$$

for N sets of sites.

If Eqs. (15) and (16) are to be used for calculating rates at arbitrary temperatures, the proper temperature dependence of k_j, $K_{A,j}$, $K_{\mathrm{H},j}$ must be introduced.

Comparison of the Models

Equations (10) and (16) can now be fitted to the data reported by Rogers *et al.* (*1*) by the standard technique of least squares. Many pertinent references on this subject may be found, e.g., in a recent review by Bard and Lapidus (*19*). Before carrying out the least squares analysis, the number of different sets of active sites to be taken into account, i.e., the value to be assigned to N in Eqs. (10) and (16), must be chosen. In principle, the value of N may be fairly large, but where the rate measurements have been carried out over only a rather small range, as in the present case where the ratio of the highest to the smallest partial pressure is only about 30, it is likely that taking into account the existence of two sets of active sites is sufficient. The problem has been discussed in some detail earlier (*12*). In cases where the reactant pressure range is wider it may be necessary to involve a larger number of sets of active sites, as was the case for isopropyl alcohol dehydrogenation over zinc oxide (*13*–*15*), but in that case the ratio of highest to lowest reactant pressure was 3000 [later extended to 20 000 (*20*)].

In accordance with the above, least squares analyses have been carried out for Eqs. (10) and (16) with $N = 1$ and $N = 2$ for the propylene as well as the isobutylene data of Rogers *et al.* (*1*). It has been pointed out previously (*12*) that when the probable error is proportional to the measured value rather than constant, one should minimize the sum of squared percentage errors (strictly speaking the sum of squared logarithmic differences) rather than the sum of squared errors.

An immediate result of the curve fitting was that neither Eq. (10) nor Eq. (16) with $N = 1$ would give a satisfactory fit. On the other hand, Eq. (16) with $N = 2$ appears to be consistent with the experimental results. The main results of the curve fitting of Eqs. (10) and (16) are given in Tables 1 and 2. The parameters given there were obtained by a simultaneous parameter evaluation, i.e., all the data points for a given reactant system were simultaneously used for the parameter evaluation.

The following features are apparent from Tables 1 and 2:

The mean deviation between calculated and observed values is considerably smaller for the dissociative model than for the associative model. An F test (see any textbook on statistics) on the variance estimates for the rate data shows the rate equation for the dissociative model to be significantly better than the rate equation for the associative model. The latter rate equation is therefore not consistent with the experimentally measured rates; as shown in the discussion below, the adsorption entropy estimates are also unsatisfactory. On the other hand, it appears likely that Eq. (16) is consistent with the experimental data.

TABLE 1

PARAMETER ESTIMATES FOR THE DISSOCIATIVE MODEL [from Eqs. (15) and (16)]

	Propylene	Isobutylene
E_1	14 770.	12 690.
$\mathcal{K}_1$	26.80	22.58
E_2	13 180.	13 180.
$\mathcal{K}_2$	23.94	23.63
$\Delta H_{A,1}$	−3263.	−1680.
$\Delta S_{A,1}$	−5.09	+0.74
$\Delta H_{A,2}$	+587.	3522.
$\Delta S_{A,2}$	+1.732	+10.22
$\Delta H_{\mathrm{H},1}$	−3677.	−455.
$\Delta S_{\mathrm{H},1}$	−12.44	−1.184
$\Delta H_{\mathrm{H},2}$	−2007.	5367.
$\Delta S_{\mathrm{H},2}$	−8.34	+15.89
SD estimate of rate measurements (%)		
	$s = 3.70$	$s = 4.61$
Mean deviation between calc and obs values (%)		
	2.46	2.79

TABLE 2

PARAMETER ESTIMATES FOR HORIUTI'S ASSOCIATIVE MODEL [from Eqs. (9) and (10)]

	Propylene	Isobutylene
E_1	14 670.	9874.
$\mathcal{K}_1$	26.70	18.00
E_2	12 510.	14 800.
$\mathcal{K}_2$	23.92	27.49
$\Delta H_{A,1}$	−1.	−2066.
$\Delta S_{A,1}$	+15.69	+8.54
$\Delta H_{A,2}$	0	−1905.
$\Delta S_{A,2}$	+3.40	−4.09
$\Delta H_{\mathrm{H},1}$	+925.	+6612.
$\Delta S_{\mathrm{H},1}$	+5.20	+21.32
$\Delta H_{\mathrm{H},2}$	+3825.	+13 390.
$\Delta S_{\mathrm{H},2}$	+5.03	+37.00
$\Delta H_{EQ,1}$	−8011.	−3330.
$\Delta S_{EQ,1}$	−34.64	−17.64
$\Delta H_{EQ,2}$	−9099.	−7693.
$\Delta S_{EQ,2}$	−32.54	−26.64
SD estimate of rate measurements (%)		
	$s = 8.20$	$s = 7.99$
Mean deviation between calc and obs values (%)		
	4.55	4.35

Having established that Eq. (10) is not consistent with the experimental results when $N = 2$, an obvious step might be to investigate what happens when $N = 3$. These computations have not been carried through, however, partly for the reason given above, partly because the number of parameters was considered excessive for the number of experimental points, and partly from a consideration of the limiting behavior of Eqs. (9) and (15) at high propylene pressures. In the limit where $K_{A,j} \cdot p_A \gg 1$ and $K_{A,j} p_A \gg (K_{\mathrm{H},j} p_{\mathrm{H}})^{1/2}$, Eq.

(15) (for the dissociative scheme) reduces to $r_j = \text{const.} \times p_H^2 p_A^{-2}$ and Eq. (9) (for the associative scheme) reduces to one of the forms $r_j = \text{const.} \times p_A^{-1}$ or $r_j = \text{const.} \times p_H$. It is seen immediately that the limiting form for the dissociative scheme rises faster with increasing hydrogen pressure and decreases faster with increasing olefin pressure than do the limiting forms for the associative reaction scheme. Study of the individual pairs of observed and calculated rates suggests that Eq. (10) fails because calculated rates do not increase fast enough with p_H and decrease fast enough with p_A. Addition of more terms will not change this feature when the constraint that all terms shall be positive is imposed.

Although the models proposed by Rogers *et al.* (*1*) and Mezaki (*3*) are unable to explain the isotopic exchange which takes place in olefin hydrogenation, a short comparison between the various models and their consistency with the experimentally measured rates may be warranted. A precise comparison is difficult because the criteria for obtaining the least squares estimates have been different. Mezaki (*3*) minimized the sum of squared deviations. Rogers *et al.* (*1*) first minimized the sum of squared deviations for the data at a constant temperature, and then finally from Arrhenius plots determined the preexponential factors and reaction enthalpies. Computations carried out by this author, however, indicate that the models involving competitive–noncompetitive adsorption and the dissociative model with two sets of reaction sites give essentially the same fit to the experimental data, the dissociative model being somewhat better than the other two.

To be fully acceptable, the parameter estimates of the dissociative model must be physically reasonable. The most conspicuous property of the data given in Tables 1 and 2 is that the adsorption enthalpies are small and the adsorption entropies are also small, and some of them are even estimated to be positive. This observation is in accordance with a dissociative model where a considerable energy must be expended to break chemical bonds, and where no great entropy loss is to be expected from adsorption because the loss of translational degrees of freedom is offset by an increase in entropy due to the creation of more particles upon adsorption. De Boer (*21*) has pointed out that, in cases of dissociative adsorption, one may even find that the adsorption may be an endothermic process because of an entropy gain.

Eley (*5*) has calculated adsorption enthalpies for the adsorption of ethylene on a nickel surface for various models of chemisorption and found that the dissociative adsorption gives a very small adsorption enthalpy. Hirota and Hironaka (*22*) concluded from NMR work that at least part of the isotopic exchange in propylene over a platinum catalyst took place via a dissociative mechanism.

Since the hydrogenation of propylene and isobutylene are two very similar reactions, one would like the parameters estimated for the two reactions to be rather similar. This similarity is in fact found in Table 1 where only the estimates for $\Delta H_{H,2}$ and $\Delta S_{H,2}$ are severely different (the one is a consequence of the other). This difference is not significant, however. It is evidently due to a wide confidence interval for these parameters. This is apparent from Table 3 where joint parameter estimates for propylene and isobutylene hydrogenation are given, i.e., the parameters for hydrogen adsorption have been made equal for the two reactions (choosing essentially the mean values), and enthalpy estimates having a tendency for turning out positive have been put equal to zero to see if that more satisfactory result still leads to a satisfactory fit between observed and calculated hydrogenation rates. The standard deviation estimates which have been obtained show that this is still the case. There are in all 18 parameters which have been estimated in Table 3, i.e., 9 parameters per set of experimental data.

It may be pointed out that the associative model gave a less good fit than the dissociative model (Tables 2 and 3) in spite of the considerably higher number of adjustable parameters in the rate equations

TABLE 3

JOINT PARAMETER ESTIMATES FOR THE DISSOCIATIVE MODEL. [Eq. (16)]

The standard deviation estimates have been obtained by assuming that there are 9 parameters in each data set.

	Propylene		Isobutylene
E_1	13 620.		13 260.
$\mathcal{K}_1$	24.77		23.60
E_2	11 590.		16 050.
$\mathcal{K}_2$	21.14		28.30
$\Delta H_{A,1}$	−3601.		−2690.
$\Delta S_{A,1}$	−6.26		−2.76
$\Delta H_{A,2}$	0		0
$\Delta S_{A,2}$	−0.28		−1.31
$\Delta H_{\mathrm{H},1}$		−1700.	
$\Delta S_{\mathrm{H},1}$		−5.54	
$\Delta H_{\mathrm{H},2}$		0	
$\Delta S_{\mathrm{H},2}$		−1.37	
SD estimate of rate measurement (%)	$s = 4.10$		$s = 4.70$
Mean deviation between calc and obs values (%)	2.87		2.90

for the associative model (16 compared to 9). This emphasizes the point that a high number of parameters in a model is not by itself assuring a good fit with experimental values. The number of parameters employed here is essentially the same as was used in Mezaki's model (*3*), where there are 10 parameters.

Besides the Horiuti–Polanyi version (*10*) of the associative reaction model, an associative model proposed by Bond *et al.* (*17*, *18*) has been investigated. Assuming two sets of active sites which leads to a kinetic equation containing 14 parameters, a fairly satisfactory fit between observed and calculated rates was obtained (similar to, but slightly less good than, the dissociative model), but the adsorption enthalpy and entropy estimates appeared too small to be really satisfactory. It is possible that other reaction schemes may be formulated which lead to kinetic equations consistent with the experimentally measured rates of Rogers *et al.* (*1*). The number of reaction schemes proposed for the associative mechanism is rather high so it was not considered profitable to study them all. A really meaningful discrimination between various alternatives may be difficult until experimental data are available for a much wider range of reaction conditions, and possibly until simultaneous adsorption measurements have been carried out.

To the author's knowledge, there are no other experimental data on hydrogenation of olefins over metal catalysts which have been obtained with sufficient accuracy and over a sufficiently wide range of reactant pressures to warrant a detailed investigation of consistency with rate equations as has been done here. It is believed that when such experiments are eventually carried out—preferably concurrently with adsorption and isotopic exchange measurements—they will help much in clarifying the question of reaction mechanisms for olefin hydrogenation and isotopic exchange.

APPENDIX: DERIVATION OF THE KINETIC EQUATIONS

The general reasoning of Hougen and Watson (*2*) is followed so the treatment given here will be rather condensed.

A. The associative model

There is a total surface concentration L of adsorbing sites of the jth kind, and C_l of these are free. The following equations are then obtained from Eqs. (5)–(8). The subscript a means that the species is adsorbed).

$$\frac{[H_a]^2}{p_{H_2} \cdot C_l^2} = K_H, \tag{A1}$$

$$\frac{[(C_3H_6)_a]}{p_A \cdot C_l^2} = K'_A \tag{A2}$$

$$\frac{[(C_3H_7)_a]\, C_l^2}{[(C_3H_6)_a][H_a]} = K'_E, \tag{A3}$$

$$r = k'[(C_3H_7)_a][H_a]. \tag{A4}$$

The total surface concentration is given by the following equation

$$L = 2[(C_3H_6)_a] + [H_a] + [(C_3H_7)_a] + C_l \tag{A5}$$

Combination of Eqs. (A1)–(A5) leads to Eq. (9) after transforming the constants in Eqs. (A1)–(A4) as follows.

$$2LK'_A = K_A, (K'_E/2L) = K_E, L^2k' = k$$

B. The dissociative model

Equations (11) to (14) lead to

$$\frac{[H_a]^2}{p_{H_2} \cdot C_l^2} = K_H, \tag{A6}$$

$$\frac{[(C_3H_5)_a][H_a]}{p_A \cdot C_l^2} = K_A, \tag{A7}$$

$$r = k'[(C_3H_5)_a][H_a]^2, \tag{A8}$$

$$\frac{p_{C_3H_8}\, C_l^2}{[(C_3H_7)_a][H_a]} = K_D, \tag{A9}$$

$$L = C_l + [H_a] + [(C_3H_5)_a] + [(C_3H_7)_a]. \tag{A10}$$

Because it is known that an alkane is adsorbed only to a small extent from gas phase, and because the conversion to alkane was low, $[(C_3H_7)a]$ in Eq. (A10) is neglected. Combination of Eqs. (A6)–(A8), and (A10) gives Eq. (15) ($k'\ L^3$ is replaced by k).

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