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Studies in Catalytic Reactions

II. The Oxidation of Some Hydrocarbons over Noble Metal Catalysts

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The previous paper has described an improved method of selecting the Hougen-Watson rate equation which most accurately fits the experimental data for a given catalytic reaction. This method has now been applied to four systems, namely; (i) oxidation of benzene on platinum on silical gel; (ii) oxidation of *n*-heptane on platinum on silica gel; (iii) oxidation of benzene on palladium on glass balls; and (iv) oxidation of cyclohexane on palladium on glass balls. In addition, the rates of adsorption and the adsorption isotherms have been determined for the separate reactant species on the two catalysts.

The analysis of these results shows clearly that the oxidation of benzene and of cyclohexane on the same catalyst is controlled by different slow steps. In the former case, reaction between molecularly adsorbed oxygen and molecularly adsorbed benzene on the catalyst surface is rate-determining, whereas in the latter the dissociative adsorption of cyclohexane limits the overall rate.

The significance of these results, and the equilibrium constants, enthalpy changes, and entropy changes in the adsorption processes are discussed in relation to two types of chemisorption known, respectively, as Type A and Type C.

SYMBOLS

A	Initial mole fraction of oxygen (this symbol is also used to refer generally to oxygen)
a	Stoichiometric coefficient for oxygen
B	Initial mole fraction of fuel (this symbol is also used to refer generally to the fuel)
b	Stoichiometric coefficient for fuel
b_1 to b_5	Regression coefficients in polynomial
E	Activation energy of reaction, activation energy for the formation of an active site
F	Total flow rate (ml/min)
ΔH	Enthalpy of adsorption, with subscript
k	Rate constant of reaction (moles/min)
k_1, k_2	Constants in rate-conversion equation
K	Adsorption equilibrium constant (atm^{-1}), with subscript
L	Total number of active centers
M	Product
m	Stoichiometric coefficient for product
p	Partial pressure, with subscript
r	Reaction rate (moles/min)
ΔS	Entropy of adsorption, with subscript
T	Temperature (°K)
V_m	Molar volume of reactants at entry conditions to reactor (ml/mole)
x	Fractional conversion (moles fuel converted/initial moles fuel present)
π	Total pressure (atm)

Subscripts

A	Oxygen
B	Fuel
M	Product

INTRODUCTION

Although catalytic reactions have been studied for many years and although in several cases the mechanisms have been elucidated with a considerable degree of certainty, it remains true to say that it is difficult to decide on the mechanism of a given catalytic reaction. There are several reasons why a study of catalytic reactions is complicated; these all stem from the fact that the catalyst surface "hides" and "disguises" (*1*) the reactants so that their behavior on the surface can only be inferred by indirect methods.

For example, in a kinetic study the surface concentrations of the reactants are deduced from their gas-phase concentrations using the Langmuir isotherm, which leads to the Hougen-Watson rate equations. Since these equations are relatively complex, their use requires that the data should both be accurate and conform to an experimental design (*2*). However, in practice it is very difficult to do this, since catalysts are prone to slight and irregular activity changes which can invalidate an analysis using complex Hougen-Watson equations. Furthermore, it may only be possible to make measurements over a narrow range of concentrations or temperatures. This region is likely to be inconsistent with the region an experimental design shows to be most favorable to the accurate fitting of a complex rate equation (*3*). The problems involved in the fitting of complex rate equations to data have been dealt with in more detail in a previous paper (*4*), where an improved method of treating them is described.

The practical difficulties associated with the use of complex rate equations have, however, meant that they have been relatively little used, although, as will be illustrated in this paper, they can provide much information about the catalyst surface and the adsorbed reactants.

Many of the catalytic oxidation studies carried out so far have been concerned simply with improving the yield of one of the products (e.g., *5*, *6*, *7*), and no real attempt has been made to determine the mechanism of reaction. The advent of catalytic combustion detectors and automobile exhaust afterburners has motivated investigations of hydrocarbon oxidation at low hydrocarbon concentrations, and in some cases, on noble metal catalysts where complete oxidation is important (*8*, *9*). However, in very few cases has the reaction been treated in a mechanistic way, employing Hougen-Watson rate equations (*10*). The present study attempts to fill this gap.

EXPERIMENTAL

a. Integral rate data. A standard flow apparatus has been used to measure integral reaction rate data. A measured stream of nitrogen was passed through a bubbler maintained at room temperature containing the hydrocarbon, and then through two cold traps at 0°C containing glass ballotini. The vapor pressure of the hydrocarbon in this nitrogen stream was thus reduced to its value at 0°C. This was independently confirmed. By a suitable adjustment of the flow rates of this stream, a further nitrogen stream, and an oxygen stream, it was possible to produce a measured total flow rate at any required concentration of hydrocarbon or oxygen, which was then fed to a tubular flow reactor placed in a furnace.

The total reactant flow rates were between 25 and 250 ml/min.

A sampling valve enabled a constant known amount of either the reactor inlet or exit streams to be injected reproducibly into a gas chromatograph. Therefore the conversion of hydrocarbon was easily determined by comparison of the peak areas of the fuel measured before and after passage through the catalyst bed.

The gas chromatograph employed a katharometer, helium was used as the carrier, and the columns were packed with 5% polyethylene glycol on Embacel at 100°C for benzene, 5% polyethylene glycol on Embacel at 35°C for cyclohexane, and 10% squalane on Embacel at 108°C for *n*-heptane.

Two types of reactor were employed. For the porous, highly active platinum on silica gel catalyst a microreactor was used, the bed dimensions of which were 0.5 cm diameter × 0.5 cm deep. The palladium on glass atalyst was less active and consequently a larger quantity was required; here the bed dimensions were 1.66 cm diameter × 3 cm deep.

In this way, measurements of conversion of hydrocarbon as a function of flow rate were made for a series of oxygen concentrations at constant fuel concentrations, and for a series of fuel concentrations at con-

TABLE 1
PROPERTIES OF CATALYSTS

Description	Catalyst (i) Platinum on silica gel	Catalyst (ii) Palladium on glass balls
BET surface area (m^2/g)	246	0.131
Mean pore size (Å)	26	Nonporous
Fraction of surface active	0.025	0.30
Mean pellet size (cm)	0.075	0.0997
Weight of catalyst (g)	0.043	26.55
Total active surface area (m^2)	26.4	10.4

stant oxygen. These measurements were repeated at several temperatures and in all cases isothermal data were obtained. It was also demonstrated that the homogeneous reaction was negligible under the experimental conditions.

b. Measurement of rates and amounts of adsorption. A conventional high-vacuum adsorption apparatus incorporating greaseless valves wherever appropriate was used to measure surface areas by the BET method, and also to determine the adsorption isotherms of benzene and oxygen on the catalysts at the reaction temperatures. The rates of adsorption were also measured in the same apparatus.

The rate of adsorption measurements were thus not made at constant pressure, but were extrapolated to give the initial rate of adsorption by use of the Elovich equation (*11*).

c. Preparation and properties of the catalysts. Two catalysts were used: (i) platinum on silica gel; (ii) palladium on glass balls. The method of preparation and deposition of the catalyst onto the carrier involved the reduction of the complex chloride to the metal using formaldehyde and followed the method described by Berkmann, Morrell, and Egloff (*12*).

The properties of the resulting catalysts are given in Table 1.

The fraction of the surface which is active was determined by comparison of the monolayer volume of chemisorbed oxygen at about 300°C with the monolayer volume of physically adsorbed nitrogen at $-197°C$ (*13*), while the pore size was obtained from the desorption curve (*14*). It is noteworthy that the rates of benzene oxidation per unit surface area on these catalysts under the same reactant concentrations and temperature differed only by a factor of 5 (Table 2).

d. Diffusion effects. The mass-transfer coefficient for bulk diffusion was calculated (*14, 15*) and compared with the rate of reaction. For the platinum on silica gel catalyst and the palladium on glass catalyst the rates of diffusion to the catalyst surface were found to be, respectively, 100 times and 2500 times the rate of reaction. Hence the effect of bulk diffusion on the rate of reaction was negligible.

The effectiveness factor (*16*) for the platinum on silica gel catalyst was also calculated and was found to be 1. Thus pore diffusion effects are absent. The other catalyst was, of course, nonporous.

As the temperature is increased, the rate of chemical reaction increases exponentially, whereas the rate of diffusion increases only with $T^{\frac{1}{2}}$. Consequently, if diffusion effects are negligible at low temperatures, as the temperature is raised they may become rate-limiting and in that case the Arrhenius plot would show a change of slope.

The fact that in the present case over a temperature range of 100°C the Arrhenius plots were good straight lines confirms the conclusion that the effects of both bulk and

TABLE 2
COMPARISON OF RATES OF REACTION AND SURFACE AREA

Temperature, 267°C		Oxygen mole fraction,	0.25
Benzene mole fraction,	8.4×10^{-3}	Nitrogen mole fraction,	0.74

Catalyst	Rate of oxidation (moles/min)	Surface area of catalyst (m^2)	Rate of oxidation (moles/min m^2)
Platinum on silica gel	2.8×10^{-6}	26.4	1.06×10^{-7}
Palladium on glass	5.2×10^{-6}	10.4	5.00×10^{-7}

pore diffusion are negligible under experimental conditions used in this work.

RESULTS

A. *Reaction Mechanisms*

The reaction mechanism has been determined by the application of Hougen-Watson rate equations to integral data (*4*). These data were measured over the following range of conditions:

Hydrocarbon concentration (mole fraction): 0.5×10^{-3} to 1.0×10^{-3}

Oxygen concentration (mole fraction): 0.06 to 0.50

Temperatures: 240° to 450°C

The data were analyzed using the method developed in the previous paper (*4*). The 104 possible mechanisms, as represented by 104 Hougen-Watson rate equations, were expressed in terms of the conversion (x). Thus a Hougen-Watson rate equation such as

$$r = \frac{kK_{\mathrm{O}_2}K_{\mathrm{B}}p_{\mathrm{O}_2}p_{\mathrm{B}}}{\{1 + K_{\mathrm{O}_2}p_{\mathrm{O}_2} + K_{\mathrm{B}}p_{\mathrm{B}}\}^2} \tag{1}$$

on rearrangement becomes the rate conversion equation

$$r = \frac{(A - aBx)(1 - x)}{(k_1 + k_2x)^2} \tag{2}$$

where

$$k_1 = \frac{1 + AK_{\mathrm{O}_2}\pi + BK_{\mathrm{B}}\pi + MK_{\mathrm{M}}\pi}{(kK_{\mathrm{O}_2}K_{\mathrm{B}}B\pi^2)^{1/2}} \tag{3}$$

$$k_2 = \frac{(mK_{\mathrm{M}} - aK_{\mathrm{O}_2} - K_{\mathrm{B}})B\pi}{(kK_{\mathrm{O}_2}K_{\mathrm{B}}B\pi^2)^{1/2}} \tag{4}$$

In all there are 28 distinct rate equations such as Eq. (2), each of which corresponds to roughly four Hougen-Watson rate equations. These four Hougen-Watson equations produce rate conversion equations of the same form but with different values of k_1 and k_2.

A computer program has been written to fit the 28 equations to the measured integral data, i.e., fractional conversion (x) vs. reciprocal flow rate ($1/F$), and thus calculate the constants k_1 and k_2. This has been done by first fitting a polynomial

$$\frac{B}{V_{\mathrm{m}}}\left(\frac{1}{F}\right) = b_1x + b_2x^2 + b_3x^3 + b_4x^4 + b_5x^5$$

to the measured x vs. $1/F$ data. Differentiation of this polynomial and substitution of suitable values of x within the range of experimental measurements thus generates a set of data

$$\frac{1}{r} = \frac{B}{V_{\mathrm{m}}}\frac{d(1/F)}{dx} \text{ vs. } x$$

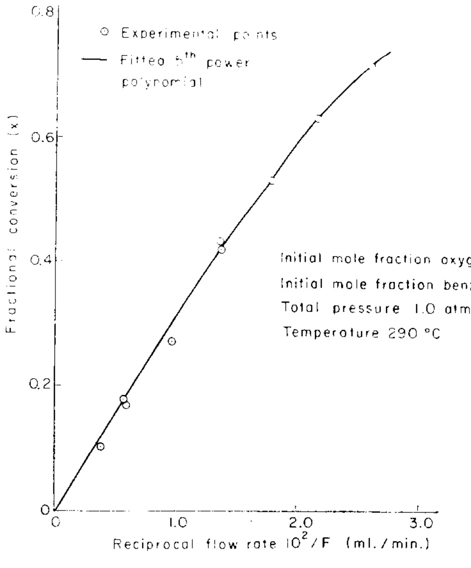

FIG. 1. The fit of a fifth power polynomial to measured conversion vs. reciprocal flow rate data on the oxidation of benzene on a glass-supported palladium catalyst.

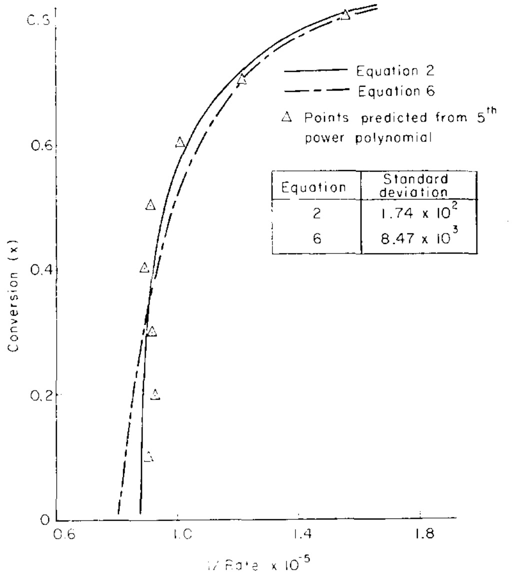

FIG. 2. The fit of Eqs. (2) and (6) to conversion vs. reciprocal rate data obtained by fitting a fifth power polynomial to the conversion vs. reciprocal flow rate data shown in Fig. 1.

to which equations such as (5) [a rearranged form of Eq. (2)] may be fitted, thereby giving the constants k_1 and k_2

$$\left(\frac{1}{r}\right)^{1/2} = \frac{k_1}{(A - aBx)^{1/2}(1 - x)^{1/2}} + \frac{k_2 x}{(A - aBx)^{1/2}(1 - x)^{1/2}} \quad (5)$$

From the behavior of k_1 and k_2 with the initial concentrations (A and B), for the 104 Hougen-Watson rate equations it is possible to decide which of the 104 mechanisms is applicable.

A typical set of integral data is shown on Fig. 1, together with the fifth power polynomial which has been fitted by least-squares to this data. Differentiation of this polynomial and substitution of suitable values of conversion produces the empirical conversion vs. reciprocal reaction rate data shown in Fig. 2. The fit of two typical rate-conversion equations (2) and (6) to this data is also shown in Fig. 2.

$$r = \frac{(A - aBx)(1 - x)}{k_1 + k_2 x} \quad (6)$$

Equation (2) is the rate-conversion equation derived from the Hougen-Watson model in which fuel and oxygen are molecularly adsorbed, and the rate-controlling step is the surface reaction between them, while Eq. (6) is derived from model systems in which the rate-determining step is surface reaction between gaseous fuel and adsorbed molecular oxygen (or vice versa).

The values of k_1 and k_2 obtained from this fitting are given in Table 3.

TABLE 3
VALUES OF k_1 AND k_2 OBTAINED BY FITTING EQS. (2) AND (6) TO DATA SHOWN IN FIG. 2

	Eq. (2)	Eq (6)
k_1	2.08×10^2	4.07×10^4
k_2	-1.13×10^2	-3.40×10^4

It is clear from Fig. 2 that Eq. (2) provides a better fit to the data than does Eq. (6) and this is reflected in the values of the standard deviation [the square root of the residual variance (*7*)] for the two fitted curves.

Values of k_1 and k_2 were obtained in a similar way for all the 28 rate conversion equations. An initial selection of the rate equations was made on the basis that k_1 must be positive; Eq. (3) shows that as K_{O_2}, K_B, and K_M are always positive, which is axiomatic since they are all equilibrium constants, then k_1 must also be positive. From the remaining equations, the correct Hougen-Watson rate equation is selected from the dependence of k_1 and k_2 on the initial concentrations. Since this derived data in the form of k_1 and k_2 for all 28 rate equations and reaction conditions is rather lengthy (*18*), it is inappropriate to present all of it. Consequently only those values of k_1 and k_2 calculated for Eq. (2) are shown, the selection procedure having de-

TABLE 4
VALUES OF k_1 AND k_2 FOR EQ. (2)—BENZENE OXIDATION ON PALLADIUM ON GLASS AT 290°C

Benzene mole fraction	Oxygen mole fraction	k_1	k_2
8.4×10^{-3}	0.25	1.92×10^2	-1.11×10^2
8.4×10^{-3}	0.50	2.03×10^2	-1.13×10^2
6.72×10^{-3}	0.25	1.76×10^2	-8.94×10
6.72×10^{-3}	0.50	1.94×10^2	-8.91×10

monstrated that this is the only equation capable of representing the data.

These data are presented in Table 4 and reference to Eqs. (3) and (4) shows that the values of k, K_{O_2}, K_B, and K_M may be calculated from k_1, k_2, A, and B. The values of k, K_{O_2}, K_B, and K_M so obtained are presented in Table 7 and all are positive.

In this way mechanisms were obtained for the four reactions studied, as follows:

(i) *Benzene oxidation on platinum on silica gel*

Reaction conditions: Temperature 267°C
Weight of catalyst 0.043 g

Rate-controlling step: Surface reaction between molecularly adsorbed oxygen and adsorbed benzene.

Hougen-Watson rate equation:

$$r = \frac{kK_{O_2}K_Bp_{O_2}p_B}{\{1 + K_{O_2}p_{O_2} + K_Bp_B\}^2}$$

TABLE 5
VALUES OF THE RATE PARAMETERS OBTAINED FOR BENZENE OXIDATION OVER PLATINUM

Rate parameter	Value
k	5.78×10^{-5} moles/min
K_{O_2}	1.47 atm^{-1}
K_B	1.65×10^2 atm^{-1}

(ii) *n-Heptane oxidation on platinum on silica gel*

Reaction conditions: Temperature 244°C
Weight of catalyst 0.0767 g

Rate-controlling step: Surface reaction between molecularly adsorbed oxygen and adsorbed *n*-heptane

Hougen-Watson rate equation:

$$r = \frac{kK_{O_2}K_Bp_{O_2}p_B}{\{1 + K_{O_2}p_{O_2} + K_Bp_B\}^2}$$

TABLE 6
VALUES OF THE RATE PARAMETERS FOR *n*-HEPTANE OXIDATION OVER PLATINUM

Rate parameter	Value
k	9.21×10^{-5} moles/min
K_{O_2}	13.8 atm^{-1}
K_B	20 atm^{-1}

(iii) *Benzene oxidation on palladium on glass*

Weight of catalyst: 26.55 g

Rate-controlling step: Surface reaction between molecularly adsorbed oxygen and benzene.

Hougen-Watson rate equation:

$$r = \frac{kK_{O_2}K_Bp_{O_2}p_B}{\{1 + K_{O_2}p_{O_2} + K_Bp_B + K_Mp_M\}^2}$$

The activation energy and entropy of reaction and the enthalpy and entropy of adsorption have been calculated:

$\Delta H_{O_2} = 56$ kcal/mole $\quad \Delta S_{O_2} = 102$ cal/mole°K
$\Delta H_B = 182$ kcal/mole $\quad \Delta S_B = 199$ cal/mole°K
$\Delta H_M = 88$ kcal/mole $\quad \Delta S_M = 171$ cal/mole°K
$E = 22$ kcal/mole $\quad \Delta S = 4.62$ cal/mole°K

(iv) *Cyclohexane oxidation on palladium on glass*

Weight of catalyst: 26.55 g

Rate-controlling step: The dissociative adsorption of cyclohexane

Hougen-Watson rate equation:

$$r = \frac{kp_B}{\{1 + K_{O_2}p_{O_2}\}^2}$$

The enthalpy and entropy adsorption of

TABLE 7
VALUES OF THE RATE PARAMETERS OBTAINED FOR BENZENE OXIDATION ON PALLADIUM

Temp. (°C)	K_{O_2} (atm^{-1})	K_B (atm^{-1})	mK_M (atm^{-1})	k (moles/min)
290°	15.4	5.73×10^3	2.27×10^3	1.04×10^{-4}
274°	3.88	4.64×10^2	2.30×10^2	5.85×10^{-5}

TABLE 8

VALUES OF THE RATE PARAMETERS OBTAINED FOR CYCLOHEXANE OXIDATION ON PALLADIUM

Temp. (°C)	k (moles/min)	K_{O_2} (atm^{-1})
456°	1.5×10^{-3}	0.57
406°	7.49×10^{-4}	0.72

oxygen and the activation energy and entropy of reaction are

$$\Delta H_{O_2} = -4.62 \text{ kcal/mole},$$
$$E = 13.9 \text{ kcal/mole},$$
$$\Delta S_{O_2} = -7.45 \text{ cal/mole°K}$$
$$\Delta S = 6.08 \text{ cal/mole°K}$$

B. *Chemisorption Studies*

The chemisorption of the individual reactants on the surface of the catalyst at temperatures of approximately 300°C was studied in two ways. Firstly, the adsorption isotherms of the reactants were determined at two temperatures. The differential enthalpies of adsorption were then determined by the application of the Clausius-Clapeyron equation. The variation of the enthalpies of adsorption with surface coverage are shown in Figs. 3 and 4.

Secondly, the initial rates of adsorption have been measured by fitting the Elovich equation (*11*) to the plot of volume adsorbed vs. time. The Elovich equation represents the rate of adsorption measurements very well and consequently the adsorption may be classified as "slow" (*11*). It was found that several hours were required for equilibration.

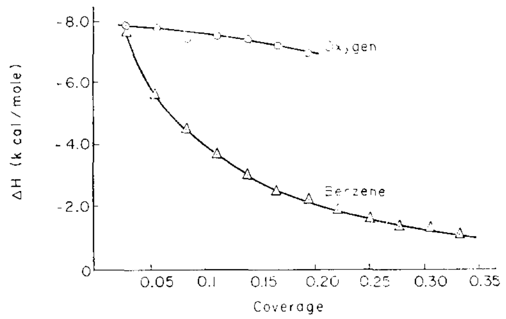

FIG. 3. The variation of the enthalpy of adsorption with surface coverage on the platinum on silica gel catalyst.

After allowing for the different weights of catalyst in the adsorption vessel and catalyst bed it is possible to compare the minimum rate at which adsorption must take place during reaction and the rate at which it has been observed to take place in this separate adsorption study (see Table 8). From Table 8 it is seen that the rate at which adsorption is taking place during reaction is approximately 100 times faster than the rate at which it has been observed to take place in this separate chemisorption study.

DISCUSSION

Reaction occurs on the surface of a catalyst because the reactants are adsorbed on "active" centers, thereby becoming activated. For this adsorption to take place it is necessary that the surface should possess unused valencies. The possible types of un-

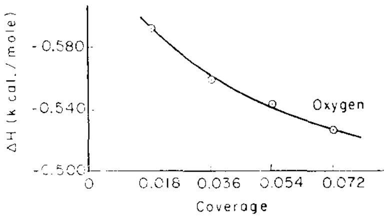

FIG. 4. The variation of the enthalpy of adsorption with surface coverage on the palladium on glass catalyst.

TABLE 9

COMPARISON OF RATES OF ADSORPTION

Rate of adsorption	Platinum on silica gel Temperature = 267°C		Palladium on glass Temperature = 290°C
	Oxygen	Benzene	Oxygen
Minimum rate of adsorption during reaction (Equivalent to rate of reaction) (ml/min)	49.3	6.57	1.93
Rate of adsorption (static adsorption measurements) (ml/min)	0.128	3.67×10^{-2}	5.9×10^{-3}

TABLE 10
Types of Surface Unsaturation

Type of unsaturation	Electron bond theory	Valence bond theory
Type A		
Surface only (all metals)	Unfilled surface states	Vacant (*dsp*) or (*sp*) hybrid orbitals
Type C		
Bulk and surface (transition metals only)	Unfilled *d* band	Vacant atomic *d* orbitals

saturation present in metals (*20*) are summarized in Table 10. It is possible to express these unsaturations in terms of the electron band theory or the valence bond theory (*21*, *22*). It is concluded that both types of unsaturation are involved in chemisorption and the degree of participation of the two types will depend on the nature of the adsorbate.

The free electrons of an unsaturated hydrocarbon should be capable of entering the vacant *d* orbital of a transition metal; thus it would be expected that an unsaturated hydrocarbon would be quite readily adsorbed by a transition metal having a vacant *d* orbital. It is considered (*23*, *24*) that this type of chemisorption (Type C) may be molecular in nature. In contrast, the finding that saturated hydrocarbons are not as readily chemisorbed as hydrogen may mean they are not capable of Type C chemisorption. The importance of the type of adsorbent is supported by some results obtained when a search was made for a nonporous catalyst. It was found that while platinum, palladium, and copper were active towards benzene oxidation, silver was not. This is to be expected since silver does not possess a vacant *d* orbital, while platinum, palladium, and copper do. This difference between palladium and silver has been interpreted (*21*) in the following way with respect to the chemisorption of hydrogen: It has been observed that there is a formidable activation energy for the adsorption of hydrogen on silver but not for the adsorption of hydrogen on palladium. It is proposed that this is because palladium possesses a partly vacant *d* orbital while silver does not. This is illustrated by plotting the potential energy curves for the two metals (Fig. 5).

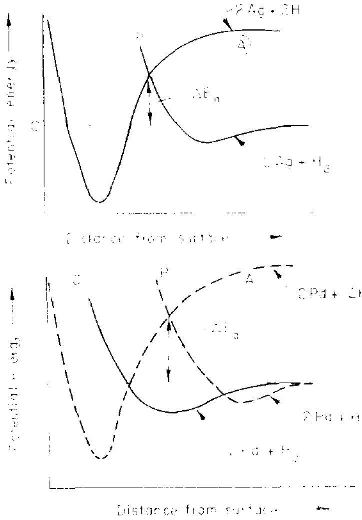

FIG. 5. Diagrammatic potential energy curves for adsorption of hydrogen on silver and palladium. Curve A, Type A chemisorption; Curve C, Type C chemisorption; Curve P, physical adsorption.

The curves P and A represent physical and Type A chemisorption, the distance is that from the catalyst surface, and E_a the activation energy for the transition from physical to Type A chemisorption. E_a is thus the activation energy of Type A chemisorption and the diagram shows how this activation energy is removed for Type C chemisorption.

An attempt will now be made to relate these chemical factors to the reaction mechanisms obtained and the rates, enthalpies, and entropies of adsorption. This will show how fundamental information about catalytic reactions may be obtained by the application of Hougen-Watson rate equations.

A. *The Significance of the Rate-Controlling Steps and Values of the Adsorption Equilibrium Constants*

The first point of note is that the adsorption equilibrium constants for oxygen are all of approximately the same magnitude (see Tables 5 to 8). Secondly, in the two studies on benzene oxidation the equilibrium constants for benzene are greater by a factor of

10^2 than those for oxygen, while the equilibrium constant for n-heptane is of approximately the same order as that for oxygen. This indicates that benzene is bonded much more strongly to the surface than oxygen, while the bonding strengths of oxygen and n-heptane are of much the same magnitude.

The relatively strong bonding of benzene to the surface is to be expected since it is unsaturated and is readily able to form a bond with unpaired d-band electrons. n-Heptane, being saturated, would not be expected to form so strong a bond with the surface. However, the rate-controlling step for these three oxidations (benzene and n-heptane oxidation on platinum on silica gel and benzene oxidation on palladium on glass) is the surface reaction between molecularly adsorbed reactants. The adsorption steps would thus be expected to be capable of proceeding much faster than the reaction rate and therefore be nonactivated. Thus, these nonactivated adsorptions which are molecular in nature, would be expected to be of Type C.

The position is somewhat different in the case of cyclohexane oxidation (iv). The rate-controlling process is the dissociative adsorption of cyclohexane, and this is clearly activated since it only takes place at higher temperatures. Furthermore, the activation energy for reaction must be the activation energy of the dissociative adsorption and this has been found to be 13.9 kcal/mole. Thus this type of chemisorption would be expected to be of Type A, firstly, because it is activated and secondly, because it is dissociative.

B. *Rates of Adsorption and Rates of Reaction*

The foregoing discussion has indicated that for benzene and n-heptane oxidation the rate of adsorption is much faster than the rate of reaction.

Yet when the rates of adsorption of the individual reactants on the surface of the catalyst were measured in a "static" adsorption system they were found to be lower by a factor of about 100 than the minimum rate at which adsorption must take place during reaction (see Table 9). Thus there must be a fundamental difference between the type of adsorption taking place during reaction and the type of adsorption observed in an adsorption study of the individual reactants where the surface coverages are high (up to a monolayer average).

In the application of the Elovich equation to many systems (*11*) it was observed that there are two types of chemisorption. First, there is a very fast chemisorption, the kinetics and statics of which are virtually inaccessible, and this is followed by a subsequent slow process, the kinetics of which may be described by the Elovich equation. This behavior has been interpreted (*26*, *27*) as being Type C chemisorption which is nonactivated (and therefore fast) involving d-orbital bonding, followed by Type A chemisorption which is activated and involves dsp-orbital bonding.

Thus it is considered that the adsorption taking place during the oxidation of benzene and n-heptane is Type C. When the adsorption of these materials is studied separately in a "static" adsorption system it is believed that the surface properties of the adsorbent are modified due to the extensive adsorption and the adsorption is now of Type A.

These conclusions about the differing types of adsorption will now be expanded by a discussion of the enthalpies and entropies of adsorption.

C. *The Enthalpies and Entropies of Chemisorption*

A consideration of the rates of adsorption has shown that the type of adsorption taking place during reaction is quite different from that observed in an adsorption study of the individual reactants, where the surface coverages of the individual reactants are quite high. In view of this distinction it would not be surprising if the enthalpies of adsorption measured under the two differing conditions were widely divergent. This is found to be so. The enthalpies of adsorption determined under reaction conditions have been found to be positive for benzene oxidation on palladium on glass and negative for cyclohexane oxidation on palladium on glass. In contrast the enthalpies of adsorption determined from static adsorption measurements have been shown to be negative (Figs. 3 and 4).*

While negative enthalpies of adsorption and negative entropy changes are easily explained, it is more difficult to account for a positive enthalpy of adsorption and a positive entropy change.

The negative enthalpy of adsorption signifies that the quantity adsorbed is decreasing with increase in temperature. This is to be expected for an activated adsorption and desorption and is supported by the bulk of the literature. The negative entropy change (decrease in entropy) is to be expected since on adsorption the adsorbate molecule is confined to the surface so that certain degrees of freedom are lost.

However, positive enthalpies of adsorption have been reported for measurements in static adsorption systems. One example relates to a study (*28*) of the chemisorption of oxygen on a series of three NiO-MgO solid solutions. The enthalpies of oxygen adsorption were found to be positive. Furthermore (*29*), the enthalpies of adsorption of oxygen and sulfur dioxide on a vanadium catalyst have been found to be positive. The reported values are $\Delta H_{\mathrm{O}_2^{1/2}} = 6.41$ kcal/mole and $\Delta H_{\mathrm{SO}_2} = 28.8$ kcal/mole. However the most important fact about these adsorptions is that they were "fast" and appeared to obey the Langmuir isotherm.

Positive enthalpies of adsorption (*30*, *31*) have been widely reported in the applications of Hougen-Watson rate equations, although so far no significance has been attached to them. There are several possible explanations. Firstly, the particular Hougen-Watson rate equation used may be inadequate and its deficiencies are falsely causing the enthalpies of adsorption to become positive. This, however, is unlikely to be the complete explanation, since applications of Hougen-Watson rate equations to widely differing reactions by various workers have given positive enthalpies of adsorption. Furthermore, similar types of reaction tend to give similar values of enthalpies of adsorption (*32–36*). In addition, positive enthalpies of adsorption have occasionally been reported (*27*, *28*) for adsorption studies in static adsorption systems. In these cases, the adsorption has been observed to be "fast."

There thus appears to be no reason why chemisorption should not be endothermic. This view is supported by de Boer (*37*), who considers that—

> "The statement that all adsorption processes starting from the gas phase are exothermic can be considered to be always true only if it is restricted to physical adsorption phenomena. It is true that in chemisorption the heats of chemisorption are usually much larger than in physical adsorption, an in all those cases chemisorption is truly exothermic. Chemisorption is, on the other hand, nothing but a chemical reaction of the adsorbed molecules with the outer layer of the adsorbent. As endothermic compounds are well known in chemistry one might consider endothermic chemisorption phenomena to be possible."

It is then shown how in one or two cases where a transient chemisorption takes place to a very limited extent, an endothermic process may be involved.

There is then no serious objection to the concept of endothermic adsorption. However, so far there has been no mention of the entropy change on adsorption. In this respect, it is remarkable that negative heats of adsorption are invariably associated with negative entropy changes on adsorption and vice versa. An increase in entropy on adsorption is not so easily explained as a positive enthalpy of adsorption.

However, further to de Boer's suggestion that "one might consider endothermic adsorption phenomena to be possible," Volkenstein (*39*) has advanced another explanation which may help to explain the entropy changes on adsorption.

It is suggested that the classical conception of activated adsorption requiring an

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* The enthalpies of adsorption during reaction have been calculated by expressing the adsorption equilibrium constant in the form

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

The enthalpies of adsorption during "static" adsorption measurements have been determined by the application of the integrated Clausius-Clapeyron equation to the isotherm at two temperatures

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

activation energy for the formation of the adsorbed complex may be replaced by the idea of an activationless adsorption on active centers which increase in number with the temperature. This is represented by a relationship of the type

$$\frac{d \ln L}{dT} = \frac{E}{RT^2}$$

where L is the total number of active centers and E is the energy of activation for the formation of an active center.

This theory then explains three facts: firstly, since the adsorption is nonactivated it is very fast and this is what has been observed during reaction for benzene on palladium. Secondly, the enthalpy of adsorption will be positive, since it is the activation energy for the formation of an active site. Lastly, since the formation of an active site is effectively increasing the randomness of the system it would be expected that the entropy change on adsorption would be positive.

It is worthwhile repeating that for the oxidation of benzene on palladium the adsorptions have been observed to be "fast," and the enthalpies and entropies of adsorption are positive.

It has thus been concluded that the Type C chemisorption which has already been observed to be molecular in nature and nonactivated may also be such that the number of active centers will increase in temperature.

Consideration of the rates of adsorption, the rate-controlling step, and the values of the adsorption equilibrium constants, has thus shown that there are two types of adsorption depending on the nature of the adsorbate and adsorbents.

The first, known as Type C, is nonactivated, very fast, and molecular in nature. It involves covalent bonding with the vacant *d* band of a transition metal. Consequently unsaturated hydrocarbons have been found to be strongly adsorbed.

The second type of chemisorption (Type A) has been found to be activated (and thus slow) and dissociative in nature, involving *dsp* bonding. Cyclohexane has been found to take part in this type of adsorption, possibly because the electrons in the C–H bond are localized and thus prevented from taking part in Type C chemisorption.

Finally, by a consideration of the enthalpy and entropy changes during adsorption, it is shown that in Type C chemisorption the number of active centers may possibly increase with increase in temperature.

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