Catalytic Hydrogenation of Cyclohexene:

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Part II. Liquid Phase Reaction on Supported Platinum in a Gradientless Slurry Reactor

The areal rate of liquid phase hydrogenation of cyclohexene on supported platinum catalysts does not depend on the nature of the support. Nor does it depend on particle size of the metal. The rate constant is independent of the nature of the solvent when the concentration of hydrogen in it is expressed as its measured or calculated solubility. All observations are compatible with the idea that the measured rate is that of chemisorption of dihydrogen on a metal surface covered with reactive hydrocarbon intermediates.

SCOPE

The effect of the dimensions of metallic particles on the catalytic activity of supported metals is of theoretical and practical importance. The present work was undertaken to examine the effect of platinum particle size on the liquid phase hydrogenation of cyclohexene in a rocking slurry reactor. The reaction was studied in a static system at constant hydrogen pressure, normally atmospheric pressure, between 275° and 316°K. As diffusion coefficients in the liquid phase are often two or more orders of magnitude lower than in the vapor phase, diffusional influence can play a substantial role in slurry reactors. It is thus imperative that reactions studied in slurry reactors be examined for diffusional effects and proof be given that observed rates have not been disguised by either intraparticle or interphase mass transport. We set out to obtain true kinetic data devoid of either the influence of transport phenomena or catalyst deactivation during an experimental run.

The present study also focused on two important aspects of liquid phase reactions. When heterogeneous catalytic reactions are carried out in the gas phase, ideal gas behavior is ordinarily assumed. However, for kinetics in the liquid phase, as in a slurry or trickle bed reactor, it is necessary first of all to ascertain whether concentrations or activities of dissolved reactants should be used in rate expressions. Second, it is also important to check whether different solvents affect the reaction rate or the rate constant. The literature of catalytic reaction engineering offers few experimental or theoretical guidelines bearing on these two important questions.

CONCLUSIONS AND SIGNIFICANCE

Kinetic data have been obtained for the liquid phase hydrogenation of cyclohexene on supported platinum catalysts in a rocking slurry reactor. First of all, values of the turnover frequency N, defined as molecules reacted per site per second, were obtained on catalysts containing different amounts of platinum of the same dispersion, defined as the ratio of surface metal atoms to total metal atoms. Values of N were found to be identical. As this result was obtained at two different temperatures, it offers sufficient proof that rates were not masked by artifacts such as the influence of interphase and intraparticle heat and mass transfer, or deactivation and poor contacting of the catalyst by reactants.

The main result of this work is that values of N were identical on nine different supported platinum catalysts where the metal particle size varied from about 1 to 7 nm. There was also no effect on N of the nature of the support (SiO_2, η-Al_2O_3, and γ-Al_2O_3); hence, no metal support interactions were encountered.

The rate was found to be zero order with respect to cyclohexene and first order with respect to hydrogen. The second significant result of this work is that the first-order rate constant remained unchanged in seven different sol-

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vents (cyclohexane, benzene, *n*-heptane, *p*-dioxane, methanol, ethyl acetate, and neat cyclohexene), provided that concentration, rather than activity, of dissolved hydrogen was used in the rate expression. To explain the above observation, a sequence of steps is proposed similar to that originally proposed by Horiuti and Polanyi for hydrogenation of ethylene. It appears that a small constant number of sites is available for the dissociative chemisorption of dihydrogen among bulky hydrocarbon intermediates which cover the surface almost completely. The transition state of the hydrogen chemisorption step was postulated to closely resemble the parent hydrogen molecule, each being affected by the local environment in a very similar way.

Boudart (1969) has grouped reactions on metal catalysts into two classes: structure sensitive and structure insensitive reactions, depending on whether turnover frequency, defined as molecules reacted per second per surface metal atom, is affected by surface structure. It has been pointed out (Poltorak and Boronin, 1966) that one way to study this effect is to study the effect of metal particle size on reaction rate in a critical size range of metal particles from 1 to 5 nm. In this range, the average coordination number of a surface atom goes up with particle size and approaches that of an atom in the surface of the bulk metal. A convenient measure of particle size is the dispersion (Boudart, 1969), defined as the ratio of two numbers: the number of surface metal atoms and the total number of metal atoms. Dispersion D may be obtained by selective chemisorption of a gas to titrate surface atoms of a given kind (Benson and Boudart, 1965; Whyte, 1973). Naturally, it is important, before classifying a reaction to be either structure insensitive or structure sensitive, that no artifacts such as metal support interactions, catalyst deactivation and poisoning, or transport effects play any role while determining the catalytic activity.

As indicated by reviews of Bond and Wells (1964) and Horiuti and Miyahara (1968), a large amount of work on catalytic hydrogenation of alkenes, especially in the vapor phase, has been carried out to elucidate the sequence of elementary steps on metal catalysts. However, comparatively little work (Boudart et al., 1966; Poltorak and Boronin, 1966; Aben et al., 1970; Oliver and Wells, 1973; Schlatter and Boudart, 1972; Coenen et al., 1973) has been done to examine the particle size effect on hydrogenation reactions, especially in the case of heavier, more complex molecules where liquid phase operation becomes necessary. Just as systematic studies regarding the deuteration of olefins and exchange reactions with alkanes, by Kemball and co-workers on metal films and Burwell and co-workers using supported metal catalysts, have contributed importantly to the understanding of elementary processes occurring in the hydrogenation and exchange reactions, examination of the sensitivity of a reaction to surface structure of a metal particle may contribute to the ultimate goal of optimizing a catalyst for a particular reaction.

Controversy still exists as to how olefin molecules are bound to a metal surface. First, an alkene can retain its olefinic character (the doubly bonded carbons being sp^2 hybridized) with π bonding to a single metal atom. Second, it can maintain a single bond between the carbon atoms, which rehybridize to sp^3 hybridization, while bonding via σ bonds to two adjacent metal atoms with the surface intermediate in eclipsed configuration (Burwell et al., 1957). Finally, a π-allylic species bonded to one surface atom can exist if there is a chain of three or more carbon atoms, none of which is quaternary nor occupies a bridgehead position (Rooney, 1963). We shall not concern ourselves with this question here except by indicating that Roth, Geller, and Burwell (1968) have summarized the situation by saying that the relative contributions of the forms of surface intermediates discussed above for alkenes and alkanes on metal catalysts may vary with the hydrocarbon, the metal, and the local site.

Let us now consider the investigations of the liquid phase hydrogenation of cyclohexene on supported platinum catalysts reported in the literature.

Dimitrienko et al. (1966) carried out the liquid phase hydrogenation of cyclohexene at 298°K, using absolute ethanol as solvent, on two 2.43 wt % platinum/silica catalysts with dispersions of 0.98 and 0.40. Before each experiment, the catalyst was oxidized in air at either 293°, 373°, or 673°K and then reduced under atmospheric pressure of hydrogen at 298°K. The authors reported that the rate per unit surface area of the metal, referred to as areal rate, varied approximately twofold as platinum dispersion varied from 0.98 to 0.40. Hence, the reaction can be considered as structure insensitive. However, the authors concluded that there was a significant effect of the temperature at which the catalyst was initially oxidized and that oxygen seemed to behave as an activator. Recently, Schlatter and Boudart (1972) indicated that a possible problem with platinum catalysts supported on silica was the contamination of platinum by residues resulting from desorption of contaminants from silica. In turn, these contaminants could be removed by a short oxidation at 573°K. The data of Dmitrienko et al. (1966) indicate that higher rates were observed when the catalyst was oxidized at higher temperatures. This could mean that cleaner platinum metal was available for the reaction owing to the burning off of carbonaceous impurities at the higher temperatures. This argument may be viewed as an explanation of the role of oxygen as an activator following Poltorak and Boronin (1966).

Hussey et al. (1968) reported reaction rates for the liquid phase hydrogenation of cyclohexene on platinum/aluminum oxide catalysts using cyclohexane as the solvent. Unfortunately, the surface area of platinum metal was not given by these authors who also acknowledge the possibility of mass transfer effects in their work. Thus, no quantitative comparison of this work with ours can be made, and these results will not be discussed further. But the results of Dmitrienko et al. (1966) on the liquid phase hydrogenation of cyclohexene on supported platinum catalysts will be compared to our results in a later section, together with the observations of Phillipson and Burwell (1970) and Smith and Swoap (1966), relative to liquid phase deuteration of cyclohexene on supported platinum catalysts.

EXPERIMENTAL

A mercury diffusion pump backed by a roughing pump was used to provide vacuum and was connected via a trap at 80°K

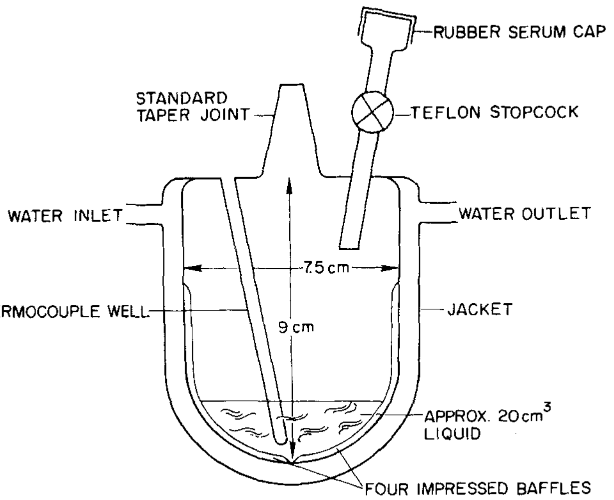

Fig. 1. Laboratory slurry reactor.

TABLE 1. TURNOVER FREQUENCY N OBTAINED ON DIFFERENT SUPPORTED PLATINUM CATALYSTS

Conditions: N corrected for 101.3 kPa H_2; $T = 307^\circ K$
Solvent—20 cm³ cyclohexane; 0.5 cm³ cyclohexene

No.	Catalyst	Dispersion (D)	N (s^{-1})
1	1.5% Pt/SiO_2	1.00	9.16
2	0.38% Pt/SiO_2	1.00	9.02
3	1.46% Pt/SiO_2	0.80	7.67
4	0.6% $Pt/\gamma\text{-}Al_2O_3$	0.70	8.61
5	2.3% Pt/SiO_2	0.62	8.67
6	0.53% Pt/SiO_2	0.56	8.51
7	0.8% Pt/SiO_2	0.34	8.92
8	1.96% $Pt/\eta\text{-}Al_2O_3$	0.23	8.21
9	3.7% Pt/SiO_2	0.14	8.62

to a manifold. Hydrogen (Liquid Carbonic), 99.94% pure with an oxygen impurity of 8 ppm, was passed through an Engelhard Deoxo purifier and a 13X molecular sieve trap before use. A mercury manometer and burette which had a reservoir containing mercury were used in conjunction with a manostat to perform kinetic work at constant pressure. The detailed design of the manostat has been discussed elsewhere (Boudart et al., 1970). Another trap at 80°K and a gold trap were placed just before the point where the reactor was connected to the system.

A Pyrex reactor (Figure 1), 170 cm³ total capacity, had a jacket for constant temperature water, a thermocouple well which dipped into the reactants, a standard taper joint, an arm for injecting fluid into the reactor, and four impressed baffles. The baffles were necessary to break up the swirling liquid and hence provided good agitation. The arm was provided with a tight fitting rubber serum cap held firmly in place with copper wire and changed for every experiment. A Teflon stopcock isolated the serum cap from the reaction zone. The reactor was connected by means of standard taper joints and a flexible Teflon tube to the main apparatus and sat on a specially designed seat which was rocked by a combination of a 40 cm arm attached to the seat at one end and at the other end to a point 2.5 cm off center on a 7 cm diameter wheel which was affixed to a Bodine 1/60 HP series wound right angle gearmotor whose speed was adjusted by a Powerstat variable autotransformer. The usual frequency of agitation was about 6 s^{-1}.

The catalysts used are listed in Table 1 with the corresponding values of platinum dispersion which were measured by the hydrogen-oxygen titration technique described by Benson and Boudart (1965).

Catalysts 1, 2, 5, and 6, prepared according to the method of Benesi et al. (1968), were provided by Dr. H. A. Benesi. The catalysts had been prereduced at 673°K in hydrogen.

Catalyst 4, a commercial reforming catalyst, was obtained from Cyanamid-Ketjen N.V. Its method of preparation is unknown. A small amount of the sample was evacuated at 423°K for 1 hr and reduced under flowing hydrogen at 673°K for 2 hr.

Catalyst 8 was supplied by Exxon Research and Engineering Company. The η alumina, prepared from β alumina trihydrate (Davison Chemical Company) by calcining in air at 866°K for 4 hr, was impregnated with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ and calcined again for 4 hr in air at 866°K. A portion of the sample was evacuated at room temperature and then sintered under flowing hydrogen at 973°K for 9 hr.

Catalysts 3, 7, and 9 were made by the incipient wetness impregnation technique. The silica gel used (60 to 200 mesh, Davison Chemical Company, grade 62) was first tested to find the amount of water required to just reach a point of incipient wetness (about 0.5 cm³ water to 1 g silica). The amount of the platinum compound used was fixed by the desired platinum content.

For catalyst 3, the required amount of $(NH_4)_2Pt(NO_2)_4 \cdot 2H_2O$, obtained from Engelhard, was weighed and dissolved in 2 cm³ of concentrated nitric acid (J. T. Baker Chemical Company) warmed slightly over a hot plate. Double distilled water was added to this solution to the amount required to wet silica gel. The solution was introduced into the silica gel and mixed thoroughly. The sample was then dried overnight in an oven at 353°K. A portion of the sample was evacuated for 1 hr at 423°K and reduced in flowing hydrogen at 673°K for 4 hr. The sample was outgassed while it cooled to room temperature and was then stored.

Catalyst 7 was prepared by impregnating the silica gel by an aqueous solution of chloroplatinic acid (Baker and Adamson). The method of preparation was otherwise unchanged from that used to make catalyst 3. A portion of the same was evacuated at room temperature for ½ hr and then reduced for 2 hr under flowing hydrogen at 673°K. The sample was outgassed while it cooled to room temperature and was then stored.

Catalyst 9 was prepared exactly like catalyst 7. A portion of the sample was evacuated at room temperature for ½ hr, and hydrogen was then passed over it for ¼ hr. The temperature of the sample was then started to be raised, and the flow of hydrogen stopped immediately. The temperature was raised to 673°K, and the sample was kept in static hydrogen for 2 hr. Hydrogen was then passed over the sample at 673°K for 2 more hr. The reduced sample was outgassed and cooled simultaneously and stored.

The chromatoquality grade cyclohexene obtained from Matheson, Coleman, and Bell (MCB) was 99.7+% pure. Chromatoquality grade *p*-dioxane and spectroquality grade ethyl acetate, *n*-heptane, and cyclohexane were obtained from MCB and were all 99+% pure. The methanol used was Baker analyzed spectrophotometric reagent grade from J. T. Baker Chemical Company. The benzene (MCB reagent grade) was distilled over a sodium-potassium alloy in a nitrogen atmosphere before use. All reagents, except cyclohexene, were used without purification. The deuterium (Matheson Gas Products) used had a minimum isotopic purity of 99.5% with an oxygen impurity of 5 ppm.

The deactivation of supported platinum catalysts has been noticed when cycloalkenes have been used, and hydroperoxides have been stated to be the main cause of poisoning (Hussey et al., 1968; Price and Shiewetz, 1957). The cyclohexene was purified by passing it through dry 300 m^2g^{-1} surface area η-γ transitional alumina powder (Kaiser Chemicals) activated at 673°K in flowing helium (Liquid Carbonic, 99.995% pure) which was first passed over copper turnings at 673°K and a trap at 80°K. The cyclohexene was stored under helium in a specially designed flask but not for more than 4 days at a time, after which a new batch of cyclohexene was purified.

Usually 20 to 50 mg of a catalyst sample, of powder size smaller than 70 μm, was used in each experiment. The sample, after being placed in the reactor, was outgassed at room temperature for 2 hr. Enough hydrogen to reach approximately atmospheric pressure was introduced and the catalyst kept in the presence of hydrogen at room temperature for 1/6 hr, after which it was outgassed for ½ hr.

After the outgassing was stopped, hydrogen was added slightly below the pressure at which the reaction was to be carried out (usually atmospheric pressure). The solvent was now introduced via the serum cap and the teflon stopcock. Long stainless steel needles and ground glass syringes were used to introduce liquids into the reactor.

After the solvent achieved a steady temperature (time needed <300 s), purified cyclohexene was added, and hydrogen was introduced until the required pressure was reached, the manostat meanwhile having been switched on.

The agitation and timer were started simultaneously after the initial level of the mercury in the burette had been noted. Zero time was the time when the agitation was started. The elapsed time between the introduction of cyclohexene and the commencement of agitation was less than 60 s. The reaction rate was obtained from the initial slope of the plot of hydrogen consumed vs. time, and as the plot was always linear, the determination of the initial slope was straightforward.

RESULTS

Before we enumerate the various results obtained, it must be shown that the reaction rates reflect only chemical events and that heat and mass transfer do not interfere with the kinetics in this investigation. The criterion used was that proposed by Koros and Nowak (1967) and discussed more fully elsewhere (Madon, 1974).

For two catalysts with platinum loadings of 2.3 and 0.53% and platinum dispersion of 0.62 and 0.56, respectively, the turnover frequency was 8.67 and 8.51 s^{-1} at 307°K and 2.40 and 2.33 s^{-1} at 275°K, respectively. For two other catalysts with platinum loadings of 1.5 and 0.38%, each having a platinum dispersion of 1.00, the turnover frequency was 9.16 and 9.02 s^{-1} at 307°K and 2.67 and 2.51 s^{-1} at 275°K, respectively. The above two batches of catalyst were used for the criterion as their preparation and pretreatment procedures had been identical, and the platinum dispersion for each batch was either identical or almost the same. As the turnover frequency for each set of catalysts was found to be the same within experimental error at two different reaction temperatures, the criterion was satisfied. Thus, there is sufficient reason to neglect all concentration and temperature gradients. Also, there cannot be any significant poisoning or catalyst deactivation influencing the above results (Madon, 1974).

When the hydrogenation of cyclohexene was carried out to completion, it was observed (Figure 2) that after about 80%+ conversion, the plot percent cyclohexene converted vs. time was not linear. This is similar to observations made during the vapor phase hydrogenations of cyclohexene (Segal et al.) and ethylene (Schlatter and Boudart, 1972). Explanation due to poisoning and catalyst deactivation may be rejected, as a second introduction of cyclohexene, after the first sample had been completely reacted, gave the same reaction rate as that observed for the first cyclohexene sample. As it was easy to obtain data in the high conversion regime, in the liquid phase work they were noted and analyzed by the equation (Boudart, 1968)

$$-\ln(1-\bar{x}) = \bar{k}t$$

A straight line was obtained on plotting $-\ln(1-\bar{x})$ vs. t only for points approximately above the 80% conversion mark. This indicates that the order of reaction with respect to olefin changes from zero to first. This may simply be explained by external diffusion, which is a first-order process. The catalyst surface is starved of olefin molecules at very low concentrations, that is, high conversions. Hence, a reactant molecule coming to the surface reacts immediately, and the surface has to wait for more cyclohexene to diffuse to it. Our work is concerned only with the linear portion of the plot in Figure 2, where the reaction rate is zero order with respect to cyclohexene. Figure 3 indicates that rate was first order with respect to hydrogen within experimental error. The rate was also found to be directly proportional to the catalyst weight.

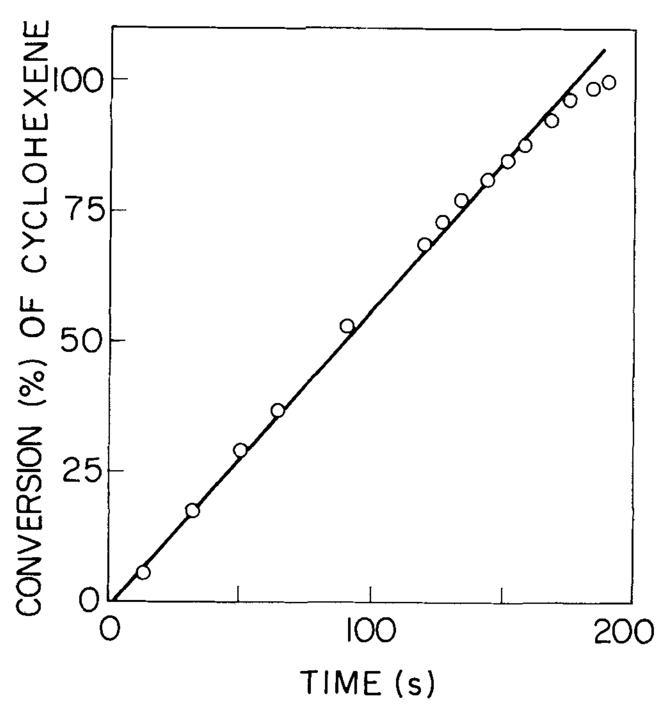

Fig. 2. Conversion (%) of cyclohexene vs. time (s) Catalyst: 1.5% platinum/silica. Dispersion = 1.00. Total pressure: atmospheric pressure. Temperature: 275°K. Solvent: 20 cm^3 *n*-heptane. Reactant: 0.2 cm^3 cyclohexene.

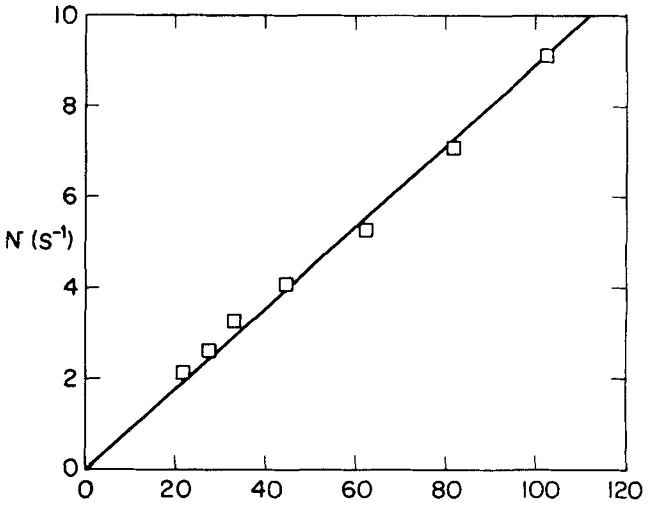

Fig. 3. *N* (s^{-1}) vs. hydrogen pressure (kPa). Catalyst: 2.3% platinum/silica. Dispersion = 0.62. Solvent: 20 cm^3 cyclohexane. Temperature: 307°K.

The hydrogenation of cyclohexene was also carried out in various solvents. Activation energies and pre-exponential factors were obtained for the reaction using four solvents where experimental values for the solubility of hydrogen were available (Gjaldbaek, 1952; Maxted and Moon, 1936; Kruyer and Nobel, 1961; Cook et al., 1957) and in the neat olefin. When experimental values could not be found, the solubilities were calculated according to the method of Gjaldbaek (1952). The rate constant was obtained by multiplying N by the average surface site density of platinum (10^{15} cm^{-2}) and dividing by Avogadro's constant and X. Table 2 gives the values of N and k at 307°K. The values of E and A are summarized in Table 3.

TABLE 2. TURNOVER FREQUENCY N AND RATE CONSTANTS FOR THE HYDROGENATION OF CYCLOHEXENE IN DIFFERENT SOLVENTS

Conditions: $T = 307°K$, values of N corrected for 101.3 kPa H_2
Catalyst—2.3% Pt/SiO_2, Dispersion = 0.62

Solvent	N (s^{-1})	$r \times 10^8$ (mol s^{-1} cm^{-2})	$X \times 10^6$ (mol cm^{-3})	$k \times 10^3$ (cm s^{-1})
Cyclohexane	8.67	1.44	3.97	3.63
n-heptane	12.57	2.09	4.85	4.30
p-dioxane	4.84	0.80	1.90*	4.23
Ethyl acetate	10.15	1.69	3.77	4.47
Methanol	7.92	1.32	3.40*	3.87
Benzene	6.86	1.14	3.07	3.71
Cyclohexene	8.40	1.39	3.57*	3.91

* Calculated values.

TABLE 3. ACTIVATION ENERGIES AND PREEXPONENTIAL FACTORS

Solvent	E_N (kJ mol^{-1})	E_k (kJ mol^{-1})	A_k (cm s^{-1})
Cyclohexane	28.28	24.20	49
n-heptane	32.26	28.32	299
Ethyl acetate	28.17	25.71	111
Benzene	28.44	24.33	54
Cyclohexene	27.91	26.03	112

TABLE 4. THE KINETIC ISOTOPE EFFECT FOR THE HYDROGENATION OF CYCLOHEXENE

Conditions: Values corrected for 101.3kPa H_2 or D_2
Solvent—20 cm^3 *n*-heptane; 0.5 cm^3 cyclohexene
Catalyst—2.3% Pt/SiO_2, dispersion = 0.62

Temperature (°K)	275	283	307	315
$k_{H_2} \times 10^3$ (cm s^{-1})	1.18	1.55	4.30	5.49
$k_{D_2} \times 10^3$ (cm s^{-1})	1.02	1.37	4.45	6.89
k_{H_2}/k_{D_2}	1.16	1.13	0.97	0.80

The activation energy E_k is obtained on plotting k vs. reciprocal temperature, whereas E_N is the activation energy obtained on plotting N vs. reciprocal temperature. Solubility and hence the hydrogen concentration may be written in terms of the Ostwald coefficient which is the volume of gas (cubic centimeters) dissolved in 1 cm^3 of the liquid at a given temperature and pressure and $\beta \propto \exp(-\Delta H_s/R_gT)$ (Gjaldbaek, 1952). For the dissolution of hydrogen in *n*-heptane and benzene, Cook, Hanson, and Alder (1957) report ΔH_s to be 4.2 and 6.3 kJ mol^{-1}, respectively. The addition of the above values of ΔH_s to E_k (Table 3) gives the values 32.5 and 30.6 kJ mol^{-1} which are close to the observed values of E_N within experimental error, that is, 32.3 and 28.4 kJ mol^{-1} for *n*-heptane and benzene, respectively. This may be expected as there is a first-order rate dependence on hydrogen. The variations of the preexponential factors may be due to their sensitivity to experimental errors present in rate determination and hydrogen solubilities. Table 1 gives values of turnover frequency at 307°K obtained with nine supported platinum catalysts. Table 4 gives values of the kinetic isotope effect k_{H_2}/k_{D_2} at various temperatures.

DISCUSSION

Nine catalysts listed in Table 1, with different modes of preparation and pretreatment and dispersion varying from 1.00 to 0.14 corresponding approximately to average platinum particle sizes of 1 to 7 nm, respectively, were used for the liquid phase hydrogenation of cyclohexene. The turnover frequency was found to be independent of the platinum particle size within experimental error (Table 1). Accordingly, the liquid phase cyclohexene hydrogenation reaction on platinum can be considered to be structure insensitive. It is also interesting to note that the catalytic activity of the metal was independent of the nature of the support with silica gel and two different forms of alumina. This observation rules out any significant contribution of the support to the observed rate by hydrogen spillover from the metal to hydrocarbon species adsorbed on the support (Schlatter and Boudart, 1972).

We shall now discuss whether the concentration of hydrogen or its activity should be used in the rate expression and then the sequence of elementary steps involved in the hydrogenation of cyclohexene on supported platinum catalysts.

For a gas-liquid system to be in equilibrium, the chemical potential of each component of the system must be identical in both phases. An alternative criterion for equilibrium is the equality of fugacity of a component in both phases or

$$f^g = f^l$$

Activity may be defined as

$$a = f/f^o$$

where f^o is the standard fugacity. From the above equations, it may be noted that the identity of the activity of a component in the liquid and gas phase may be a condition for equilibrium if the standard state is chosen to be the same in both phases:

$$a^g = a^l$$

As activity can also be defined as the product of the concentration and the activity coefficient, we have

$$\gamma^g c^g = \gamma^l c^l$$

If we choose the standard state to be the ideal gas at 1 atm, the activity coefficient of the gas (in our case hydrogen) may be taken as unity:

$$c^g = \gamma^l c^l = a^l$$

Hence, if we write

$$r = k a^l_{H_2}$$

we have

$$r = k c^g_{H_2}$$

From Table 2 it can be seen that the rates (N or r), all corrected for 101.3 *kPa* hydrogen pressure vary; therefore, the rate constant in the above equation will depend on the solvent.

However, if we write

$$r = k c^l_{H_2}$$

then again, from Table 2, it is seen that k, in this case, is a constant (within ±10%) and is independent of the solvent. This constancy in the value of the rate constant leads us to believe that the concentration of hydrogen in the liquid, rather than its activity, should be used in the rate expression.

The sequence of the elementary steps proposed by Horiuti and Polanyi (1934) for alkene hydrogenation on metal catalysts has been modified to explain the hydrogenation of cyclohexene on supported platinum catalysts as follows:

$$\mathrm{H_2}^l \rightleftarrows \mathrm{H_2}^p \tag{1a}$$

$$\mathrm{H_2}^p + {**} \longrightarrow 2\mathrm{H}{*} \tag{1b}$$

$$R + {**} \rightleftarrows {*}R{*} \tag{2}$$

$${*}R{*} + \mathrm{H}{*} \rightleftarrows R\mathrm{H}{*} + 2{*} \tag{3}$$

$$R\mathrm{H}{*} + \mathrm{H}{*} \longrightarrow R\mathrm{H_2} + 2{*} \tag{4}$$

where p denotes the hydrogen in a precursor state before it undergoes dissociative chemisorption, and the symbol $\rightleftarrows$ denotes equilibrium.

Phillipson and Burwell (1970) have reported the following observations when cyclic olefins are reacted with deuterium in the liquid phase on platinum/aluminum oxide catalysts at 298°K and atmospheric pressure, conditions close to those used in our experiments: 1. there is formation of some isotopically exchanged olefin, 2. there is exchange-addition deuteration leading to cycloalkanes with a range of deuterium contents of 0, 1, 2, and more than 2 deuterium atoms per product molecule, and 3. there is no formation of HD. Phillipson and Burwell further postulate that the only source of deuterium in olefin exchange is given at sites for hydrogenation, and hence alkene exchange and alkene hydrogenation occur at the same sites.

Observations 1 and 2 and similar observations by Smith and Swoap (1966) permit us to treat steps (2) and (3) as being in quasiequilibrium. Step (1*b*) may be taken to be irreversible as no HD formation is observed, the $\mathrm{H_2}$-$\mathrm{D_2}$ exchange being inhibited by the presence of the olefin. The adsorption on platinum at ambient conditions is known to be as follows: alkenes > hydrogen >> alkanes. Alkanes do not chemisorb on metals at temperatures at which our hydrogenation reaction is carried out, as shown by the absence of exchange with deuterium (Burwell, 1969). This, plus the fact that rates are identical when the reaction is carried out in the presence or absence of a large quantity of product alkane, enables us to assume that the product does not play any significant role in the reaction and that step (4) is irreversible.

It is neither necessary for us to assume here whether ${*}R{*}$ or $R\mathrm{H}{*}$ is the most abundant surface intermediate, nor to assume whether the cyclohexene is adsorbed on a single site or is diadsorbed on two adjacent sites, though we have indicated a diadsorbed cyclohexene surface species in step (2).

The hydrogenation process may be envisaged as follows. Since there is a zero-order dependence on cyclohexene, the platinum surface is assumed to be almost completely saturated with hydrocarbon species. Furthermore, a small constant number of unspecified sites located among the bulky hydrocarbon species is accessible for hydrogen chemisorption. Above the chemisorbed layer is a layer of physisorbed solvent. The hydrogen from the gas phase first dissolves in the solvent and then enters the physisorbed solvent layer, the hydrogen now being in a molecular state which is a precursor of the final dissociative chemisorption as $\mathrm{H}{*}$ at low surface coverage. The hydrogenation process then results from the independent addition of two surface hydrogen atoms, the addition being of the cis type, on the side of the double bond which faces the catalyst (Burwell, 1969). The hydrogen molecules in the gas, liquid, and precursor states are in equilibrium with each other.

In accord with the above discussion, we assume that the reaction rate constant measured by us is that for the chemisorption of hydrogen. At the steady state

$$r = r_{1b} = k_{1b} c^p{}_{\mathrm{H_2}} ({**}) \tag{5}$$

where $({**})$ is the concentration of two neighboring active sites which may be expressed (Boudart, 1968) as

$$({**}) = \frac{1}{2} z({*}) \frac{({*})}{(L)} \tag{6}$$

and hence

$$r = k_{1b} c^p{}_{\mathrm{H_2}} \frac{1}{2} z({*}) \frac{({*})}{(L)} \tag{7}$$

From Equation (1*a*)

$$K = c^p{}_{\mathrm{H_2}} / c^l{}_{\mathrm{H_2}} \tag{8}$$

where K is the equilibrium constant for step (1*a*).

On substituting for $c^p{}_{\mathrm{H_2}}$ in Equation (7) and absorbing K and the constant values $1/2\ z\ ({*})/(L)$ and $({*})$ in the rate constant, we get

$$r = k c^l{}_{\mathrm{H_2}} \tag{9}$$

where

$$k = k_{1b} K \frac{1}{2} z({*}) \frac{({*})}{(L)}$$

We shall now try to explain the observation that the rate constant k is independent of the solvent (Table 2) when concentration of dissolved $\mathrm{H_2}$ is used in the rate expression.

Fugacity may be defined as

$$R_g T d(\ln f_i) = d\mu_i \quad (\text{constant } T)$$

or, on integration

$$\mu_i - \mu_i{}^o = R_g T \ln \frac{f_i}{f_i{}^o}$$

where $\mu_i{}^o$ is a constant and a function of temperature only and is the chemical potential of a component at the conditions where $f_i = f_i{}^o$ (the standard state fugacity).

Step (1*b*) may be written using a transition state

$$\mathrm{H_2}^p + {**} \rightleftarrows \ddagger \longrightarrow 2\mathrm{H}{*} \tag{10}$$

For the equilibrium step, we can write

$$\sum_i \nu_i \mu_i = 0 = \sum_i \nu_i \mu_i{}^o + \sum_i \nu_i R_g T \ln f_i / f_i{}^o \tag{11}$$

where the sum is over the species $\mathrm{H_2}^p$, $**$, $\ddagger$. It is convenient to choose the standard state conditions so that the $\mu_i{}^o$'s are solvent independent. Assuming that the solvents do not adsorb onto $**$, we can set

$$f_{**} = f^o{}_{**}$$

However, the hydrogen molecules and transition state may be affected by the solvent, so we choose a hypothetical standard state of pure component at unit fugacity:

$$f^o_{\ddagger} = f_{\mathrm{H_2}P} = f_{\mathrm{H_2}l} = f^o{}_{\mathrm{H_2}g} = 1$$

For mixed systems where the concentrations are very low (or the species are nearly pure), the fugacity is proportional to the concentration

$$f_i = c_i \mathcal{H}_i$$

where $\mathcal{H}_i \equiv \lim\limits_{c_i \to 0} f_i / c_i$ is equivalent to Henry's constant for gases and is solvent dependent. For the very dilute transition state

$$f_{\ddagger} = c_{\ddagger} \mathcal{H}_{\ddagger}$$

while for the hydrogen which is sparingly soluble

$$f^p{}_{\mathrm{H_2}} = c^p{}_{\mathrm{H_2}} \mathcal{H}^p{}_{\mathrm{H_2}} = f^l{}_{\mathrm{H_2}} = c^l{}_{\mathrm{H_2}} \mathcal{H}^l{}_{\mathrm{H_2}} = f^g{}_{\mathrm{H_2}} = x^g{}_{\mathrm{H_2}} P \tag{12}$$

In our experiments, $f^g{}_{H_2}$ is a constant or is solvent independent.

From Equations (11) and (12)

$$c_{\ddagger} = \exp\left[\frac{\mu^o{}_{\circ\circ} + \mu^o{}_{H_2P} - \mu^o{}_{\ddagger}}{R_gT}\right]\frac{c^p{}_{H_2}\mathcal{H}^p{}_{H_2}}{\mathcal{H}_{\ddagger}}$$

$$= \frac{F(T)\mathcal{H}^l{}_{H_2}c^l{}_{H_2}}{\mathcal{H}_{\ddagger}}$$

The rate of reaction may be written as (Boudart, 1968)

$$r = \frac{k_BT}{h}c_{\ddagger}$$

To express the rate in units of mole second^{-1} centimeter^{-2} there should be an additional constant factor α which is the volume of physisorbed solvent per unit area of the platinum. Therefore

$$r = \frac{k_BTF(T)\alpha\mathcal{H}^l{}_{H_2}c^l{}_{H_2}}{h\mathcal{H}_{\ddagger}} \tag{13}$$

Two cases may be developed from the above discussion, and we shall first examine the case which enables us to explain the proportionality of the rate to the liquid phase concentration of hydrogen in the hydrogenation of cyclohexene in several solvents. The transition state may be pictured as one where the hydrogen-hydrogen bond is strong, but the hydrogen-surface bonds are weak. The influence of the surface on the transition state appears to be small, and the complex closely resembles the parent hydrogen molecule. A particular solvent then seems to affect the complex and a hydrogen molecule in an identical way; hence $\mathcal{H}^l{}_{H_2} = \mathcal{H}_{\ddagger}$. Then Equation (13) may be written as

$$r = \text{constant } c^l{}_{H_2}$$

which corresponds to the observations.

The second case may be important when the transition complex is strongly influenced by the catalyst surface and not by the surrounding solvent. In such a case, $\mathcal{H}^l{}_{H_2}$ is not equal to $\mathcal{H}_{\ddagger}$, and $\mathcal{H}_{\ddagger}$ is independent of solvent. Moreover, as shown in Equation (12), $\mathcal{H}^l{}_{H_2}c^l{}_{H_2}$ is also solvent independent. Equation (13) may then be written as r = constant.

In conclusion, it seems that the hydrogen adsorption step which is known to be dissociative (Twigg, 1950; Bond and Wells, 1964; Burwell, 1969), for alkene hydrogenation, takes place, in our case at least, not directly on platinum but on the chemisorbed hydrocarbon species which almost completely cover the metal. Though platinum is necessary, it may not be directly involved in the hydrogen adsorption step, and this concurs with the observation that the hydrogenation reaction is insensitive to the structure of platinum, and also with our proposal that the environment of the hydrogen in the transition state, in our model, is very similar to that of the parent hydrogen molecule in the bulk solvent.

These speculative ideas are closely related to a new interpretation of catalytic hydrogenation of olefins on metals discussed by Thomson and Webb (1976). According to these authors, a general unifying mechanism of these reactions is one in which hydrogen transfer takes place between an adsorbed hydrocarbon species and the adsorbed olefin rather than directly between adsorbed hydrogen and the adsorbed olefin.

A further interesting observation, given in Table 4, indicates that the kinetic isotope effect k_{H_2}/k_{D_2} over the temperature range studied is small. A similar result has been reported by Smith and Burwell (1962) for the hydrogenation of 1-hexene at 298°K on an Adam's platinum catalyst. Our result is particularly intriguing because the classical diving mechanism of activated adsorption with dissociation predicts the rate of hydrogen adsorption to be at least 1.4 times larger than the corresponding adsorption rate for deuterium (Boudart and Taylor, 1952). However, it has been observed in the past that hydrogen and deuterium do chemisorb with identical rates on certain materials such as zinc oxide-chromium oxide, chromium oxide gel, nickel on kieselguhr, and zinc oxide (Pace and Taylor, 1934; Parravano et al. 1959). An explanation offered by Boudart and Taylor (1952) for the identity of hydrogen and deuterium chemisorption rates involves the importance of the active site generation step in the chemisorption process. Such an argument may be applicable in our case where the dissociative chemisorption of $H_2{}^p$ has been proposed to be the kinetically significant step, and where the observed kinetic isotope effect is small. Hence the adsorption sequence is postulated to involve the initial formation of $H_2{}^p$ which interacts with activated sites. Such activation or generation of sites is independent of whether hydrogen or deuterium is used, the type of solvent present, or the platinum surface structure, but may depend on the chemisorbed hydrocarbon species which almost completely cover the metal. Thus, the dissociative chemisorption of $H_2{}^p$ and site activation may both be important steps, in our case, in the adsorption process. This picture of the adsorption process agrees (Madon, 1974) with the kinetic analysis and the explanation regarding the solvent effect given previously.

Finally, we shall compare our data for the liquid phase cyclohexene hydrogenation on supported platinum catalysts to those of Dmitrienko et al. (1966). The hydrogenation rates on platinum/silica catalysts obtained by Dmitrienko et al. are at least one order of magnitude lower than those obtained by us. Dmitrienko et al. observed that the order of reaction with respect to cyclohexene was zero order only up to 50% conversion; this could mean that owing to poisons present in the liquid reagents, the activity of the catalyst decreased as the hydrogenation reaction progressed (Hussey et al., 1968). This could be one reason for observing low rates of reaction. Another reason could be that the data of Dmitrienko et al. may have been influenced by diffusion; unfortunately, no mention was made of precautions taken or tests made to check for mass transport effects.

NOTATION

a = activity
A_k = preexponential factor of rate constant cm s^{-1}
c = concentration, mol cm^{-3}
D = dispersion
E = activation energy, kJ mol^{-1}
f = fugacity
f^o = standard state fugacity
$\mathcal{H}$ = Henry's constant
ΔH_s = enthalpy of solution, kJ mol^{-1}
h = Planck's constant
K = equilibrium constant
k = rate constant, cm s^{-1}
$\bar{k}$ = constant, s^{-1}
k_B = Boltzmann's constant
(L) = total number of surface sites/cm^2
N = turnover frequency, s^{-1}
P = total gas pressure, kPa
R = cyclohexene
RH = half hydrogenated intermediate

R_g = gas constant
r = reaction rate, mol s^{-1} cm^{-2} of metal
T = temperature, °K
t = time, s
X = solubility, mol cm^{-3}
x = mole fraction
$\bar{x}$ = fractional conversion
z = number of nearest neighbors of a surface atom

Greek Letters

α = volume of physisorbed solvent per unit area of platinum
β = Ostwald coefficient, dimensionless
γ = activity coefficient
μ = chemical potential
μ^o = standard chemical potential
ν = stoichiometric coefficient

Symbols

$\ddagger$ = transition state
$*$ = vacant site
$**$ = adjacent dual vacant sites
$\rightleftarrows$ = equilibrium

Superscripts

g = gas
l = liquid
p = physisorbed layer precursor state

Subscript

i = component 1, 2, 3 . . . . . .

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