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Catalytic Hydrogenation of Cyclohexene

3. Gas-Phase and Liquid-Phase Reaction on Supported Palladium

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The hydrogenation of cyclohexene was studied in both gas and liquid phases on six different palladium catalysts supported on silica gel and alumina between 264 and 308 K at hydrogen pressures from 4 to 89 kPa, cyclohexene partial pressures from 0.46 to 1.5 kPa, and cyclohexene concentrations from 0.15 to 3.0 *M*. Under these conditions the turnover frequency is independent of particle size (1.5 to 10 nm) in both liquid and gas phases, of the nature of the support, and of the nature of nonaromatic solvents (methanol, *n*-heptane, ethyl acetate, and cyclohexene). The order of reaction was one-half with respect to hydrogen for the reaction in both liquid and gas phases and zero with respect to cyclohexene partial pressure (gas phase) or with respect to cyclohexene molar concentration (liquid phase). At the same temperature and hydrogen pressure, the turnover frequency was about twice as high in the gas phase as in the liquid phase.

INTRODUCTION

The mechanism of the hydrogenation of alkenes on metal catalysts has been the subject of many investigations (*1*). In 1934, Polanyi and Horiuti (*2*) proposed a mechanism for the hydrogenation of ethylene on the surface of metallic nickel. This mechanism still appears to give a good representation of many aspects of catalytic hydrogenation and related reactions on metals of group VIII, particularly nickel, platinum, palladium, and rhodium.

Information obtained from studies using isotopic hydrogen both in exchange reaction with saturated hydrocarbons (*3–5*) and in the hydrogenation of alkenes (*6–9*) has contributed particularly to the present state of understanding of these reactions. On the other hand, kinetic data, especially areal rates, are relatively scarce, especially for the hydrogenation of cyclic olefins. In particular, with supported metals, it is of interest to determine the effect of metal particle size on turnover frequency. We have reported recently the lack of such an effect for the hydrogenation of cyclohexene, in both gas (*10*) and liquid phases (*11*) on different supported platinum catalysts. The present paper reports similar work on supported palladium. Among previous investigations of the hydrogenation of cyclohexene on supported palladium catalysts (*12–16*) only one (*12*) gives the surface area of palladium metal. At any rate, earlier results will be discussed below together with our own results.

REACTION IN GAS PHASE

Experimental Apparatus

The gas-phase reaction of cyclohexene with hydrogen was studied in a Pyrex batch-recirculation system (*17*) under con-

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ditions designed to obtain kinetic data free from all transport influences. The reactor was a glass chamber 25 mm in diameter and about 15 mm high with a medium-grade fritted disk to support the catalyst in amounts between 3.5 and 10 mg. A glass coil above the reactor served to preheat or precool the reaction gases. The reactor was immersed in a Dewar through which was flowed a 50% v/v solution of water and ethylene glycol, from a thermostated bath. The temperature was measured with a thermocouple inserted into a well extending through the reactor wall to a point just above the center of the fritted disk. The gases were circulated by a noncontaminating gas-recirculating pump (*18*). A flow rate of 960 cm^3 min^{-1} was used in a system of 2.34 liters total volume, and 23-cm^3 samples were withdrawn at approximately 8-min intervals for chromatographic analysis. A bypass in the system made it possible to introduce and mix the reactant gases in the loop while the catalyst in the reactor was still in pretreatment stages. In order to facilitate sampling, another bypass permitted samples to be taken without interruption of the flow over the catalyst. The samples were obtained with a Varian–Aerograph XA-210 six-way sample valve and were analyzed in a Varian–Aerograph A-90-P chromatograph equipped with a 3-m column of 70% Chromosorb P and 30% dibutylphtalate which operated at 373 K.

Matheson, Coleman and Bell chromatoquality cyclohexene was used after purification through an activated alumina column in order to remove peroxides and traces of oxygen. The Al_2O_3 column was treated with flowing He at 693 K for 1 h, and a bulb with cyclohexene was then attached to the column, after which a freeze–pump–thaw technique was used to bring the cyclohexene to the storage bulb. The hydrogen, 99.932% pure, was further purified by diffusion through a Milton Roy hydrogen diffuser. Helium (99.995% pure) was used after passage through a glass coil at 78 K.

TABLE 1

Koros and Nowak Criterion[a]

Catalyst	Dispersion (%)	Turnover frequency (sec^{-1})	
		273 K	283 K
3.75% Pd/SiO_2	55	0.72	1.36
0.57% Pd/SiO_2	60	0.76	1.42

[a] See Ref. (*23*). Conditions: hydrogen pressure, 10.64 kPa; cyclohexene pressure, 1.0 kPa.

Catalysts

The amount of palladium in the six supported catalysts described below was determined by atomic absorption. It is reported as a weight percentage. A catalyst from Engelhard Industries, 4.88% Pd/Al_2O_3, was reduced at 773 K in hydrogen, outgassed at that temperature, and cooled down to room temperature. Then it was exposed to air prior to use. The dispersion of palladium was determined to be 0.21 by the titration method of Benson *et al.* (*19*) which was used for all other catalysts as well. Values of dispersion are given in Table 2. A 2.84% Pd/SiO_2 catalyst was prepared by impregnation using a measured amount of $PdCl_2$ dissolved in a small quantity of concentrated HCl. The resulting solution was evaporated to boil off excess acid and distilled water was added to obtain the required amount of salt solution to just reach the point of incipient wetness of the support (Davison silica gel, Grade 62). The catalyst was calcined for 4 h in air at 723 K and reduced in hydrogen at 773 K. Four catalysts, 0.57% Pd/SiO_2, 1.39% Pd/SiO_2, 1.45% Pd/SiO_2, and 3.75% Pd/SiO_2, were prepared by cation exchange (*20, 21*). The first step of preparation was to exchange NH_4^+ from a 1:1 diluted NH_4OH solution to the surface of the silica gel. The silica gel was 50/100-

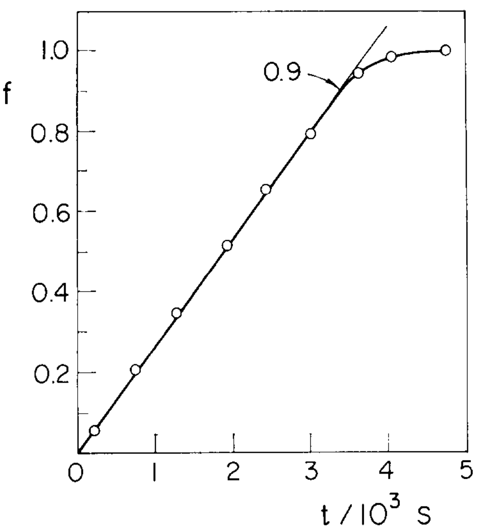

FIG. 1. Hydrogenation of cyclohexene: fractional conversion f versus time t. Catalyst: 4.88% Pd/Al_2O_3; dispersion: 21%; Temperature: 273 K; $P_{H_2}/P_{cyclohexene}$: 100.

mesh Davison Grade 62. The second step was the cation exchange between the $Pd(NH_3)_4^{2+}$ ion from the solution and the surface NH_4 ions. The $Pd(NH_3)_4Cl_2$ solution was prepared by dissolving $PdCl_2$ in concentrated NH_4OH solution at 348 K and then diluting to obtain a 0.01 *M* solution. The palladium salt solution was slowly added to a slurry of the support in 1:1 dilute NH_4OH solution. The slurry was stirred for 2 h at 348 K. The next step of preparation was to filter the slurry. The filtrate was washed with distilled water and dried *in vacuo* in an oven overnight at room temperature. The catalysts were calcined in air at 723 K for 4 h and reduced at 773 K in hydrogen.

Procedure

The standard pretreatment of the catalysts listed above consisted of a 3-h outgassing at room temperature (pressure: 1.3×10^{-3} Pa), followed by 1-h reduction in flowing hydrogen (75 cm^3 min^{-1}) at room temperature. After the reduction, the two stopcocks of the reactor were closed to maintain the catalyst saturated with hydrogen (adsorbed and absorbed) and the rest of the system was outgassed for 0.5 h. As the catalyst was being reduced, the reactant gases were added and circulated through the system, bypassing the reactor. The gases were introduced in the following order: cyclohexene (0.46 to 1.46 kPa), hydrogen (4.52 to 88.3 kPa), and helium (to balance the system at atmospheric total pressure). The circulation of the thermostatic bath solution was started. When the reactor had reached the reaction temperature, the reactants were admitted to the catalyst chamber. The first sample for chromatographic analysis was taken after 3 min, allowing for thorough mixing within the recirculating system loop. The subsequent samples were taken at time intervals ranging from 480 to 600 sec, depending upon the reaction rate. The reaction rate was taken as the average between the initial slopes of the plot of quantity of product (cyclohexane) and quantity of reactant (cyclohexene) versus time.

Results

The reaction rate is given as turnover frequency (*22*) defined as the average number of molecules of cyclohexane produced

TABLE 2

Effect of Palladium Dispersion[a]

Condition	Gas phase	Liquid phase
Temperature (K)	273	308
Hydrogen pressure	10.64 kPa	Atmospheric
Cyclohexene pressure or concentration	1.0 kPa	0.24 *M* in cyclohexane

Loading (%)	Support	Dispersion (%)	Turnover frequency (sec^{-1})	
			Gas phase	Liquid phase
2.84	SiO_2	11	0.58	6.54
4.88	Al_2O_3	21	0.97	7.95
3.75	SiO_2	55	0.72	6.54
0.57	SiO_2	60	0.76	6.47
1.39	SiO_2	70	0.80	8.25
1.45	SiO_2	76	0.90	7.96

and cyclohexene consumed per surface palladium atom per second (N sec^{-1}) under the conditions indicated. The rate was zero with respect to cyclohexene (Fig. 1) and one-half order with respect to hydrogen (Fig. 2).

The absence of both internal and external heat and mass transfer limitation are indicated by the values of N shown in Table 1. The absence of any significant change in N at two different temperatures, with two different catalysts that differ sevenfold in metal loading but have similar dispersion, is a convincing test that the reaction rates are correctly measured (*23, 24*).

No effect of metal dispersion on the reaction rate was found as shown in Table 2 so that the hydrogenation of cyclohexene on supported palladium can be regarded as a structure-insensitive reaction (*25–27*).

The temperature dependence of the rate constant k, i.e., the apparent activation energy E_g, was found to be 38.90 kJ mol^{-1} (Fig. 3) and the preexponential factor was 8.45×10^6 sec^{-1} kPa$^{-\frac{1}{2}}$.

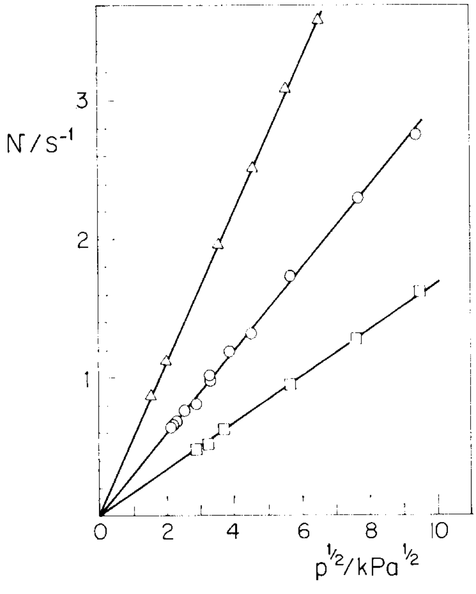

FIG. 2. Effect of hydrogen partial pressure on the turnover frequency for the gas-phase hydrogenation of cyclohexene. Catalyst: 4.88% Pd/Al_2O_3; dispersion: 21%. (□) 264 K, (○) 273 K, (△) 283 K.

TABLE 3

Hydrogenation of Cyclohexene is Zero Order in Hydrocarbon Molar Concentration[a]

Cyclohexene concentration (M)	Turnover frequency (sec^{-1})
3.01	7.79
1.88	7.77
1.10	7.85
0.69	7.69
0.24	7.73
0.15	7.74

[a] Conditions: hydrogen pressure, atmospheric; temperature, 308 K; catalyst, 4.88% Pd/Al_2O_3; $D = 0.21$; solvent, cyclohexane.

REACTION IN LIQUID PHASE

Apparatus

The apparatus described earlier (*11*) and shown in Fig. 4 was used to study the liquid-phase hydrogenation of cyclohexene. The vacuum was provided by a roughing pump and a mercury diffusion pump connected to the system via a trap at 78 K. The reaction temperature was controlled by pumping water from a thermostatic bath, through the reactor jacket. The water flow rate was controlled with a variable transformer. The temperature of the reactor mixture was measured by a thermocouple inserted into a well through the reactor wall, which dipped into the reactants. The reactor (180 cm^3, total capacity) was connected to the apparatus via a standard taper joint and a flexible Teflon tube. It also had an arm with a Teflon stopcock and a rubber serum cap through which the reactant (cyclohexene) and the solvents were introduced. The reactor was agitated at a frequency of 350 min^{-1}. The total pressure in the system was controlled by a constant-pressure device (*24, 28*). Hydrogen was passed through an Engelhard Deoxo purifier and a 13× molecular sieve trap. Helium, used in the treatment and storage of cyclohexene, was passed through

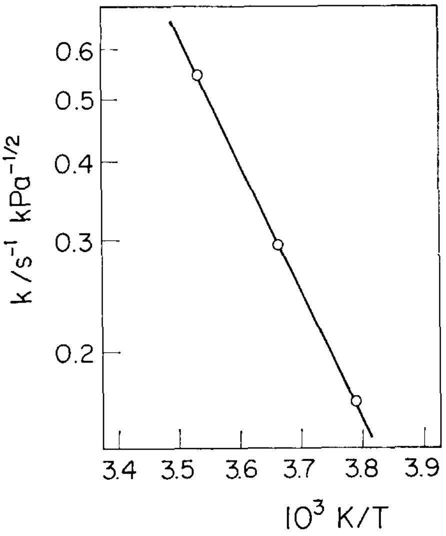

FIG. 3. Arrhenius plot for the gas-phase hydrogenation of cyclohexene. Catalyst: 4.88% Pd/Al_2O_3; dispersion: 21%.

a trap at 723 K containing copper turnings and then through a 13X molecular sieve trap at 78 K. The cyclohexene was purified as described above and elsewhere (*11, 24*) from the hydroperoxides. The solvents (spectroquality) were used without any additional purification.

The catalysts used were the same as those described above. The reaction was carried out with catalyst particles smaller than 44 μm (greater than 325 mesh). It was found that, with particle sizes greater than 100 μm (lower than 200 mesh), mass transport effects play a dominant role (*11, 24*).

Procedure

The catalyst was dried *in vacuo* in an oven overnight at 383 K, weighed, and placed in the reactor which was connected to the apparatus (Fig. 4). The temperature of traps A and B was at 78 K whereas the 13X molecular sieve (C) was at room temperature. Stopcocks 3, 4, and 5 were kept closed. The line connecting trap C with the rest of the apparatus was isolated from the vacuum line. Stopcock 6 was opened and the reactor and catalyst were evacuated for 10 min while the Teflon stopcock on the reactor was open. Stopcock 6 was then closed, the liquid nitrogen Dewar on trap B was removed, and the trap was evacuated for 15 min in order to remove oxygen and water vapor collected in the trap. The Dewar with liquid nitrogen was placed on the trap and the whole apparatus was then evacuated (stopcock 6 and Teflon stopcock on the reactor were open while the catalyst outgassed for 2 h at room temperature pressure, 1.3×10^{-2} Pa). After turning stopcock 1, to stop evacuation, hydrogen was admitted into the apparatus. The catalyst was kept in the presence of hydrogen at room temperature for 1 h. At this time, stopcocks 4 and 5 were opened to fill up the burette with hydrogen while the pressure was controlled by observing the Hg manometer.

The hydrogen was introduced until the total pressure was near to the reaction pressure. The water from the thermostatic bath at the reaction temperature was circulated around the reactor. The solvent was now introduced, through the serum cap and the Teflon stopcock, with a 15-cm-long stainless steel needle and glass syringe.

Agitation of the reactor was started to make it easy for the solvent to achieve a steady temperature and saturation in hydrogen. After 10 min, agitation was stopped, purified cyclohexene was added, and hydrogen was introduced until the total pressure reached the desired value. Meanwhile the manostat controlling the total pressure was switched on. Stopcock 1 was turned to isolate the apparatus from the arm connected with trap C and the vacuum system. After the initial level of the Hg in the burette had been noted, the agitation and the timer were started simultaneously. The reaction rate, at constant pressure, was calculated by taking the initial slope of the plot of the volume of hydrogen consumed versus time.

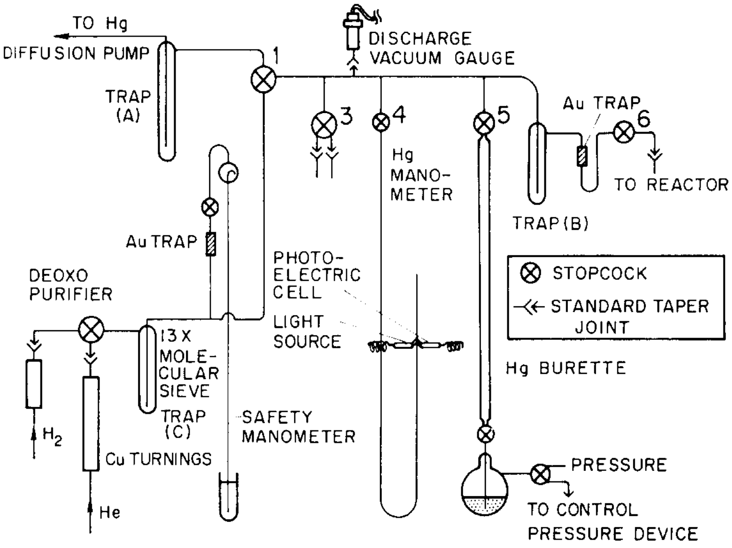

Fig. 4. Main apparatus for liquid-phase hydrogenation.

Results

The rates are given as turnover frequency as previously defined. The initial rates of reaction of cyclohexene with hydrogen have been corrected for the changes in the partial pressure of hydrogen in the reaction flask resulting from the solvent vapor pressure.

As in the gas phase, we used the Koros–Nowak criterion to examine the gradientless behavior of the reacting system. For two catalysts with palladium loadings of 0.57 and 3.75% and palladium dispersions of 60 and 55%, respectively, values of N were 6.47 and 6.54 $\sec^{-1}$ at 308 K. Corresponding values were 2.70 and 2.79 $\sec^{-1}$ at 288 K. Thus our kinetic data are free from all transport influences and besides the catalyst was perfectly suspended in the liquid mixture (Fig. 5).

The order was one-half with respect to hydrogen pressure (Fig. 6). The dependence of the reaction rate on substrate concentration corresponds to zero order. The hydrogenation of cyclohexene was also carried out in different solvents (Table 5). The apparent activation energy E_1 was obtained from an Arrhenius plot (Fig. 7) and it was found to be 31.81 kJ mol^{-1}. The preexponential factor was 1.96×10^5 $\sec^{-1}$ $\text{kPa}^{-\frac{1}{2}}$. The six catalyst supports listed in Table 2, with different modes of preparation and dispersion varying from 11 to 76%, were used. The average palladium particle size of the catalysts varied from 1 to 8 nm (*21*). The turnover frequency was found to be independent of palladium dispersion (Table 2), just like in the gas phase.

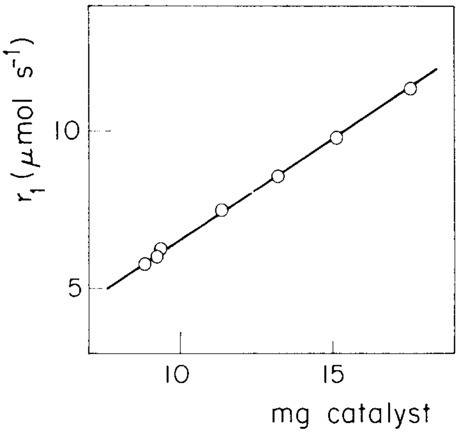

Fig. 5. Reaction rate r as a function of the weight of catalyst for the liquid-phase hydrogenation of cyclohexene. Catalyst: 4.88% Pd/Al_2O_3; dispersion: 21%; temperature: 308 K; solvent: cyclohexane; hydrogen pressure: atmospheric.

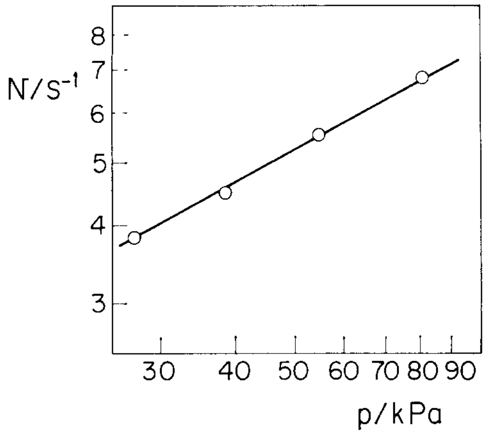

FIG. 6. Hydrogenation of cyclohexene: effect of hydrogen pressure on turnover frequency. Catalyst: 4.88% Pd/Al_2O_3; dispersion: 21%; temperature: 308 K; solvent: cyclohexane.

DISCUSSION

Using the Koros–Nowak criterion, we have shown that our catalytic data, in both liquid and gas phases, are free from transport influences. With confidence in our rate data, we think the salient result of the work is the observation that, with values of palladium dispersion from 11 to 76% corresponding to average particle size from 1 to 8 nm, the turnover frequency is independent of the palladium particle size within experimental error, in both liquid and gas phases (Table 2). Thus the hydrogenation of cyclohexene on palladium is structure insensitive as it was found to be on platinum (*10, 11*). In addition the catalytic activity of the metal is independent of the nature of the support when silica gel and alumina are used as supports.

According to Polanyi and Horiuti (*2*) the addition of hydrogen to an olefin is described by the following elementary process.

$$\mathrm{R} + 2* \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} *\mathrm{R}* \qquad (1)$$

$$\mathrm{H_2} + 2* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2\mathrm{H}* \qquad (2)$$

$$*\mathrm{R}* + \mathrm{H}* \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{RH}* + 2* \qquad (3)$$

$$\mathrm{RH}* + \mathrm{H}* \xrightarrow{k_4} \mathrm{RH_2} + 2* \qquad (4)$$

It has been shown that cycloalkanes do not dissociatively chemisorb on palladium catalysts under our conditions (*3, 5*), hence the addition of the second hydrogen in step 4 can be regarded as irreversible. But the formation of large amounts of exchanged alkene when deuterium is used is enough evidence that addition of the first hydrogen and olefin adsorption are highly reversible (*5, 6, 13*). The appearance of a small amount of HD in the gas phase shows that hydrogen adsorption is also reversible (*6, 13*).

We now assume that hydrogen chemisorption, step 2, is in equilibrium with constant k_2 and that the most abundant surface intermediate is the half- hydrogenated state, RH*, covering almost en-

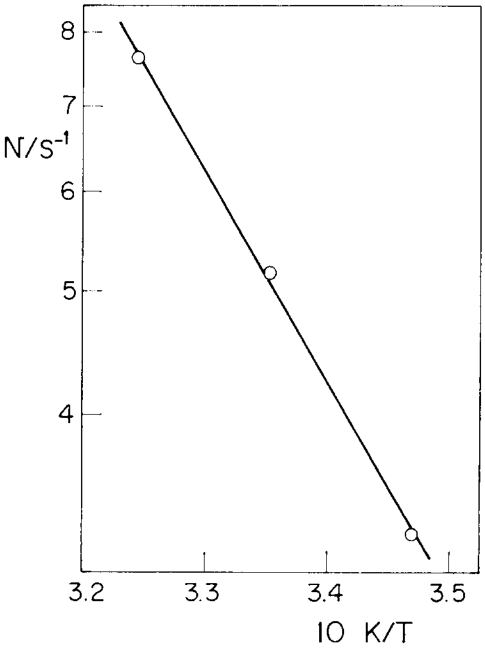

FIG. 7. Arrhenius plot for the liquid-phase hydrogenation of cyclohexene. Catalyst: 4.88% Pd/Al_2O_3; dispersion: 21%; hydrogen pressure: 101.1 kPa; solvent: cyclohexane.

tirely the available surface. These assumptions are compatible with the small amount of HD found in the gas phase, the appearance of deuterium in the olefin when deuterium is used, and the zero order of reaction with respect to hydrocarbon.

With the additional assumption that chemisorbed hydrogen covers only a small fraction of the free sites, we have

$$(L) \simeq (\mathrm{RH}*) \quad \text{and} \quad (\mathrm{RH}*) \gg (*) \gg (\mathrm{H}*),$$

where (L) is the number of active sites per unit area of metal and (RH*), (*), and (H*) are the concentrations of the half-hydrogenated state, the free active sites, and the atomic hydrogen adsorbed, respectively.

Under these conditions the rate r of reaction is that of step 4 and is given by

$$r = r_4 = (L)k_4k_2^{\frac{1}{2}}(\mathrm{H}_2)^{\frac{1}{2}},$$

in agreement with the kinetic results.

No solvent effect was found with nonaromatic solvents, polar or nonpolar, which did not compete for the sites with the cyclohexene or with the hydrogen shown by our results with methanol, ethyl acetate, cyclohexane, and *n*-heptane, and also by the results of others with acetone and *n*-hexane (*14*, *15*). But with aromatic solvents such as benzene and toluene the reaction rate depended strongly on the relative concentration of the cyclohexene and benzene (Table 4). The more basic solvent xylene competes more strongly for the surface than benzene. Neither benzene nor xylene are hydrogenated under our experimental conditions.

TABLE 4

Cyclohexene Hydrogenation in Different Solvents[a]

Solvent	Turnover frequency (sec^{-1})
Methanol	7.85
n-Heptane	7.98
Ethyl acetate	7.93
Cyclohexane	7.80
Benzene	0.58
Benzene[b]	2.78
Xylene[b]	2.49

[a] Conditions: hydrogen pressure, atmospheric; temperature, 308 K; catalyst, 4.88% Pd/$\mathrm{Al_2O_3}$; $D = 0.21$; cyclohexene concentration: 0.24 M.

[b] Cyclohexene concentration: 3.01 M.

In Table 5 we report the value of the turnover frequency for the hydrogenation of cyclohexene in liquid and gas phases, under the same conditions of temperature and hydrogen pressure. The turnover frequency for gas-phase hydrogenation is twice the turnover frequency for liquid-phase hydrogenation.

Although the fraction of the surface covered by the half-hydrogenated state appears to be almost unity, increasing the cyclohexene concentration should increase the surface coverage of the half-hydrogenated state with a reduction in the available surface area for hydrogen chemisorption. In the liquid phase, the cyclohexene concentration was from 0.2 to 3 M, but in the gas phase the largest concentration was only about 6×10^{-4} M. Thus it appears that the difference between the turnover frequency in liquid and gas phases is due to the difference in the fraction of the surface covered by the half-hydrogenated

TABLE 5

Turnover Frequency for Cyclohexene Hydrogenation in Liquid and Gas Phases[a]

	Turnover frequency (sec^{-1})	
	Gas phase	Liquid phase
(a) Temperature: 283 K Hydrogen pressure: 53.2 kPa	4.0	1.9
(b) Temperature: 288 K Hydrogen pressure: 53.2 kPa	5.32	2.40

[a] Conditions: catalyst, 4.88% Pd/$\mathrm{Al_2O_3}$; $D = 0.21$.

state, because of the different cyclohexene concentrations used in liquid and gas phases. We are not aware of any other clear-cut quantitative comparison between catalytic rates in both gas and liquid phases.

Finally, our data for the hydrogenation of cyclohexene on palladium catalysts will be compared to those of others.

The hydrogenation rates in liquid phase on palladium black catalysts were reported by Spitsyn *et al.* (*12*). The value of the turnover frequency (assumption: 1.2×10^{15} sites cm^{-2}) are $N = 1$ sec^{-1} for a palladium black prepared by the Zelinskii method and $N = 0.7$ sec^{-1} for the palladium black prepared by a method involving radiation, both at atmospheric hydrogen pressure and at 293 K. The turnover frequency obtained by us for the same experimental conditions is 4.1 sec^{-1}, which is four times greater than that obtained by Spitsyn *et al.* (*12*). These authors also report reaction orders in complete agreement with ours, with respect to the kinetic order of both cyclohexene and hydrogen.

Hussey and Nowack (*13*) studied the liquid-phase hydrogenation of cyclohexene on two Pd/Al_2O_3 catalysts. Unfortunately, as no palladium dispersion was reported, a turnover frequency could not be obtained from their data. The reaction orders found by Hussey and Nowack were 0.2 to 0.3 with respect to cyclohexene and 0.45 ± 0.05 with respect to hydrogen pressure. But Hussey and Nowack state that their rates reflect an intrinsic zero-order process upon which a first-order hydrogen pore-diffusion process is superimposed. Hussey and Nowack used 150- to 200-mesh particles, and, with this size of catalyst particles, the rates of liquid-phase hydrogenation of cyclohexene on platinum are indeed influenced by intraparticle diffusion (*24*).

Druz *et al.* (*14*) studied the hydrogenation of cyclohexene in mixtures of methanol and *n*-hexane on palladium black. The surface area of the metal catalyst is not given. They found that the reaction rate does not depend on solvent composition. The same authors (*15*) carried out the reaction of hydrogenation of a mixture of cyclohexene and acetone on palladium. They found that the rate of cyclohexene hydrogenation does not depend on solvent composition and that acetone is hydrogenated to a negligible extent. Our results with nonaromatic solvents are in agreement with those of Druz *et al.* (*15*).

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