The Kinetics of the Hydrogenation of Cycloalkenes on Palladium–Alumina Catalysts[1]

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Reaction rates for the hydrogenation of bicyclo[2.2.1]heptene, cyclopentene, cyclohexene, cycloheptene, and cyclooctene from solution in cyclohexane on alumina-supported palladium catalysts are reported. The observed rates at 25.0° near 1 atm are first order in catalyst but they exhibit a fractional order dependence both upon the concentration of the cycloalkene and also upon the hydrogen pressure. The apparent activation energy for cyclohexene is 5.7 ± 0.5 kcal mol^{-1}. The fractional order dependence of the rates upon the cycloalkene concentration is explained in terms of a reversible chemisorption of the alkene, while the fractional order dependence upon hydrogen pressure is viewed to reflect an intrinsic zero-order dependence upon which is superimposed a first-order pore diffusional process involving hydrogen.

We have recently reported on the kinetics of the hydrogenation of a number of cycloalkenes from solution in cyclohexane using alumina-supported platinum catalysts near room temperature and hydrogen pressures near 1 atm.[2] Very considerable care was found to be essential to guarantee the absence of catalyst-poisoning impurities; otherwise the reaction rates were not reproducible. These reactions with platinum catalysts were found to be first order in hydrogen pressure and in the amount of catalyst added, but to be zero order in cycloalkene concentration. These findings led us to modify the Horiuti–Polanyi mechanism[3] for hydrogenation at platinum surfaces to have chemisorption of the alkene irreversible.

Our attention quite naturally turned to palladium catalysts. These are about as popular as platinum catalysts for the hydrogenation of nonaromatic carbon unsaturation. Indeed, for nonconjugated double bonds the two catalysts are often used interchangeably. The two are, however, quite different in several ways. Palladium is very selective in promoting the stepwise addition of pairs of hydrogen atoms to alkynes, allenes, and 1,3-dienes while platinum is not.[4] Platinum, on the other hand, promotes the isomerization only of exceptional alkenes under hydrogenation conditions;[2] in contrast, isomerization of alkenes on palladium is extensive and is even appreciably faster than hydrogen addition with some.[5] Likewise, the two catalysts differ considerably in stereochemical specificity where *cis-* and *trans*-dialkylcycloalkanes can be formed,[5a,b] in their ability to exchange deuterium for protium in alkenes and alkanes,[6] and in their promotion of the disproportionation of cyclohexenes.[7]

The reason for such differences in catalytic activity is obscure. One inference is that the details of the surface reactions which take place on these two catalysts differ considerably at the least; it is possible that there are fundamental differences in the surface reactions on the two catalysts.

A knowledge of the kinetics of a reaction being an important component of any meaningful discussion of its mechanism, we report here the results of kinetic studies of hydrogen addition to cycloalkenes from the liquid phase at palladium surfaces. These are counterpart to our earlier studies using platinum catalysts.[2]

Experimental Section

The Apparatus.—The hydrogenation apparatus used in this study was that developed for studies using platinum catalysts.[2]

Catalysts.—Hot aqueous solutions of *trans*-dinitrodiammine-palladium(II),[8] which had been several times recrystallized from water, were stirred for several hours with η-alumina[9] on the steam bath, following which the impregnated supports were filtered at the water pump and dried at 100°. These were then heated in a stream of oxygen in a muffle furnace, cooled under high purity nitrogen, and activated with purified electrolytic hydrogen at 350° as before.[2]

Two 150–200 mesh alumina supports were used in the research reported here. One had a surface of 208 m^2 g^{-1}; the other, 227 m^2 g^{-1}. Both were prepared by the method of Selwood[10] but the higher surface support was washed exhaustively with *hot* distilled water before being fired. This support also differed from the lower surface one by having much less alkaline material (traces *vs.* 2%) which could be extracted by boiling water.

One catalyst used in this research (PDG-1) was prepared using the lower area support. It had 0.74% palladium[11] but was appreciably less active than a second (PDG-2) which was prepared from the higher area support. The metal content of the latter as only 0.57%.

Solvents and Substrates.—The same painstaking care as before[2] was found to be required for the observed rates to be reproducible. If anything, these palladium catalysts are even more sensitive to catalyst-poisoning impurities than the platinum catalysts used in the previous study.

Catalyst and Cycloalkene Dependence.—In a typical experiment, 21.64 ± 0.05 mg of PDG-1 catalyst was placed in the reaction flask. The system was evacuated and flushed five times with hydrogen, then the hydrogen pressure was set near 760 mm, and 0.700 ± 0.005 ml of highly purified[2] cyclohexane was injected *via* the entry port. After 20-min agitation to equilibrate the catalyst and to attain temperature equilibrium at $25.0 \pm 0.1°$, 0.080 ± 0.005 ml of high purified[2] cyclohexene was added. The pressure was readjusted close to 760 mm, agitation was begun, and hydrogen volumes were noted and recorded at 30-sec intervals.

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[1] We make grateful acknowledgment for support of this research from the National Science Foundation (GP 4656).

[2] A. S. Hussey, G. W. Keulks, G. P. Nowack, and R. H. Baker, *J. Org. Chem.*, **33**, 610 (1968).

[3] M. Polanyi and J. Horiuti, *Trans. Faraday Soc.*, **30**, 1164 (1934).

[4] See W. G. Young, R. L. Meier, J. Vinograd, H. Bollinger, L. Kaplan, and S. L. Linden, *J. Amer. Chem. Soc.*, **69**, 2046 (1947). See also E. F. Meyer and R. L. Burwell, Jr., *ibid.*, **85**, 2877 (1963).

[5] (a) S. Siegel and G. V. Smith, *ibid.*, **82**, 6087 (1960); (b) J-F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **83**, 3874 (1961); (c) G. V. Smith and J. R. Swoap, *J. Org. Chem.*, **31**, 3904 (1966); (d) A. W. Weitkamp, *J. Catal.*, **6**, 431 (1966).

[6] See (a) E. F. Meyer and C. Kemball, *J. Catal.*, **4**, 711 (1965), and (b) K. Schrage and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **88**, 4549 (1966), for recent examples.

[7] A. S. Hussey, T. A. Schenach, and R. H. Baker, *J. Org. Chem.*, **33**, 3258 (1968).

[8] N. L. Cull and H. B. Jonassen, *Inorg. Syn.*, **4**, 179 (1953).

[9] H. C. Stumpf, A. S. Russell, J. W. Newsome, and C. M. Tucker, *Ind. Eng. Chem.*, **42**, 1398 (1950); see also H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, **82**, 2471 (1960).

[10] P. W. Selwood, *Advan. Catal.*, **3**, 41 (1951).

[11] We are indebted to Dr. G. R. Lester, Universal Oil Products Co., Des Plaines, Ill., for the determination of the palladium content of these catalysts and the pore distribution in the supports.

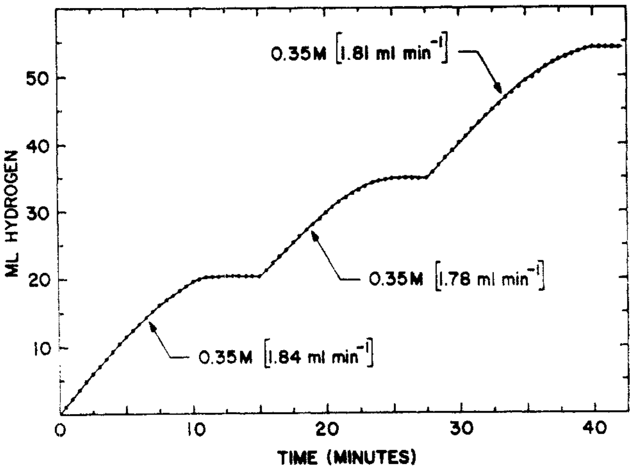

Figure 1.—Rate of hydrogen absorption: cyclohexene in cyclohexane; 21.64 mg of 0.74% Pd catalyst; 25.0°; 760 ± 1 mm. Initial concentrations: (a) 1.07 *M*; (b) 0.70 *M*; (c) 0.085 *M*.

When the hydrogenation of this first sample was complete, a second sample of 0.060 ± 0.005 ml of cyclohexene was injected and its hydrogenation was followed as above. A third 0.080 ± 0.005 ml sample of cyclohexene was then injected and the course of its hydrogenation was followed in the same way. These data are presented in graphical form in Figure 1, and the results from a number of experiments with cyclohexene as the substrate are presented in Table I. The data from experiments where poisoning was extensive (relatively very slow rates) were discarded. The data from experiments in which the hydrogen absorption rates for the second and third samples were appreciably slower than the rate for the first sample were also discarded because such a progressive slowing of rate reflects the accumulation of catalyst-poisoning impurities.[2]

The initial specific rates for hydrogen addition to the several cycloalkenes are summarized in Table II.

Pressure and Temperature Studies.—Similar three-sample experiments were employed in pressure and temperature studies. However, many of the pressure dependence studies were also carried out with a single 0.300 ± 0.005 ml sample of the cycloalkene in 0.300 ± 0.005 ml of cyclohexane. Reaction rates were observed at two or three *increasing* total pressure settings, one of which was near 760 mm. When somewhat slow rates were observed near 760 mm, the rates at the several pressures were normalized by this factor. Data from experiments where poisoning was extensive were discarded.

Typical data for the pressure dependence studies are summarized in Figure 2 and in Table III.

The initial rates of reaction of cyclohexene at different temperatures (Table IV, first sample of three-sample experiments) have been corrected for the change in solubility of hydrogen in cyclohexane with temperature[12] and for the change in the partial pressure of hydrogen in the reaction flask which results from the change in vapor pressure of cyclohexane with temperature.[13] From the slope of a log rate *vs.* T^{-1} plot the apparent activation energy is calculated to be 5.7 ± 0.5 kcal mol^{-1}.

Deuterium Addition.—A solution of 0.30 ml of cyclohexene in 0.60 ml of cyclopentane with 10.24 mg of PDG-2 catalyst was shaken under 1 atm of deuterium (99.7%) for 50 sec. The material was flash evaporated (liquid nitrogen trap) and then separated into solvent, cyclohexane (3.4%), and cyclohexene (96.6%) by glpc. Mass spectrometric analysis (Consolidated Electrodynamics Model 21-104, 15-V ionization potential) furnished parent peak data from which the deuterium distributions were calculated (corrected for natural abundance of hydrogen and carbon isotopes): cyclohexane, d_0 (17.2), d_1 (37.4), d_2 (38.9), d_3 (4.16), d_4 (1.25), d_5 (0.50), d_6 (0.24), d_7 (0.12), d_8 (0.07), d_9 (0.06), d_{10} (0.03), d_{11} (0.02), d_{12} (0.01), d_{av} (1.39); cyclohexene, d_0 (96.7), d_1 (2.8), d_2 (0.3), d_3 (0.2), d_4 (trace), d_{av} (0.40).

TABLE I

INITIAL RATES OF HYDROGENATION OF CYCLOHEXENE USING PALLADIUM CATALYSTS[a]

Pressure, mm	Catalyst, mg	Rate, ml min^{-1}	Specific rate[b]
		PDG-1[c]	
756	9.39	1.17	73
765	10.12	1.17	69
753	12.59	1.49	69
760	12.77	1.44	66
750	13.47	1.70	73
750	15.53	1.80	67
756	18.96	2.23	69
753	25.15	2.90	67
750	34.50	4.45	75
			Av 70 ± 3[d]
		PDG-2[e]	
757	8.81	2.36	204
763	10.47	2.39	175
758	10.98	3.00	208
762	11.75	3.19	208
763	12.08	2.82	179
761	12.92	3.11	184
762	13.20	3.60	208
			Av 195 ± 14[d]

[a] From solution in cyclohexane, 25.0 ± 0.1°. [b] Rates expressed as mol min^{-1} g-atom^{-1}. [c] 0.74% Pd. [d] Standard deviation. [e] 0.57% Pd.

TABLE II

INITIAL RATES OF HYDROGENATION OF CYCLOALKENES USING PALLADIUM CATALYSTS[a]

Cycloalkene[b]	Initial rate[c,d] PDG-1[e]	PDG-2[f]
Bicyclo[2.2.1]heptene	450 ± 20 (2)	
Cyclopentene	129 ± 10 (9)	400 ± 20 (4)
Cyclohexene[g]	70 ± 3 (9)	195 ± 14 (7)
Cycloheptene	66 ± 4 (4)	218 + 12 (3)
Cyclooctene	4.0 ± 0.2 (4)	18 ± 1 (2)

[a] From solution in cyclohexane, 25.0 ± 0.1°, 760 ± 5 mm total pressure. [b] Concentration $\sim$1 *M*. [c] Number of experiments in parentheses. [d] Rates expressed as mol min^{-1} g-atom^{-1}. [e] 0.74% Pd. [f] 0.57% Pd. [g] Apparent activation energy, 5.7 ± 0.5 kcal mol^{-1}.

Results

The collection of the rate data reported here has been beset with the frustrating experimental problem of the necessity for the complete exclusion of rate-slowing impurities. The palladium catalysts appear to be even more sensitive to trace impurities than were the platinum catalysts used in our previous kinetic study. Moreover, when platinum catalysts are used, the rates of hydrogenation are zero order in cycloalkene concentration; hence a divergence of the rate plots from linearity immediately signals the presence of rate-slowing impurities.[2] The rates of hydrogenation of cycloalkenes at palladium surfaces, however, are functions of their concentrations. Consequently, as the rate plots have an inherent curvature (Figure 1), traces of catalyst poisons simply superimpose some additional curvature to these plots and the presence of poisons is not immediately obvious.

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(12) P. Frohlich, E. J. Tauch, J. J. Hogan, and A. A. Peer, *Ind. Eng. Chem.*, **23**, 548 (1931); see also M. W. Cook, D. N. Hanson, and B. J. Alder, *J. Chem. Phys.*, **26**, 748 (1957).

(13) "International Critical Tables," Vol. III, 1928, p 222.

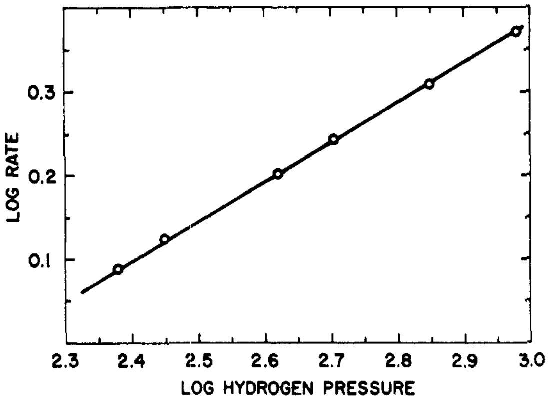

Figure 2.—Dependence of initial hydrogen absorption rate on hydrogen pressure: cyclooctene in cyclohexane; 0.57% Pd catalyst, 25.0°; concentration ≥1 *M*. (Rate in ml of H_2 min^{-1} g of catalyst^{-1} at STP.)

TABLE III

KINETICS FOR THE HYDROGENATION OF CYCLOALKENES ON ALUMINA-SUPPORTED PALLADIUM CATALYSTS[a]

$$\text{rate} = k[\text{cycloalkene}]^m[P_{H_2}]^n$$

	Catalyst			
	PDG-1[b]		PDG-2[c]	
Cycloalkene	*m*	*n*	*m*	*n*
Bicyclo[2.2.1]-heptene	0.20 ± 0.05	~1		
Cyclopentene	0.26 ± 0.05	0.57 ± 0.05	0.26 ± 0.05	0.56 ± 0.05
Cyclohexene	0.34 ± 0.05	0.45 ± 0.05	0.33 ± 0.05	0.47 ± 0.05
Cycloheptene	0.27 ± 0.05	0.43 ± 0.05	0.33 ± 0.05	0.48 ± 0.05
Cyclooctene	0.23 ± 0.05	0.23 ± 0.05	0.24 ± 0.05	0.48 ± 0.05

[a] From solution in cyclohexane at 25.0 ± 0.1°. Initial concentration ≥1 *M*. [b] 0.74% Pd. [c] 0.57% Pd.

TABLE IV

TEMPERATURE COEFFICIENT FOR THE HYDROGENATION OF CYCLOHEXENE ON PALLADIUM[a]

$1/T \times 10^3$	Log rate[b,c]
3.47	1.889
3.36	2.058
3.30	2.112
3.25	2.177
3.20	2.243
3.14	2.276

[a] From solution in cyclohexane. [b] At STP, ml of hydrogen min^{-1} g of catalyst^{-1}, corrected for change of hydrogen solubility and hydrocarbon partial pressure with temperature. [c] Using 0.74% Pd catalyst (PDG-1).

In the platinum-catalyzed study,[2] a sample-bracketting procedure allowed us to compare the rates of hydrogenation of the several alkenes with considerable confidence because it was so easy to tell when rate-slowing impurities were present. However, in the studies reported here using palladium catalysts, the presence of such impurities is not obvious (except when it is extensive) until the data have been analyzed. As a consequence we found it impractical to use the sample-bracketting procedure which we had used before. Rather, we have resorted to a three-successive-sample procedure through which the presence of rate-slowing impurities is detectable because of its cumulative effect on the rates observed for the second and third samples.

Because we were not able immediately to detect the presence of traces of rate-slowing impurities, the total data collected for the palladium-catalyzed hydrogenations are somewhat less precise than those which were obtained using platinum. We have, in effect, collected hydrogen absorption data which converge toward the maximum rate of a completely poison-free system. In the experiments where poisoning was extensive the initial rates were relatively very slow, tending toward one-half the fastest initial rates. Apparently, about one-half of the catalytic activity of these palladium catalysts is very sensitive to such poisons but the remainder of the catalytic activity is much less sensitive. These slow initial rate data were discarded.

Where the presence of poisons was not immediately obvious, the rates observed for the first sample tended to fall into the lower range of a group of very fast initial rates, but the rates for the second and third samples became progressively slower. We therefore applied the requirement that the initial rates of the second and third samples be very close to that of the first. This criterion allowed us to identify experiments in which rate-slowing impurities were significant. We were then able to discard all of the low values in the high-rate group in good conscience, leaving the edited data which are summarized in Table I and II. The initial rates (mol min^{-1} g-atom^{-1}) are the slopes of the tangents of rate plots of the experimental data at the beginning of the hydrogenations when hydrogen absorption rates are nearly linear. We summarize them in this form in Table II simply for convenient comparison with the specific rates reported earlier for platinum catalysts.[2]

Dependence of Rate on Amount of Catalyst.—The data of Table I include initial rates using a range of catalyst weight from *ca.* 5 to 35 mg. The rates are clearly first order in the amount of catalyst and, within experimental error, doubling the amount of catalyst doubled the initial rate of hydrogen absorption. Likewise the slopes of tangents at equal cycloalkene concentrations along the curving hydrogen uptake plots (Figure 1) gave rates which were first order in the amount of catalyst. Thus, neither hydrogen transport from the gas phase into the liquid phase nor diffusion of hydrogen through the solution to the catalyst surface[2,14] limits the rates which we observe under our experimental conditions. The possibility of diffusional limitations within the catalyst pores remains, however. It will be discussed later.

Notice that it would probably not be possible to hydrogenate bicyclo[2.2.1]heptene using our more active PDG-2 catalyst without imposing serious hydrogen transport or hydrogen diffusion limitations on the rates of hydrogen absorption observed.

Dependence on Substrate Concentration.—From rate data such as that presented in Figure 1 one can obtain values for the exponent *m* in the rate expression

$$\text{rate} = k[\text{E}]^m[P_{H_2}]^n[\text{catalyst}] \qquad (1)$$

where *k* is the rate constant for the over-all reaction, $[\text{E}]^m$ is the molar cycloalkene dependence, and $[P_{H_2}]^n$ is the hydrogen dependence. These values for *m* are summarized in Table III. They are about 0.3 and

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(14) H. S. Davis, G. Thomson, and G. S. Crandall, *J. Amer. Chem. Soc.*, **54**, 2340 (1932); H. C. Yao and P. H. Emmett, *ibid.*, **81**, 4125 (1959).

are not greatly different. These data *for a particular hydrogen pressure* can be accommodated by Langmuir–Hinshelwood kinetics and the rate expression

$$\text{rate} = k'K_E[E]/(1 + K_E[E] + K_H[H_2]) \qquad (2)$$

where k' is the over-all rate constant at the particular hydrogen pressure, K_E is the chemisorption constant of the alkene, [E] is its molar concentration, K_H is the chemisorption constant for hydrogen from solution, and $[H_2]$ is its molar concentration. The kinetics do not allow a choice between eq 2, however, and a simpler rate expression

$$\text{rate} = k'K_E[E]/(1 + K_E[E]) \qquad (3)$$

which assumes that hydrogen does not interfere with the chemisorption of alkene.

Dependence of Rate on Hydrogen Pressure.—The data from experiments using cyclooctene and our PDG-2 catalyst are summarized in Figure 2 which is a plot of log initial rate *vs.* log P_{H_2}. The slopes of such plots for the several cycloalkenes give values for n, the order of hydrogen in rate expression 1. These values are also summarized in Table III where the rates are seen to vary within experimental error with the square root of hydrogen pressure, except for bicycloheptene and cyclooctene using PDG-1 catalyst.

Discussion

Dependence of Rate on Substrate Concentration.—We have earlier proposed that the kinetics of hydrogen addition and the nonintervention of isomerization in the face of extensively isotopically exchanged cycloalkane are best accommodated by a chemisorption of cycloalkenes on platinum surfaces which is effectively irreversible.[2,15] A reversible chemisorption of cycloalkenes on palladium surfaces, in accord with rate expression 2 or 3, would seem at first to offer a satisfactory explanation for the extensive isomerization which intervenes when palladium is the hydrogenation catalyst. It would also seem to explain the difference in stereochemical consequences with palladium compared with platinum catalysts.[5]

It has been pointed out,[16] however, that very different assumptions about the mechanism of a sequence of reactions taking place at the surface of solid catalyst, such as we deal with here, often lead to rate expressions which are of identical mathematical form as expressions 2 and 3. Hence it is not possible to make a choice among the several alternatives on the basis of the kinetic data alone and we must call upon other information in order to be able to refine the general model[17] so that it is accord with the details of palladium-catalyzed hydrogenations.

$$H_2 + 2^* \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2H^*$$

$$E + 2^* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} E^{**} \text{ (diadsorbed alkane)}$$

$$E^{**} + H^* \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} 2^* + HE^* \text{ (monoadsorbed alkane)}$$

$$HE^* + H^* \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} H_2E + 2^*$$

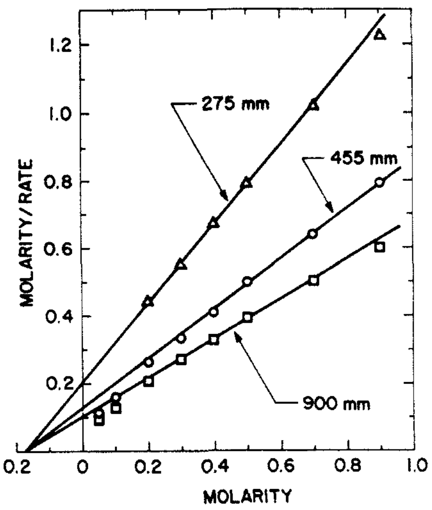

Figure 3.—Plots of cyclohexene molarity/rate *vs.* cyclohexene molarity in cyclohexane: 0.74% Pd catalyst; 25.0°. (Rate in mol $\sec^{-1}$ g-atom^{-1}.)

First, it has been shown conclusively that cycloalkanes do not dissociatively chemisorb on palladium catalyst under our conditions;[5a,b] hence the addition of the second hydrogen (associative desorption of cycloalkane) can be regarded to be irreversible. Second, the very extensively exchange product which is formed when deuterium is used (see Experimental Section and ref 5d) is compelling evidence that the addition of the first hydrogen is highly reversible. Third, the appearance of HD in the gas phase shows that hydrogen adsorption is also. We are then left only with the questions (1) whether adsorption of alkene is reversible or not and (2) whether alkene and hydrogen compete with one another in the adsorption process.

Let us ignore the question of the reversibility of alkene chemisorption for the moment to consider a variation of the general Horiuti–Polanyi model for hydrogen addition in which the adsorptions of hydrogen and alkene are independent of one another, and the addition of the first hydrogen is highly reversible but the addition of the second hydrogen is irreversible in accord with the discussion above. A steady-state treatment based on these assumptions leads to eq 4

$$\text{rate} = \frac{k_2k_3k_4[E]\Theta_H{}^2}{k_2[E](k_{-3} + k_3\Theta_H + k_4\Theta_H) + k_3k_4\Theta_H{}^2 + k_{-2}k_{-3} + k_{-2}k_4\Theta_H} \qquad (4)$$

if chemisorption of alkene is reversible. The last two terms in the denominator disappear if chemisorption of alkene is irreversible, but in either event eq 4 is of the same mathematical form as eq 2 and 3. At constant pressure, the fraction of the surface occupied by hydrogen, Θ_H, would be constant in this model and,

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(15) A. S. Hussey, R. H. Baker, and G. W. Keulks, *J. Catal.*, **10**, 258 (1968).

(16) M. Boudart, "Kinetics of Chemical Processes," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1968, p 104.

(17) M. Polanyi and J. Horiuti, *Trans. Faraday Soc.*, **30**, 1164 (1934).

if eq 4 is rearranged to eq 5 it is seen that a plot of

$$[\mathrm{E}]/\mathrm{rate} = \left[\frac{k_{-3} + k_3\Theta_{\mathrm{H}} + k_4\Theta_{\mathrm{H}}}{k_3k_4\Theta_{\mathrm{H}}^2}\right][\mathrm{E}] + \left[\frac{1}{k_2} + \frac{k_{-2}(k_{-3} + k_4\Theta_{\mathrm{H}})}{k_2k_3k_4\Theta_{\mathrm{H}}^2}\right] \quad (5)$$

[E]/rate *vs.* [E] should be linear with quite different intercepts depending upon whether adsorption of alkene is reversible or irreversible. If the latter obtains and $k_2 \gg 1$, the intercept will be at the origin. This is true for platinum-catalyzed systems[2] where $k_2 \gg k_{-2}$. If adsorption is reversible, k_{-2} will be finite and the intercept will be positive.

The data for cyclohexene at three different hydrogen pressures are plotted in this way in Figure 3, where the plots are seen to be linear, except at very low concentrations, and the intercepts to be positive. Notice, furthermore, that the data for the three pressures extrapolate to a common intercept with the abscissa in accord with an adsorption of alkene which is independent of the adsorption of hydrogen. The departure from linearity at low concentration may come about because Θ_{H} is not independent of [E]. However, we prefer an alternate explanation which will be discussed in the next section, and we propose that the hydrogen addition reaction in palladium-catalyzed systems near 1 atm involves reversible adsorptions of hydrogen and alkene which are independent of one another, a reversible addition of the first hydrogen, and an irreversible addition of the second.

The Depencence of Rate on Hydrogen Pressure and the Question of Pore Diffusion Limitations.—The empirical dependence of the observed rates on the square root of hydrogen pressure (Table III) is a matter of concern because such a dependence can be interpreted to mean that the rate-determining step of the sequence is the addition of the first hydrogen atom. The transition state for such a rate-critical step would include a *single* hydrogen atom, whence a square-root dependence on hydrogen pressure logically follows. Such an interpretation is quite at odds with our assumptions in the model which we have developed in the preceding section. Fortunately, an alternate explanation for the observed rate dependence is available.

When a catalyst with an extensive internal pore structure is used, diffusion within the torturous pores may limit the availability of reactants at the internal catalytic surfaces.[18] In our system the deficient reactant will certainly be hydrogen because its concentration in the bulk solution is so small relative to that of the cycloalkene.[13] Diffusion being a first-order process with a small activation energy, the observed orders for reaction will tend toward unity and the observed activation energies will tend to be small[19] when diffusion limitations are superimposed. Thus an intrinsic zero-order reaction will tend toward half order and half-order reactions will tend toward three-quarters order, etc. Consequently, we are led to interpret the hydrogen dependence which we observe to reflect an *intrinsic zero-order process* upon which a first-order hydrogen pore diffusion process is superimposed.

We have no single piece of unequivocal evidence to support the imposition of pore diffusion limitations upon the observed rates in these experiments but there are several implications within our experimental data which lend support. The total effect of these arguments is rather convincingly in favor of this explanation for the hydrogen dependence which is observed.

First, the very extensive exchange observed when cyclohexene is deuterated[17] would seem to require the formation of monoadsorbed alkane to be reversible. Second, the Thiele moduli and the Weisz moduli[18] as estimated from our particle size (150–200 mesh), surface areas (>200 m^2 g^{-1}), pore volumes (>2.5 cm^3 g^{-1}), D_{eff} for hydrogen (0.5 to 7.5 × 10^{-5} cm^2 sec^{-1}),[19,20] and the reaction rates (Table II) are several times larger than the maximum values below which diffusional effects can be ignored.[18] Third, the apparent activation energies are small.[19] Fourth, the hydrogen dependence falls to about one-quarter order when *slowly* hydrogenated cyclooctene is hydrogenated using our *less active* PDG-1 catalyst, but appears to approach first order when very rapidly hydrogenated bicycloheptene is the substrate (Table III).

Pore diffusional limitations are most convincingly demonstrated to be present by using catalyst particles of successively smaller size. We are not able mechanically to reduce our particle size without exposing the catalyst to rate-slowing impurities. It is possible, however, literally to explode particles of strong adsorbants by suddenly exposing them to materials which strongly adsorb on them[21] and when 1.0 to 2.0 μl of water is added in the course of a hydrogenation experiment such as that summarized in Figure 1, the rates are observed to increase. The effect is variable but is often as much as 80%.[22] The same effect is observed with acetic acid and with methanol, but not with 1,4-dioxane, and a second addition of protic solvents causes the rates to decrease. This effect seems likely to be the result of a breaking open of the catalyst particle to expose more metal surface to the reactants.

Finally, the rates of hydrogenation become much slower when the cycloalkene is nearly completely reduced (Figure 1). If pore diffusional effects are indeed involved in the initial fast rates, the hydrogen deficiency within the pores should become progressively less pronounced toward the end of the reaction. That is to say, more and more of the catalytic surface in the interior of the particle should be able to participate, up to the point where cycloalkene diffusional effects begin to be encountered. Accordingly, the rate of decrease of rate with cycloalkene concentration toward the end of the reaction should be less than that predicted by rate expressions 2, 3, and 4. Hence the existence of a pore diffusion effect is an alternate explanation for the divergence of the plots of Figure 3 from linearity.

We believe that the weight of the evidence supports

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(18) C. N. Satterfield and T. K. Sherwood, "The Role of Diffusion in Catalysis," Addison-Wesley Publishing Co., Inc., Palo Alto, Calif., 1963, pp 56–71.

(19) The activation energy for the diffusion of hydrogen in cyclohexane is 2.9 kcal mol^{-1}: N. E. Khazamora and L. R. Linshitz, *Khim. Prom.*, (8), 579 (1963). See *Chem. Abstr.*, **60**, 2348*d* (1964).

(20) See ref 18, pp 11–30.

(21) D. H. Bangham, *Proc. Roy. Soc.*, **A147**, 175 (1934).

(22) We had observed this phenomenon before when bicyclo[2.2.1]heptene was hydrogenated using our platinum catalysts.[2] After the catalysts had been used to hydrogenate this very forcefully chemisorbed alkene, they often showed *increased* activity in the hydrogenation of cyclohexene. At that time we had no understanding of why this should be so.

the contention that a pore diffusional effect superimposed on an intrinsic zero-order dependence is responsible for the square-root hydrogen dependence which is observed. A zero-order dependence on hydrogen pressure is quite consistent with hydrogen/palladium ratios of ~0.6 near 1 atm at 25°.[23] The palladium crystallites at the exterior of the support, and those close to it, can be regarded to be reservoirs of hydrogen. It follows that a zero-order hydrogen dependence should be observed on palladium films but we do not have any evidence to this point.

Registry No.—Bicyclo[2.2.1]heptene, 498-66-8; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; cyclohexane. 110-82-7.

[23] F. A. Lewis, "The Palladium Hydrogen System," Academic Press, New York, N. Y., 1967, p 4.

Base-Catalyzed Intermolecular Condensation of α,β-Unsaturated Ketones. Self-Condensation of Styryl Isobutyl Ketone to Epimeric Diketones, $C_{26}H_{32}O_2$, and a Triketone, $C_{39}H_{48}O_3$. Stereochemistry of Michael Cyclization

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The self-condensation of styryl isobutyl ketone (1) in ethanolic sodium hydroxide solution leads to a cyclic diketone dimer, all-*trans*-3,5-diphenylisopropyl-4-(3-methylbutanoyl)cyclohexanone (**2a**), and a triketone trimer, 3,5-diphenyl-2-isopropyl-4-(2-isopropyl-7-methyl-5-oxo-3-phenyloctanoyl)cyclohexanone (**4**). In aqueous sodium hydroxide, **1** produces an acyclic dimer, 1,5-diphenyl-4-isopropyl-9-methyl-1-decene-3,7-dione (**3a**), a compound shown to be a precursor of **2a**. Pyrolysis of trimer **4** produces **1** and **2b**, an epimer of **2a**. Heating **2a** in refluxing dioxane with sodium methoxide catalyst leads to a mixture of **2a**, **2b**, and a third cyclic dimer, **2c**. The configurations of these condensation products have been established by deuterium-exchange experiments and nmr spectroscopy. The stereochemistry of the relevant addition reactions and a comparison with the related Michael aldol cyclization are examined and discussed.

Study of the stereochemistry of Michael cyclization arising from an acyclic precursor appears in only one previous report.[1] Stereochemistry of the related Michael aldol cyclization (Robinson annelation reaction) has been examined; most of these reactions involve Michael addition of a cycloalkanone enolate to an α,β-unsaturated ketone, followed by aldol cyclization to form a new ring.[2] Most other studies of Michael addition stereochemistry have dealt with the formation of acyclic diastereoisomers,[2f,g,3–5] or products of an addition to an activated endocyclic double bond.[2a,c,6–8] We have extended our studies of the base-catalyzed self-condensation of α,β-unsaturated ketones[9] to an examination of the stereochemistry of Michael cyclization products obtained by self-condensation of styryl isobutyl ketone. In this example, unlike many other types of Michael addition, the mechanism does not involve the complicating features of enolization stereochemistry. Product equilibration by enolization is a post-Michael addition process in this case.

The base-catalyzed self-condensation of styryl isobutyl ketone (**1**), in contrast to reactions of other

$C_6H_5CH{=}CHCOCH_2C_3H_7\text{-}i$

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styryl alkyl ketones which have been examined,[9,10] leads to several crystalline condensation products rather than a single cyclic diketone dimer. Isomeric acyclic and cyclic diketones, $C_{26}H_{32}O_2$, and a triketone, $C_{39}H_{48}O_3$, have been prepared in the present work.

The base-catalyzed self-condensation of styryl isobutyl ketone has been studied by other workers.[9b,10c,11,12] In *ethanolic* sodium hydroxide solution the formation of a crystalline dimer, $C_{26}H_{32}O_2$, has been reported, and previously we showed its structure to be **2a**.[9b] We have now prepared dimers **2b** and **2c**, both of which have been shown to be epimers of **2a**. In *aqueous* sodium hydroxide Metayer[11] obtained a product, mp 141°, which he described as a dimer; we have shown it to be a trimer, $C_{39}H_{48}O_3$.

Condensation Products and Structure.—Self-condensation of styryl isobutyl ketone in *aqueous* sodium

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[1] F. Wingler and H. Reiff, *Ann. Chem.*, **705**, 96 (1967).

[2] (a) W. S. Johnson, S. Shulman, K. L. Williamson, and R. Pappo, *J. Org. Chem.*, **27**, 2015 (1962); (b) J. A. Marshall and W. I. Fanta, *ibid.*, **29**, 2501 (1964); (c) H. G. O. Becker, U. Fratz, G. Klose, and K. Heller, *J. Prakt. Chem.*, (4) **29**, 142 (1965); (d) A. T. Nielsen, *J. Org. Chem.*, **30**, 3650 (1965); (e) T. A. Spencer, H. S. Neel, and D. C. Ward, *ibid.*, **31**, 434 (1966); (f) M. M. Robison, M. G. Pierson, L. Dorfman, and B. F. Lambert, *ibid.*, **31**, 3206, 3213 (1966); (g) L. Jung, *Bull. Soc. Chim. Fr.*, 4692, 4696 (1967); (h) A. T. Nielsen and W. J. Houlihan, *Org. Reactions*, **16**, 11 (1968).

[3] A. Wettstein, K. Heusler, H. Ueberwasser, and P. Wieland, *Helv. Chim. Acta*, **40**, 323 (1957).

[4] M. P. Hughes, Ph.D. Thesis, Rice University, 1964; *Dissertation Abstr.*, **25**, 1570 (1964).

[5] A.-M. Baradel, J. Dreux, R. Longeray, P. Laszlo, and H. Rivière, *Bull. Soc. Chim. Fr.*, 3543 (1966).

[6] E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

[7] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 367–368.

[8] (a) R. A. Abramovitch and J. M. Muchowski, *Can. J. Chem.*, **38**, 557 (1960); (b) S. V. Kessar, J. P. Nagpal, and K. K. Khullar, *J. Indian Chem. Soc.*, **39**, 381 (1962); (c) M. E. Wall, F. I. Carroll, and G. S. Abernathy, *J. Org. Chem.*, **29**, 604 (1964); (d) N. L. Allinger and C. K. Riew, *Tetrahedron Lett.*, 1269 (1966); (e) R. A. Abramovitch and D. L. Struble, *Tetrahedron*, **24**, 357 (1968).

[9] (a) A. T. Nielsen, D. W. Moore, and K. Highberg, *J. Org. Chem.*, **26**, 3691 (1961); (b) A. T. Nielsen and H. J. Dubin, *ibid.*, **28**, 2120 (1963); (c) A. T. Nielsen, H. Dubin, and K. Hise, *ibid.*, **32**, 3407 (1967); (d) A. T. Nielsen and S. Haseltine, *ibid.*, **33**, 3264 (1968).

[10] (a) R. Dickinson, I. M. Heilbron, and F. Irving, *J. Chem. Soc.*, 1888 (1927); (b) I. M. Heilbron and F. Irving, *ibid.*, 2323 (1928); (c) I. M. Heilbron and F. Irving, *ibid.*, 931 (1929); (d) I. M. Heilbron, R. N. Heslop, F. Irving, and J. S. Wilson, *ibid.*, 1336 (1931).

[11] M. Metayer, *Rec. Trav. Chim. Pays-Bas*, **71**, 153 (1952).

[12] C. V. Gheorghiu and B. Arwentiev, *J. Prakt. Chem.*, (2) **118**, 295 (1928).