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The Role of Adsorbed Hydrogen in the Catalytic Hydrogenation of Cyclohexene*

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A gold film, electroplated on a palladium-silver alloy thimble, was used to study the mechanism of catalytic hydrogenation of cyclohexene. The rate of chemisorption of hydrogen from its gaseous molecular state is very slow on gold. Yet hydrogen adatoms can be supplied readily to the gold surface by allowing the gas to contact the palladium-silver surface, to diffuse through the bulk of the metal, and to emerge in the chemisorbed state on the gold surface. The results suggest that under our experimental conditions the rate of hydrogenation of cyclohexene on a metal surface is dependent on the square of the hydrogen adatom concentration, and is independent of the partial pressures of both the olefin and the reaction product, cyclohexane. An activation energy of 5 kcal/mole was assigned to the reaction. Under certain conditions the catalytic function of the gold surface was reversible, i.e., it catalyzed the dehydrogenation of cyclohexane to produce cyclohexene. Mechanisms for the reactions consistent with our results are suggested.

INTRODUCTION

It has been common knowledge that, as hydrogenation catalysts, the transition metals are generally superior to those outside the transition group of the Periodic Table. Consequently, studies of specific catalytic reactions, including parahydrogen conversion (*1*), hydrogenation of ethylene (*2*) and of cyclohexene (*3*), hydrogen–deuterium exchange in hydrocarbons (*4*), and hydrogen–deuterium equilibration (*5*), have been interpreted largely in terms of unpaired *d* electrons in the metal and *dsp* hybrid orbitals.

In our studies (*6*) of the kinetics of hydrogen atom recombination on surfaces, however, we observed that many nontransition metals were better catalysts than transition metals. And in a subsequent study (*7*) it was found that the rate of hydrogen–deuterium equilibration on gold at moderate temperatures was promoted by the preadsorption of hydrogen on the gold surface. The common aspect of both of these systems appeared to be the existence of a surface layer of chemisorbed hydrogen on the metal.

These observations led us to inquire about the role of chemisorbed hydrogen in the catalytic hydrogenation of an olefin. Phrased pragmatically, the question was: "Could a nontransition metal be endowed with catalytic hydrogenation activity comparable to that of a transition metal by supplying chemisorbed hydrogen to its surface?"

To answer this question we required an olefin hydrogenation catalyst on which the population of chemisorbed hydrogen is independent of the pressure of gaseous hydrogen in its environment, and on which olefin chemisorption is negligible. Gold is such a catalyst, for at temperatures below 200°C its rate of chemisorption of hydrogen from the molecular state is immeasurably slow (*8*) relative to its rate of desorption (*9*). Therefore, to establish a steady state

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* We gratefully acknowledge support of this work by a group of industrial companies.

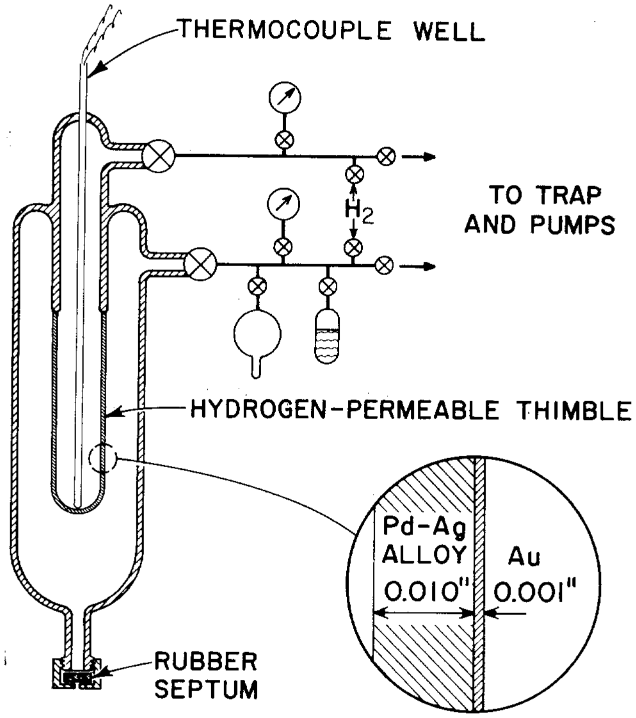

FIG. 1. Schematic diagram of apparatus.

population of hydrogen adatoms on a gold surface, hydrogen must be provided by means other than chemisorption, such as diffusion from the bulk of the metal to the surface.

In actuality, such a catalyst takes the form of a membrane of gold bonded to a transition metal, such as palladium, which readily chemisorbs gas from a hydrogen atmosphere. Hydrogen occluded in the palladium diffuses through it, across the palladium–gold interface, and through the gold to its surface. It appears there as chemisorbed hydrogen atoms which associatively desorb. The population of hydrogen adatoms will be a function of the relative rates of desorption and bulk diffusion, and will not be dependent significantly on the pressure of molecular hydrogen in contact with the gold. The use of such a catalytic surface makes possible an evaluation of the role of surface-adsorbed hydrogen on the rate of hydrogenation of an olefin.

EXPERIMENTAL APPARATUS AND TECHNIQUE

The catalytic surface in these experiments was a gold film intimately bonded to the outer side of a palladium-silver alloy thimble* by a commercial electroplating process (Fig. 1). The open end of the thimble was brazed to a Kovar-Pyrex tubular graded seal (the Kovar and the brazed joint were gold-plated also) and mounted in a glass reaction vessel in a vacuum system. The interior of the thimble constituted a separate chamber which was isolated from the reactor. (In this paper, the term "reactor" refers to the chamber enveloping the gold side of the thimble. The inner chamber, consisting of the Pd-Ag alloy side of the thimble, will be referred to simply as the "thimble;" see Fig. 1.) The vacuum system was arranged so that the thimble and the reactor could be separately evacuated or filled to any desired pressure with hydrogen or olefin vapor, or

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* Obtained from J. Bishop and Co., Malvern, Pa. This alloy was reported to be 23% silver and 77% palladium. It was used because, unlike palladium, it exhibits negligible mechanical distortion upon saturation with hydrogen, yet it is more hydrogen-porous than pure palladium. The geometric surface area of the thimble was 26.7 cm^2.

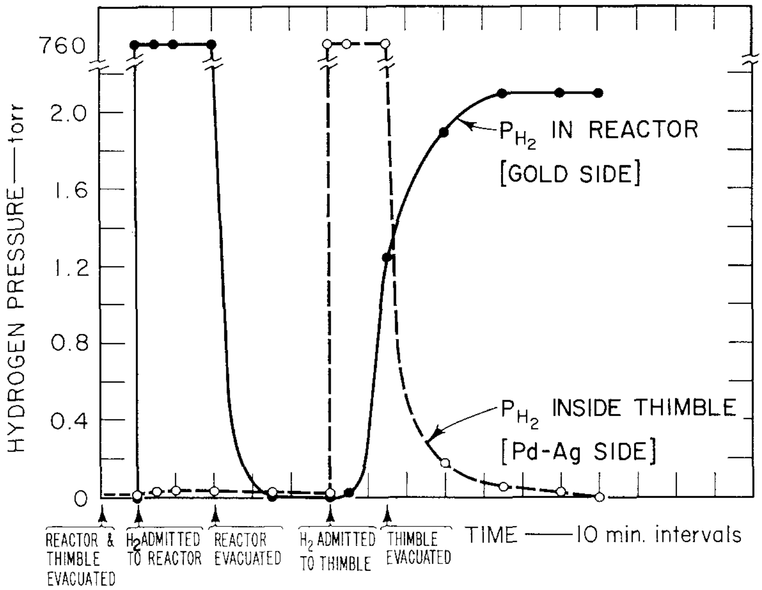

FIG. 2. Hydrogen permeability of gold-clad palladium-silver alloy thimble at 125°C.

a mixture. In addition, by means of a T configuration and two needle valves appropriately connected to the thimble, a tank of hydrogen, and a vacuum pump, the pressure of hydrogen in the thimble could be maintained at a constant value even though the gas was flowing out of the thimble by diffusion through the wall. In effect, the thimble could serve as an infinite reservoir of hydrogen at a fixed pressure.

The reactor and thimble could be maintained at an elevated temperature by enclosing the assembly in a split cylindrical electric furnace. Pressures were measured with a differential manometer (*10*) used as a null instrument, thereby eliminating mercury vapor from all parts of the system. All valves in the system had bellows-sealed stems and were made of brass. The vacuum-pumping arrangement consisted of a mechanical pump, a mercury diffusion pump, and a liquid-nitrogen-cooled trap, and was capable of attaining vacuums in the region of 10^{-6} Torr.

The olefin employed in the hydrogenation experiments was Eastman cyclohexene, treated with ferrous sulfate to remove peroxides, dried over magnesium perchlorate, vacuum-distilled, and degassed by repeated freezing, pumping, and thawing. Thus purified, the starting material contained approximately 3% cyclohexane and a trace of methylcyclopentane.

The hydrogen was Matheson prepurified grade. It was admitted to the thimble without further purification, but was diffused through a palladium-silver purification unit* before it was employed in the reactor.

After the reactants were admitted to the reactor, the course of the reaction was followed by measuring the cyclohexane/cyclohexene ratio in 1-ml samples withdrawn from the reactor in a gas-tight syringe at suitable time intervals. The analysis was carried out at 70°C on a 10-ft × ¼-inch chromatographic column containing No. 710 silicone oil impregnated on a refractory support. Helium was employed as the carrier gas. The detector was a Gow-Mac thermal conductivity cell with tungsten filaments.

EXPERIMENTAL RESULTS

In order to establish the integrity of the gold film, the characteristics of the thimble for hydrogen diffusion at 125°C were studied. As shown in Fig. 2, diffusion of hydrogen from the gold side to the palladium-silver side of the membrane is negligible at 125°C even with a pressure

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* J. Bishop & Co. Model A-1 Hydrogen Diffusion Cell.

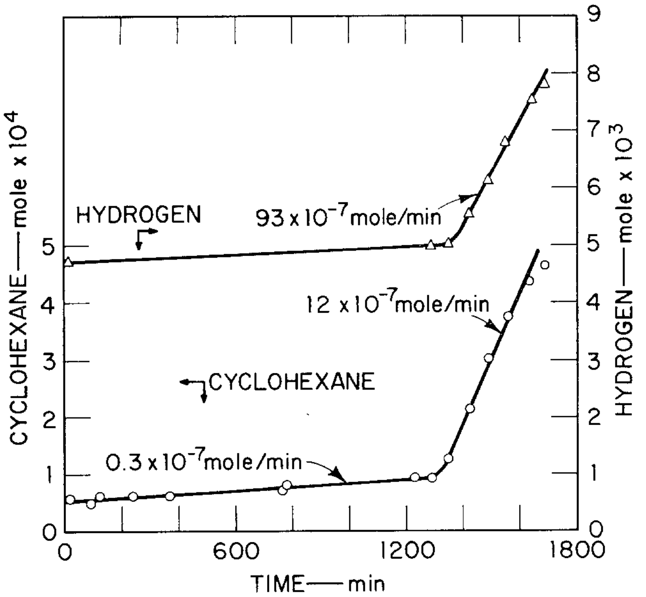

FIG. 3. Activity of gold catalyst for hydrogenation of cyclohexene at 125°C. Initial conditions: $P_{H_2} = 238$ Torr; $P_{C_6H_{10}} = 91$ Torr. At time 1300 min, hydrogen at 1 atm was admitted to thimble.

differential of 1 atm of hydrogen. Inversion of the differential, however, so that the pressure of hydrogen on the palladium-silver side is 1 atm, results in a rapid diffusional transport of hydrogen through the membrane. The thimble wall appears to be effectively semipermeable to hydrogen at 125°C.

An additional verification of the integrity of the gold film at 125°C was made by introducing a mixture of hydrogen and cyclohexene into the reactor. In this experiment (Fig. 3) the initial charge of reactants contained an excess of hydrogen (hydrogen/cyclohexene = 2.6/1). The total pressure and the ratio of cyclohexane to cyclohexene were monitored over a 22-hr period during which the thimble was continuously evacuated. The negligible change in total pressure and the small increase in the quantity of cyclohexane during this time indicated that the gold surface was essentially noncatalytic and nonpermeable to molecular hydrogen.

Catalytic activity was bestowed on the gold surface by filling the thimble with hydrogen at a constant pressure. The suddenness with which hydrogenation of the cyclohexene commenced is shown in Fig. 3 at time $t = 1300$ min, when hydrogen was admitted to the thimble at a pressure of 1 atm. The rate of formation of cyclohexane quickly increased to a constant value greater by a factor of 40 over the initial rate. Hydrogen began to diffuse into the reactor also, but the increase in partial pressure of hydrogen during the observed time span could not account for the enhanced rate of hydrogenation.

In order to investigate the kinetic dependence of the hydrogenation reaction on the partial pressures of the various components in the system, a number of similar experiments were carried out in which (1) the diffusive flux of hydrogen through the thimble was varied by adjusting the pressure in the thimble, and (2) the initial pressure of hydrogen in the reactor was varied from 0 to 300 Torr. No significant variations were made in the initial pressure of cyclohexene in the reactor, but time-linear rates of formation of cyclohexane were observed during the hydrogenation of up to 70% of the initial pressure of the olefin. The results of these experiments, summarized in Table 1, suggest that the hydrogenation rate is related to the diffusion rate of hydrogen through the mem-

TABLE 1
HYDROGENATION OF CYCLOHEXENE (C_6H_{10}) ON A GOLD SURFACE WITH CHEMISORBED HYDROGEN

Catalyst temp. (°C)	Initial pressure (Torr)			Rate of formation [(mole/min) $\times 10^7$]		Per cent C_6H_{10} converted
	Reactor		Thimble			
	$P_{C_6H_{10}}$	P_{H_2}	P_{H_2}	Cyclohexane	Hydrogen	
70°	99	280	1520	5.1	131	12
	82	298	1520	4.4	170	6
125°	91	238	0	0.31	0	2
	83	302	506	0.92	9.05	5.5
	78	0	760	1.08	28.5	9.5
	91	229	506	1.11	12.5	3
	85	267	506	1.92	22.2	2.5
	80	0	760	2.46	72.2	4
	90	670[a]	760[a]	3.2	0[a]	14
	80	219	760	11.9	92.6	15
	93	213	1520	24	342	30
	90	238	760	38	178	60
	58	140	1520	40	589	69
200°	97	280	760	9.9	1000	28

[a] Experiment carried out under special conditions; see text.

brane, but is zero order with respect to all gaseous components in the reactor—cyclohexene, cyclohexane, and hydrogen. The essential, active species required for the catalytic hydrogenation of an olefin thus appears to be chemisorbed hydrogen.

The diffusive flux of hydrogen through the membrane could be varied by increasing or decreasing the pressure of hydrogen in the thimble. At a thimble temperature of 125°C, the flux exhibited a sensitive dependence on the pressure differential between thimble and reactor (Table 1). Even with a fixed pressure of hydrogen in the thimble, however, substantial variations between experiments in the apparent porosity of the membrane were observed. The precise cause of this phenomenon is undetermined, but we attribute it to the high temperature coefficient of porosity of the alloy in the temperature range 100–150°C (*11*).

The fact that the rate of hydrogenation of cyclohexene at 125°C could be correlated with the diffusive flux of hydrogen emerging from the gold surface (Fig. 4) indicates that chemisorbed hydrogen is an intermediate in both olefin hydrogenation and hydrogen recombination on the gold surface. It suggests that the kinetic order of these reactions with respect to chemisorbed hydrogen is identical also. However, the question remains: Does the hydrogen flux govern the rate of hydrogenation directly, or indirectly by affecting the steady state concentration of chemisorbed hydrogen on the catalyst surface? In order to elucidate this point, the rate of formation of cyclohexane was measured in a situation where the net diffusive flux of hydrogen into the reactor was governed primarily by the removal of chemisorbed hydrogen from the gold surface by the cyclohexene to form cyclohexane.

This experiment was based on the observed fact that the diffusion rate of hydrogen through the membrane gradually diminished as the hydrogen pressure in the reactor approached that in the thimble. Under these conditions, the hydrogen adsorption–desorption rate differential on the gold was obviously greatly reduced, yet it could be completely restored to its original state (that depicted in Fig. 2) by heating and pumping on both sides of the membrane to remove all sorbed and occluded hydrogen from the metal. Presumably, this behavior reflects a change in the chemisorption characteristics of gold associated with

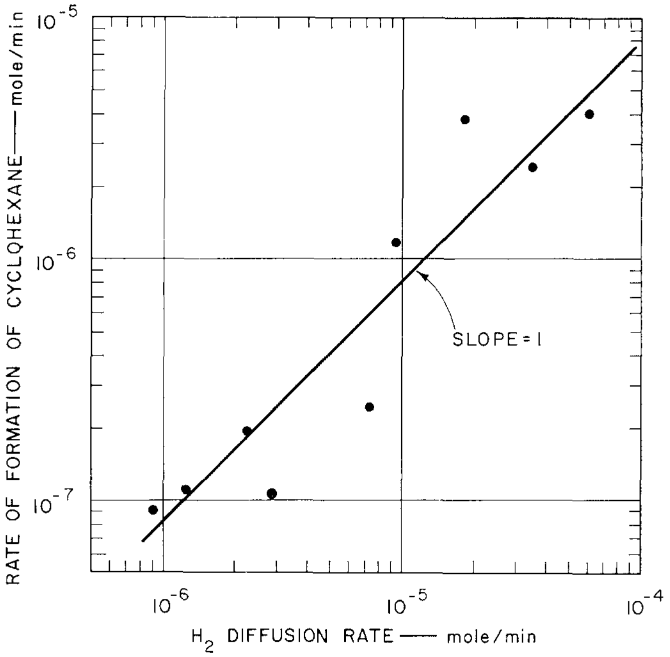

FIG. 4. Rate of hydrogenation of cyclohexene as a function of rate of diffusion of hydrogen through membrane at 125°C.

the accumulation of hydrogen on the surface or in the bulk of the metal. Diminution of the heat of adsorption $|-\Delta H_a|$ of hydrogen on tungsten (*12*) and on copper (*9*) with increasing surface coverage of chemisorbed hydrogen has been reported. Such a lowering of the magnitude of $|-\Delta H_a|$ may be accompanied by a decrease in the energy of activation for adsorption, especially in the case of a metal like gold which is reported to exhibit a small endothermic energy of adsorption (*13*). In the gold-clad membrane this would be manifested by a reversible loss of its semipermeable character so that an equilibrium state involving equal pressure of hydrogen on both sides of the membrane could be achieved.

Such a condition was attained by bathing the thimble in hydrogen at a pressure of 1 atm (on both sides) for a prolonged period of time. The reactor was then pumped out for just 5 min, and a cyclohexene/hydrogen mixture (1/7.5) was admitted to a total pressure of 1 atm. Within 2 hr the total pressure in the reactor rose to 780 Torr and remained constant. The rate of formation of cyclohexane was followed for 7 hr and found to be constant and comparable to the rate determined in the previous experiments carried out at large hydrogen fluxes.

During this experiment (identified with an asterisk in Table 1), hydrogen diffused out of a virtually infinite reservoir and into the reactor, because the thimble was connected to a large tank of compressed hydrogen through a pressure reducer and regulator. In order to test whether hydrogen could be supplied to the reactive state at the gold surface only by diffusion out of the bulk metal, the thimble, full of hydrogen at 1 atm, was isolated from the hydrogen tank. Under these conditions, the rate of formation of cyclohexane diminished, yet the total pressure in the reactor remained practically constant. Presumably, as the available hydrogen was consumed by the cyclohexene, the steady state population of chemisorbed hydrogen diminished also, necessarily on both sides of the membrane.

These results suggest that the rate of hydrogenation of cyclohexene is a function primarily of the concentration of chemisorbed hydrogen on the surface of the catalyst. This conclusion is supported further by additional experiments at other

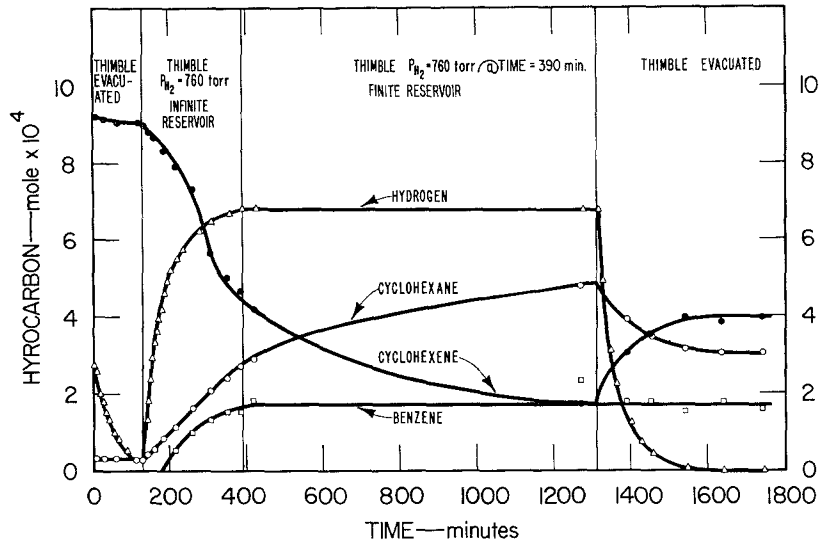

FIG. 5. Activity of gold catalyst for hydrogenation of cyclohexene at 200°C. Initial conditions: $P_{H_2} = 280$ Torr; $P_{C_6H_{10}} = 97$ Torr.

catalyst temperatures (Table 1). At 200°C the rate of adsorption of hydrogen on gold is sufficient to allow a substantial hydrogen flux into the gold membrane, yet hydrogenation activity appears only when hydrogen is supplied from the thimble to the gold surface at a high enough rate to produce a significant production rate of molecular hydrogen (Fig. 5). At this temperature, hydrogen equilibration between the membrane, reactor, and thimble occurs relatively quickly, yet the rate of formation of cyclohexane is constant and independent of the diminishing hydrogen flux, apparently because the hydrogen adatom concentration is constant.

It is of interest to note that a fraction of the hydrocarbon is converted to benzene at 200°C. The quantity of benzene formed (Fig. 5) is in line with gradual attainment of its equilibrium partial pressure (*14*).

It is especially remarkable that at 200°C the catalyst function seems to be quite reversible. When hydrogen is withdrawn from the catalyst surface by evacuating the thimble, cyclohexane begins to be converted to cyclohexene at a significant rate (Fig. 5). Even this dehydrogenation reaction, however, appears to be dependent on the existence of chemisorbed hydrogen on the surface of the catalyst, for the composition of the hydrocarbon mixture in the reactor ceases to change when the hydrogen content of the system has been reduced to a low value (Fig. 5).

Temperature variation of the catalyst affects the rates of a variety of elementary processes in this system, including adsorption, diffusion, and chemical reaction. Consequently, the significance of observed temperature coefficients of over-all reaction rate is obscure. However, hydrogenation rates at three temperatures, 70°, 125°, and 200°C, were observed for the case described above where hydrogen equilibrium between the thimble, the membrane, and the reactor was established. The attainment of a true steady state with respect to hydrogen at the lowest temperature was somewhat uncertain due to the low porosity of the membrane. Nevertheless, the three rate values satisfied an Arrhenius expression with an activation energy term of 5 kcal/mole, which is in general agreement with the values of activation energy reported for a variety of olefin hydrogenations on metal catalysts (*15*).

DISCUSSION

The catalytic activity of the gold membrane can be understood in terms of a dynamic balance between diffusive transport of hydrogen through the metal and the removal of hydrogen from the surface by adatom recombination and olefin hydrogenation. In the absence of chemical reaction, the rate of arrival of hydrogen atoms at the surface of the gold is given by (*16*)

$$\frac{dC_{\mathrm{B}}}{dt} = \frac{(C_{\mathrm{A}} - C_{\mathrm{B}})}{(S/D)} \tag{1}$$

where D is the average diffusion coefficient for hydrogen through the membrane and S is a shape factor related to the membrane thickness and geometry.* C_{A} and C_{B} are the respective surface concentrations of hydrogen on the Pd–Ag and Au sides of the membrane.

Even at temperatures as low as −78°C, hydrogen atoms chemisorbed on gold are highly mobile (*17*). Hence, hydrogen adatom recombination on gold most likely involves a bimolecular, second order reaction (*18*) with an associated rate expression

$$\mathrm{H(s)} + \mathrm{H(s)} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{H_2(g)}$$

$$d[\mathrm{H_2(g)}]/dt = -\tfrac{1}{2}(dC_{\mathrm{B}}/dt) = k_1 C_{\mathrm{B}}{}^2 - k_2[\mathrm{H_2(g)}] \tag{2}$$

Similarly, for cyclohexene hydrogenation

$$2\mathrm{H(s)} + \mathrm{C_6H_{10}} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{C_6H_{12}}$$

$$\begin{aligned} d[\mathrm{C_6H_{12}}]/dt &= -\tfrac{1}{2}(dC_{\mathrm{B}}/dt) \\ &= k_3 C_{\mathrm{B}}{}^2[\mathrm{C_6H_{10}}] - k_4[\mathrm{C_6H_{12}}] \end{aligned} \tag{3}$$

Under the conditions of our experiments on the gold surface at 125°C, the rate constants k_2 and k_4 appear to be small, and the rate of hydrogenation independent of the olefin concentration $[\mathrm{C_6H_{10}}]$. Hence, these terms may be eliminated from Eqs. (2) and (3) and, the surface concentration of hydrogen atoms, C_{B}, may be computed from their net rate of formation

$$\frac{dC_{\mathrm{B}}}{dt} = \frac{(C_{\mathrm{A}} - C_{\mathrm{B}})}{S/D} - 2k_1 C_{\mathrm{B}}{}^2 - 2k_3 C_{\mathrm{B}}{}^2 \tag{4}$$

In the steady state $(dC_{\mathrm{B}}/dt = 0)$

$$C_{\mathrm{B}} = \frac{D}{4S(k_1 + k_3)} \left\{ \left[1 + \frac{8C_{\mathrm{A}}S(k_1 + k_3)}{D} \right]^{1/2} - 1 \right\} \tag{5}$$

Substituting Eq. (5) for C_{B} in Eq. (3) (simplified by neglecting $[\mathrm{C_6H_{10}}]$ and k_4) gives an expression for the olefin hydrogenation rate as a function of C_{A} and the various rate constants

$$\frac{d[\mathrm{C_6H_{12}}]}{dt} = \frac{k_3}{16} \left[\frac{D}{S(k_1 + k_3)} \right]^2 \left\{ \left[1 + \frac{8C_{\mathrm{A}}S(k_1 + k_3)}{D} \right]^{1/2} - 1 \right\}^2 \tag{6}$$

Equation (6) is of interest because it suggests a limit where chemical reaction on the surface gives way to diffusive transport of hydrogen as the hydrogenation-rate-controlling process on the catalyst. The expression predicts that the hydrogenation rate approaches zero as C_{A} is reduced to zero, as would be expected. When the term $[8C_{\mathrm{A}}\ S(k_1 + k_3)]/D$ is much larger than unity, corresponding to $C_{\mathrm{A}} \gg C_{\mathrm{B}}$, Eq. (6) reduces to a simple linear relationship

$$\frac{d[\mathrm{C_6H_{12}}]}{dt} = \frac{k_3}{k_1 + k_3} \frac{DC_{\mathrm{A}}}{2S} \tag{7}$$

which states that the rate of formation of cyclohexane is proportional to the rate of diffusion of hydrogen, DC_{A}/S, as observed in our experiments (Fig. 4). For a membrane of given shape factor S, this condition obtains when in Eq. (6) the ratio $[(k_1 + k_3)/D] \gg 1$, that is, when the chemical reaction rate on the gold surface exceeds the diffusion rate in the metal. From our measurements of the relative rates of formation of hydrogen and cyclohexane at 125°C, we calculate $k_1/k_3 = 14 \pm 6$. It is also evident from Eq. (6) that the apparent activation energy observed in our measurements represents a combined temperature coefficient for two rate constants and a transport parameter.

In this regime, where the rate of arrival of hydrogen adatoms at the gold surface

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* For a cylindrical membrane $S = [1/(2\pi l)]\ln(b/a)$ where a and b are, respectively, the inner and outer radii of the cylinder, and l is the length. Because, in our experiments, there is diffusional transport through two metals in series, the term (S/D) actually represents the total "series resistance," analogous to the case of steady state heat conduction.

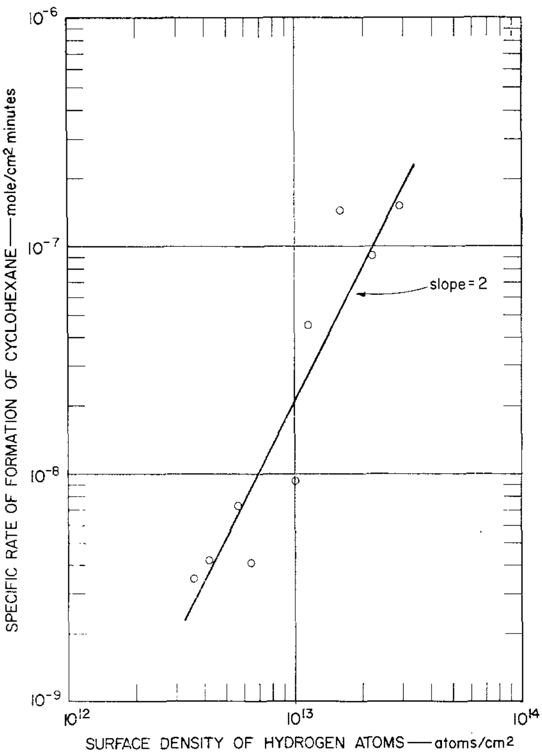

FIG. 6. Rate of formation of cyclohexane as a function of surface density of hydrogen atoms at 125°C.

is governed by the diffusional mechanism in the body of the metal and is slow relative to the specific reaction rate for adatom recombination or desorption, the rate of appearance of H_2(gas) in the reactor may be taken as a measure of the steady state surface population of hydrogen atoms. From Eq. (2) (assuming $k_2[H_2(g)]$ to be negligible)

$$C_B = k_1^{-1/2}(d[H_2(g)]/dt)^{1/2}$$

As an approximation, the numerical value of C_B may be calculated from absolute rate theory (*19*), assuming a mobile adsorbed hydrogen layer (*17*) and an activation energy for desorption of 14 kcal/mole (*13*). The results of such a calculation, based on a surface roughness factor of 2, indicate a very low surface density of hydrogen adatoms. When these values are plotted against the measured rate of formation of cyclohexane on a logarithmic grid (Fig. 6), the results suggest that the hydrogenation rate is second order with respect to chemisorbed hydrogen. The rate therefore, appears to be limited only by the surface density of hydrogen atoms.

The observed dependence of the cyclohexene hydrogenation rate on the square of the hydrogen adatom concentration (Fig. 6) may be interpreted in terms of two possible mechanisms. In the simplest, two hydrogen adatoms are removed simultaneously when the double bond of the olefin molecule is saturated

$$C_6H_{10}^* + 2H(s) \xrightarrow{k_3} C_6H_{12}$$

where the asterisk represents a weakly bound, possibly physisorbed, species. Since the rate appears to be independent of the olefin concentration, one may conclude that an abundance of olefin molecules is available for reaction. The kinetic data may be also interpreted by a two-step mechanism involving an adsorbed free radical

$$C_6H_{10} + H(s) \underset{k_{3b}}{\overset{k_{3a}}{\rightleftarrows}} C_6H^{\cdot}_{11}(s)$$

$$C_6H^{\cdot}_{11}(s) + H(s) \xrightarrow{k_{3c}} C_6H_{12}$$

where the second reaction is the slow step. Such a mechanism avoids the necessity of the termolecular encounter demanded by the one-step hydrogenation. It requires, however, a low probability for the reaction between molecular hydrogen and the free radical (Rideal mechanism), since such a reaction would replenish the hydrogen adatom population. This condition occurs in hydrogen–deuterium equilibration on gold (*7*) but was not observed in our olefin hydrogenation experiments.

The dehydrogenation reaction occurs when hydrogen is rapidly removed from the surface by diffusion into the bulk metal (Fig. 5). This suggests a "reverse hydrogenation" mechanism.

$$s^{\dagger} + C_6H_{12} \rightarrow C_6H^{\cdot}_{11}(s) + H(s)$$

$$C_6H^{\cdot}_{11}(s) + s^{\dagger} \rightarrow C_6H_{10} + H(s)$$

$$H(s) + H(s) \rightarrow H_2(g)$$

$$H(s) \rightarrow H(b)$$

where $s^{\dagger}$ represents an active surface site for chemisorption and H(b) refers to occluded hydrogen. Under the conditions of our experiments, it appears that the rate of the last step is fast relative to the other steps. Also, since the reaction requires chemisorbed hydrogen, it seems necessary that a fraction of the surface sites be initially occupied with hydrogen adatoms.

The notion that the critical factor in catalytic olefin hydrogenation is the surface concentration of hydrogen atoms is not without support in the recent literature. Erkelens *et al.* (*3*) studied the cyclohexene hydrogenation on evaporated gold films in the temperature range 150–350°C, and concluded that gold was a very poor catalyst because of the small concentration of hydrogen adatoms. Other investigators have come to similar conclusions with other metals used as catalysts and other olefins. McCabe and Halsey (*20*) correlated an enhanced ethylene hydrogenation activity on copper with the quantity of adsorbed hydrogen. Thompson and Wishlade (*21*) used C^{14}-tagged ethylene to demonstrate that preadsorbed ethylene did not hydrogenate on nickel, and Takeuchi and Asano (*22*) employed tritium to show that strongly bound hydrogen on nickel is most reactive with ethylene. Kowaka and Joncich, using a palladium thimble to study the hydrogenation (*23*) and deuteration (*24*) of ethylene, found that the reaction rate was enhanced when they supplied hydrogen to the catalytic surface by diffusing it through the thimble wall. In other catalytic experiments with palladium-silver alloys of various compositions, Kowaka (*25*) demonstrated that the catalytic activity is related to the rate at which the catalyst will occlude hydrogen. The precise relationship between all of these effects is not clear, but they all point to a dominant role of chemisorbed hydrogen in the catalytic hydrogenation of olefins.

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