JOURNAL OF CATALYSIS **11**, 30–34 (1968)

Dehydrogenation of Cyclohexane on a Hydrogen-Porous Membrane

BERNARD J. WOOD

From the Solid State Catalysis Laboratory, Stanford Research Institute, Menlo Park, California 94025

Received January 22, 1968

In the presence of hydrogen at 125°C, cyclohexane is thermodynamically stable with respect to cyclohexene. However, by forcing nonequilibrium conditions on a hydrogen-porous palladium-silver alloy membrane, cyclohexane vapor at about 0.1 atm is readily dehydrogenated to cyclohexene. The dehydrogenation occurs when hydrogen is pumped out of the reactor by diffusion through the membrane. For any fixed hydrogen pressure in the reactor and any steady rate of diffusion of hydrogen through the membrane, a corresponding steady ratio of cyclohexane to cyclohexene results, attained within a few minutes after experimental conditions are changed. According to a proposed mechanism, sorbed hydrogen atoms are required for the dehydrogenation, but their concentration on the catalytic surface is maintained far below the normal equilibrium concentration (for the external hydrogen pressure) by pumping them through the membrane.

INTRODUCTION

In a recent study (*1*) of the hydrogenation of cyclohexene on a hydrogen-porous metallic membrane, it was observed that, under certain conditions, the function of the catalytic membrane could be inverted to reverse the reaction and produce cyclohexene by dehydrogenation of cyclohexane. Since hydrogenation is the thermodynamically favored reaction in the presence of gaseous hydrogen and a metallic catalyst (*2*), such a dehydrogenation is of substantial interest. This report discusses the results of a kinetic study of the dehydrogeneration reaction.

EXPERIMENTAL APPARATUS AND TECHNIQUE

The experimental apparatus is shown schematically in Fig. 1. The catalytic surface is the outer side of a thimble, fabricated from 0.010-inch palladium-silver alloy (J. Bishop & Company, reported to be 23% silver) with a geometric surface area of 27 cm^2.

The ratio of cyclohexene to cyclohexane in the reactor at any time was determined by withdrawing a sample in a gastight syringe and analyzing it in a gas chromatograph (*1*). This ratio could be adjusted

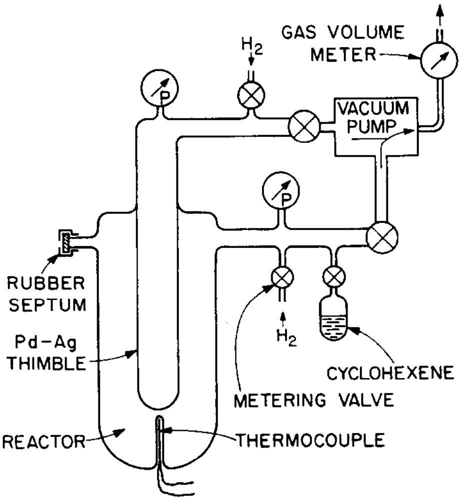

FIG. 1. Schematic diagram of apparatus for dehydrogenation of cyclohexane.

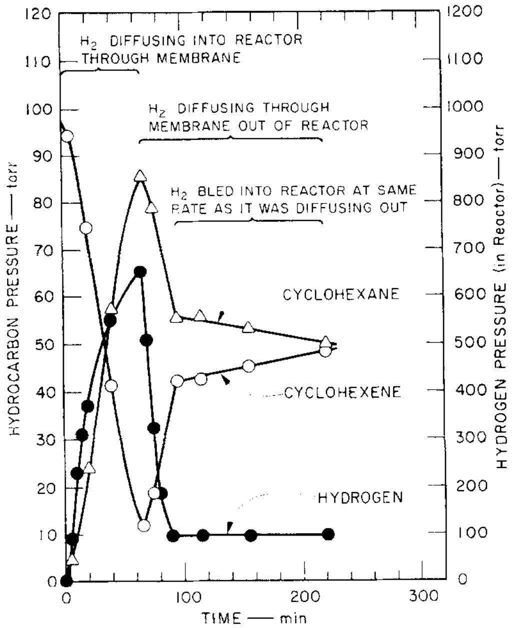

FIG. 2. Reversible hydrogenation of cyclohexene.

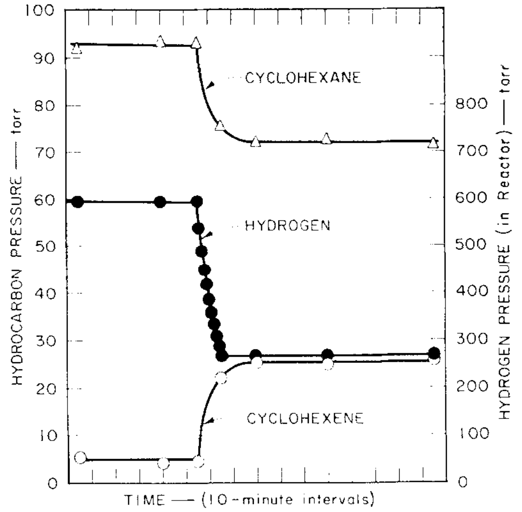

FIG. 3. Dependence of steady state pressures of cyclohexene and cyclohexane on hydrogen pressure in reactor. Diffusive flux of hydrogen through membrane changed.

by appropriate treatment with hydrogen: pumping hydrogen out of the thimble causes the gas to diffuse through the membrane out of the reactor, and cyclohexene is formed; conversely, when hydrogen is supplied to the catalytic surface by filling the interior of the thimble with this gas, cyclohexene is hydrogenated (Fig. 2).

The rate of diffusion of hydrogen through the membrane can be varied by adjusting the hydrogen pressure differential across the membrane. In our experiments, the rate of diffusion of hydrogen from the reactor was varied by throttling the vacuum pump; simultaneously the pressure of hydrogen in the reactor was fixed by leaking hydrogen through a metering valve. The temperature of the membrane and reactor was maintained at 125°C in all experiments.

EXPERIMENTAL RESULTS

Typical observed variations in the hydrogenation/dehydrogenation reactions caused by changing the sense or the magnitude of the flow of hydrogen through the membrane are shown in Figs. 2 and 3. The experiment in Fig. 2 started with only cyclohexene in the reactor. As hydrogen was supplied through the thimble, hydrogen accumulated in the reactor and the cyclohexene was hydrogenated to cyclohexane. When hydrogen was then removed from the thimble, hydrogen diffused out of the reactor and cyclohexane was dehydrogenated. When the hydrogen pressure was held constant by adding hydrogen to the reactor to balance that lost through the membrane, cyclohexane was slowly dehydrogenated to cyclohexene, even though thermodynamic equilibrium would require nearly complete hydrogenation. The results of subsequent experiments, exemplified in Fig. 3 and summarized in Table 1, show that at constant hydrogen pressure in this reactor, about 15 min is required for the concentrations of cyclohexane and cyclohexene to attain a steady state which depends linearly on the rate of diffusion of hydrogen through the thimble. The data indicate that low hydrogen pressures and/or high rates of hydrogen removal by diffusion favor large fractions of cyclohexene in the reactor. They also show that in the complete absence of hydrogen, the catalyst exhibits no detectable dehydrogenation activity for cyclohexane. Based on the initial rate of change in the ratio of cyclo-

TABLE 1
Steady-State Fraction of Cyclohexene Produced on Membrane Catalyst

P_{H_2} in reactor (torr)	H_2 diffusion rate (out of reactor) (cc/min) at 1 atm	Fraction of cyclohexene in reactor	$\frac{[C_6H_{10}]}{[C_6H_{12}]}$
800	24	0.38	0.61
713	16	0.27	0.38
	22	0.50	1.00
	24	0.56	1.27
	33	0.86	6.15
410	7	0.83	4.89
	9	0.87	6.68
218	5	0.04	0.04
	7	0.11	0.12
99	4	0.84	5.25
0	0	0[a]	0

[a] Starting from 100% cyclohexane.

hexene to cyclohexane when the pressure and diffusion rate of hydrogen are altered (Fig. 3), the molar diffusion rate of hydrogen is 14 times greater than the molar dehydrogenation rate.

Discussion

The results in Table 1 suggest that, under the conditions of these experiments, a dynamic steady state is attained between the rates of adsorption and desorption of hydrogen, the chemical reactions between hydrogen and the hydrocarbons, and the rate of diffusive transport of hydrogen away from the catalytic surface of the membrane.

The following mechanism is consistent with these observations and also with the previously reported kinetic studies of cyclohexene hydrogenation on a membrane catalyst (*1*).

$$C_6H_{12} + H(s) \xrightarrow{k_1} C_6H_{11}\cdot + H(s) + H(b) \qquad (1)$$

$$C_6H_{11}\cdot + H(s) \xrightarrow{k_2} C_6H_{12} \qquad (2)$$

$$C_6H_{11}\cdot \underset{k_4}{\overset{k_3}{\rightleftarrows}} C_6H_{10} + H(s) \qquad (3)$$

$$H_2(g) \underset{k_6}{\overset{k_5}{\rightleftarrows}} 2H(s) \qquad (4)$$

$$H(s) \rightarrow H(s') \text{ (diffusion through membrane)} \qquad (5)$$

H(s) and H(s′) refer to hydrogen atoms chemisorbed on the reactor side and on the opposite side of the thimble membrane, respectively; H(b) refers to hydrogen dissolved within the membrane. $C_6H_{11}\cdot$ is a radical sorbed on the catalyst. During reaction, the reactant and product molecules, C_6H_{12} and C_6H_{10}, are undoubtedly in sorbed states also.

The rates of steps (1) through (4) may be expressed in the usual fashion as the products of rate constants and the concentrations of the reactants. Step (5) is a mass transport process in which the rate of disappearance of H(s) depends on its concentration gradient in the membrane. This rate is expressed by a diffusion equation appropriate to transport of a gas through a thin cylindrical membrane:

$$\frac{d[H(s)]}{dt} = -D\frac{[H(s)] - [H(s')]}{S} \qquad (6)$$

where D is the diffusion coefficient for hydrogen in the palladium-silver alloy, and S is the shape factor involving the thickness of the membrane and its geometry.

If the concentrations of intermediates H(s) and $C_6H_{11}\cdot$ are small relative to those of the reactants and products and are used up as rapidly as they are formed, a steady state analysis gives an expression for the rate of formation of cyclohexene as a function of the hydrogen pressure, the diffusive flux, and the concentration of sorbed hydrogen atoms. This equation

$$\frac{d[C_6H_{10}]}{dt} = \frac{k_3(k_5[H_2(g)] - k_6[H(s)]^2 + D/S\{[H(s)] - [H(s')]\})}{2k_2[H(s)]} - k_4[H(s)][C_6H_{10}] \qquad (7)$$

may be integrated to give

$$[C_6H_{10}] = \frac{k_3(k_5[H_2(g)] - k_6[H(s)]^2 + D/S\{[H(s)] - [H(s')]\})}{2k_2k_4[H(s)]^2} \times (1 - \exp\{-k_4[H(s)]t\}) \qquad (8)$$

which shows that the quantity of cyclohexene formed increases with time in an exponential manner, but only if [H(s)] has a finite value. Thus, in the absence of sorbed hydrogen, dehydrogenation does not occur, in agreement with the experimental observations (Table 1).

At long times, the exponential term in Eq. (8) approaches zero, and the concentration of cyclohexene becomes time-independent. Thus the mechanism successfully accounts for the observed attainment of a steady state with respect to cyclohexene, cyclohexane, and hydrogen when the diffusive flux of hydrogen through the membrane is held constant. Experimentally steady states are obtained in a matter of minutes (see Fig. 3); hence the term k_4[H (s)] in Eq. (8) must be of sizable magnitude.

A similar analysis and integration gives an expression analogous to Eq. (8) for the concentration of cyclohexane:

$$[C_6H_{12}] = \frac{k_5[H_2(g)] - k_6[H(s)]^2 + D/S\{[H(s)] - [H(s')]\}}{2k_1[H(s)]} \times (1 - \exp\{-k_1[H(s)]t\}) \quad (9)$$

In the steady state, the quotient of Eqs. (8) and (9) gives a simple expression which suggests that the ratio of cyclohexene to cyclohexane is simply a linear function of the reciprocal of the concentration of sorbed hydrogen atoms.

$$\frac{[C_6H_{10}]}{[C_6H_{12}]} = \frac{k_1k_3}{k_2k_4[H(s)]} \quad (10)$$

Equation (10) predicts that the ratio of cyclohexene to cyclohexane will decrease as the concentration of sorbed hydrogen atoms increases. This is in full agreement with the reported study (*1*) of the hydrogenation of cyclohexene on a gold surface, which showed that the kinetically significant component was the sorbed hydrogen atom. It also agrees qualitatively with the results in Table 1. (The rather broad span of these results precludes any quantitative correlation.) The practical consequence of this conclusion is that the most active surface for dehydrogenation of a hydrocarbon must sustain a concentration of sorbed hydrogen atoms which is very low, but not zero.

In the case of the membrane catalyst, the concentration of hydrogen atoms can be affected in two ways: (1) lowering the pressure of hydrogen over the catalyst; (2) removing hydrogen atoms from the surface more rapidly than they are deposited by adsorption by diffusing them rapidly through the membrane. The diffusive transport of hydrogen may be enhanced by lowering the magnitude of [H(s')] (increasing the pumping speed of the system), or by altering the geometric character of the membrane (making it thinner or changing its configuration) [see Eq. (6)].

In any case, it is of interest to note that the only reactant consumed in such a reactor is the saturated hydrocarbon. Hydrogen transported through the membrane may be recycled so that after an initial charge of the gas in a flow-type reactor, only cyclohexane need be supplied. The product stream would contain cyclohexene and excess hydrogen.

If the reactants are allowed to remain in the reactor for long periods (>24 hr) at low hydrogen pressure (<100 torr), up to 24% benzene is formed. This is consistent with the equilibrium data reported ref. (*2*) for the cyclohexene-benzene system. The absence of benzene as a product in short runs suggests that only one molecule of hydrogen can be removed from each cyclohexane molecule during the catalytic dehydrogenation reaction on the membrane. Whether the membrane catalyst would, in a similar fashion, selectively dehydrogenate only one carbon-carbon linkage in a straight-chain hydrocarbon, however, cannot be predicted.

ACKNOWLEDGMENTS

I am grateful to Dr. Henry Wise and Dr. Frank Mayo for their discussions and suggestions concerning the interpretation of the data, and to Mrs. Madeline Rado for assistance in the

experimental work. The work was carried out under the Oxidation Program supported by a group of industrial companies.

REFERENCES

1. Wood, B. J., and Wise, H. *J. Catalysis* **5**, 135 (1966).
2. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Research Project 44. Carnegie Press, Pittsburgh, Pennsylvania, 1953.