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Hydrogenation of Alkenes on Gold*

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Gas-phase hydrogenation of 1-butene and cyclohexene was carried out at 383°K on a gold surface. Since molecular hydrogen for the hydrogenation reaction does not adsorb on gold at this temperature, it was supplied to the gold surface by diffusing it through a palladium–silver alloy membrane on which a gold layer was electroplated. The hydrogenation rates of the alkenes were measured individually and in admixture. The hydrogenation rates were found to be first order in alkene pressure, and second order in chemisorbed hydrogen. For the gas mixture of alkenes, the total rate of hydrogenation was found to be the sum of the individual rates.

I. INTRODUCTION

Detailed study of the kinetics of catalytic hydrogenation of alkenes led to the conclusion that the rate of hydrogenation is governed by the surface density of chemisorbed hydrogen (*1*, *2*). In one of these studies (*1*) a gold surface was employed, which was electroplated on the outer side (labelled the reactor side) of a hydrogen diffusion thimble (Pd–Ag alloy). By diffusing hydrogen through the thimble onto the gold surface, we were able to relate the alkene hydrogenation rate to the hydrogen diffusion rate, thereby demonstrating the catalytic properties of gold covered with chemisorbed hydrogen. Because of the possibility of different catalytic rates for various alkenes, it seemed desirable to explore in detail the rates of hydrogenation of two alkenes in admixture. We selected cyclohexene and 1-butene for this purpose.

II. EXPERIMENTAL DETAILS

The apparatus used in our studies has been described in Ref. (*1*). A Pd–Ag alloy thimble (8.8 cm long, 1.0 cm diam) was electroplated on its outer surface (labelled the reactor side) with a layer of gold (0.0025 cm thick). The apparatus was designed to facilitate evacuation, transfer, sampling, and pressure measurement (*3*) of the gases involved in the experiments. The thimble was enclosed in a cylindrical glass reactor, which was heated externally by electrical furnace elements whose temperature was controlled at 383 ± 2°K. The procedure we adopted was to maintain 1 atm of hydrogen on the Pd–Ag side of the thimble at all times. Immediately before introducing the alkenes the reactor side was pumped out for 2 min to rid it of accumulated hydrogen. The residual H_2 pressure in the reactor did not increase to more than 0.01 Torr during the time that the alkenes were being introduced into the reactor.

At convenient times during the reaction, gas samples of 1–5 ml were withdrawn from the 250-ml reactor and analyzed by gas chromatography. A F&M Model 5750 gas chromatograph was used for most of the analyses. Satisfactory separation of 1-butene, butane, *cis*-2-butene, *trans*-2-butene, cyclohexene, and cyclohexane was accomplished by linear temperature programming (298–343°K) of a column containing a mixture of 80% (W/W) of packing A and 20% (W/W) of packing B, where A is 20% (W/W) bis-methoxyethyl

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TABLE 1

Catalytic Hydrogenation of 1-Butene and Cyclohexene on Gold at 383°K

Reactants present[a]	Hydrogen diffusion rate R_d (mole/min) × 10^6	Hydrogenation rate (initial) R_h (mole/min) × 10^6		R_h/R_d	
		C_4H_{10}	C_6H_{12}	C_4H_{10}	C_6H_{12}
C_4H_8	29	0.34	—	0.012	—
C_4H_8	24	0.43	—	0.018	—
C_4H_8	35	0.44	—	0.013	—
				0.014 ±0.002	
C_6H_{10}	13	—	0.13	—	0.010
C_6H_{10}	18	—	0.38	—	0.021
C_6H_{10}	24	—	0.20	—	0.008
					0.013 ±0.003
C_4H_8, C_6H_{10}	11	0.20	0.19	0.018	0.017
	38	0.45	0.43	0.012	0.011
				0.013 ±0.004	0.014 ±0.003

[a] Initial pressure of each reactant was 53 ± 3 Torr.

adipate on Chromsorb W and B is 20% (W/W) diethyl sebacate on the same support. In some experiments a 10 ft × ¼ in. column containing Dow Corning No. 710 silicon oil on a refractory support was used to separate the C_6 compounds. The chromatograms were analyzed by peak-height measurements with the use of empirically determined molar response values for the compounds analyzed.

III. Experimental Results

Table 1 summarizes the results of a number of experiments carried out to measure the individual and combined hydrogenation rates of 1-butene and cyclohexene. Based on the observations described in Ref. (*1*), we have listed the ratio of the hydrogenation rate to the hydrogen diffusion rate. This ratio is given in the last column of Table 1.

To elucidate the order of the kinetics with respect to alkene concentration, we measured the hydrogenation rate of cyclohexene as a function of its initial pressure. The starting pressures of cyclohexene ranged from 22 to 83 Torr; results are given in Table 2.

Results for some experiments carried out under conditions of high diffusion rates are given in Table 3.

IV. Discussion

The results obtained in this study may be interpreted with the aid of the observed relationship between the rate of formation of alkane and the rate of diffusion of hydrogen through the catalyst thimble (*1*). Two additional observations are of interest with regard to the mechanism of alkene hy-

TABLE 2

Effect of Initial Pressure of Cyclohexene on the Hydrogenation Rate at 383°K

Initial pressure of C_6H_{10} $P_{C_6H_{10}}$ (Torr)	Hydrogen diffusion rate R_d (moles/min) ×10^6	Hydrogenation (initial) rate R_h (moles/min) ×10^6	Normalized hydrogenation coefficient R_h/R_d	$\frac{R_h/R_d}{P_{C_6H_{10}}}$ (Torr^{-1}) ×10^4
23	22	0.12	0.005	2.2
53[a]	18	0.24	0.013	2.5
83	33	0.59	0.018	2.2

[a] Average of three separate runs.

TABLE 3

HYDROGENATION OF CYCLOHEXENE AT 383°K UNDER CONDITIONS OF HIGH DIFFUSION RATES OF HYDROGEN

Initial pressure of C_6H_{10} (Torr)	Hydrogen diffusion rate, R_d (moles/min) $\times 10^6$	Hydrogenation (initial) rate, R_h (moles/min) $\times 10^6$	R_h/R_d
52	73	1.67	0.023
48	63	1.09	0.017
22	73	1.22	0.017
25	65	1.12	0.017

drogenation. The first concerns the reaction order of the catalytic reaction with respect to the alkene concentration. The data in Table 2 suggest that the process is first-order in alkene concentration, since the ratio of the normalized hydrogenation coefficient to the initial alkene pressure is constant. Secondly, when both alkenes (1-butene and cyclohexene) are present in the gas mixture, the hydrogenation proceeds at a rate equivalent to the sum of the two individual rates (last set of data in Table 1). In spite of the fact that the hydrogen atom density on the catalyst surface is low because of the competing reaction for hydrogen-molecule formation, a fraction of the incident alkene molecules capture hydrogen atoms and are converted to alkane. Also, the catalyst does not distinguish between 1-butene and cyclohexene during the hydrogenation process. Variations due to the structural differences of the two olefins are not reflected in the reaction rate, as is evidenced by the similarity of the individual hydrogenation kinetics (Table 1).

The reaction steps leading to the production of alkane may be represented as follows:

$$\text{alkene(g)} + \text{H(s)} \rightleftarrows \text{alkyl(s)}, \qquad (1)$$

$$\text{alkyl(s)} + \text{H(s)} \rightleftarrows \text{alkane(s)}, \qquad (2)$$

$$\text{alkane(s)} \rightleftarrows \text{alkane(g)}, \qquad (3)$$

$$2\text{H(s)} \rightleftarrows \text{H}_2\text{(g)}. \qquad (4)$$

The rate of production of alkane in the gas phase is given by

$$\frac{d}{dt}[\text{alkane (g)}] = k_3[\text{alkane (s)}] - k_{-3}[\text{alkane (g)}]. \qquad (5)$$

By assuming steady-state concentrations for H_s, alkyl-s, and alkane-s and by ignoring the reaction represented by k_{-3} one can derive the expression

$$\frac{d}{dt}[\text{alkane (g)}] = \frac{k_1k_2k_3[\text{H(s)}]^2[\text{alkene}]}{(k_{-2}+k_3)(k_{-1}+k_2[\text{H(s)}])}. \qquad (6)$$

From (4) we may derive

$$\frac{d}{dt}\text{H}_2\text{(g)} = k_4[\text{H(s)}]^2 \qquad (7)$$

the reverse reaction of (4) is inconsequential since H_2 does not dissociatively adsorb on Au at such low temperatures. If we assume that $k_{-1} \gg k_2$ [H(s)] we may write

$$\frac{d}{dt}[\text{alkane (g)}] = \frac{k_1k_2k_3}{k_{-2}+k_3} \frac{[\text{alkene (g)}]}{k_{-1}k_4} \frac{d[\text{H}_2\text{(g)}]}{dt}. \qquad (8)$$

Equation (8) predicts that the rate of formation of alkane should be first order in alkene and first order in H_2 production, in accordance with experimental observations. The term $d[H_2(g)]/dt$ is proportional to the diffusion rate of hydrogen through the catalyst thimble as discussed in detail in Ref. (*1*). A further simplication to (8) arises if we assume that the desorption of the product is faster than the reverse of (2). This leads to the expression

$$\frac{d}{dt}(\text{alkane (g)}] = K_1\frac{k_2}{k_4}[\text{alkene (g)}]\frac{d[\text{H}_2\text{ (g)}]}{dt}, \qquad (9)$$

where $K_1 = k_1/k_{-1}$, the equilibrium constant for (1).

It is of some interest to note that no dialkyl compound was formed in any appreciable amount. This fact indicates that the surface density of alkyl radicals is very low relative to the density of H atoms or that the alkyl radicals are much less mobile. Thus the probability of an encounter between two radicals is very much less than that between a radical and a hydrogen atom.

The diffusional mass transport of hydrogen through the membrane occasionally led to very high mass fluxes and unusually high hydrogenation rates, far in excess of those to be expected on the basis of the data shown in Table 1. The results from a series of such measurements are summarized in Table 3. The cause for the variation in catalytic behavior may be sought in the density distribution of hydrogen inside the thimble. As shown schematically in Fig. 1, the distribution of hydrogen inside the thimble becomes uniform (profile a) at saturation with a constant pressure of hydrogen on both sides of the membrane. The density profile depicted by curve b (Fig. 1) represents the type of gradient to be expected under conditions prevalent during steady state catalysis (Table 1). Finally, curve c is indicative of the type of concentration profile that causes higher mass fluxes of hydrogen and larger hydrogenation rates. Both the slope of the density curve at the catalytic surface and the surface density (C''_B) of hydrogen at the gold side have increased because of the non-steady state distribution of hydrogen within the thimble. The net result is an increased diffusion flux and a higher reaction rate which, as observed experimentally, gradually diminish to the steady state condition reproduced by curve b (Fig. 1).

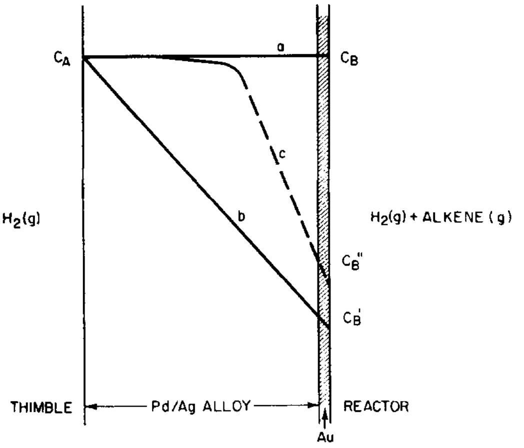

Fig. 1. Density profile of hydrogen in wall of diffusion thimble.

This work has increased the scope of our earlier studies (*1*, *2*) by showing that (a) the hydrogenation rate is approximately first-order in alkene concentration, that (b) the catalytic activity is nearly the same for the two structurally different alkenes used in this work, and (c) the two alkenes are hydrogenated in admixture as the sum of the individual rates. In addition, the results demonstrate that the hydrogenation of olefins does not require special surface-hydrocarbon interactions but only the presence of a sufficient quantity of adsorbed H atoms, which serve as sites for production of the radical intermediate.

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