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Kinetic Study of 1-Butene Hydrogenation on Supported Palladium

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The reaction between 1-butene and hydrogen on supported palladium has been kinetically investigated in order to study both the isomerization and hydrogenation. Experiments were performed at 50°, 75°, and 100°C at different 1-butene partial pressures by employing a microflow reactor. A reaction mechanism is proposed which allows a satisfactory description of the reacting system.

Introduction

The mechanism of olefin hydrogenation on transition metals has been the object of open discussion (*1*). In the present paper some kinetic results are given on the hydrogenation of 1-butene on supported palladium. Experiments have been carried out on 1-butene in order to study also the isomerization reactions, due to double-bond migration, associated with the hydrogenation process.

The work was performed with the aim of suggesting a comprehensive mechanism for the complex reaction pattern.

Experimental

Highly dispersed palladium supported on alumina was employed as a catalyst (0.484 % Pd; alumina surface area about 200 m^2/g) (*2*, *3*). The 1-butene was a Phillips Petroleum Co. pure grade product. Its content in *n*-butane was 0.5% and this was taken into account in the material balances.

The analyses of 1-butene, *cis*-2-butene, *trans*-2-butene and *n*-butane were performed by gas chromatography using an 8-m stainless steel column of benzyl Cellosolve (25%) on Carbowax 60–80 mesh at 40°C.

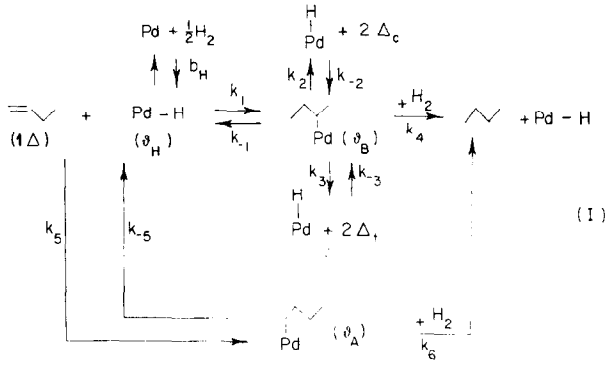
Hydrogen was a gas chromatographically pure gas. The experiments were performed in a microflow system by feeding a tublar reactor with mixtures of 1-butene and hydrogen. The stream outgoing from the reactor was directly injected into the gas chromatograph for the analysis. The fresh catalyst samples were run (at least 4 hr) with the reaction mixtures up to stationary conditions. This procedure guaranteed good reproducibility of the kinetic data.

Results and Kinetic Interpretation

Reactions were performed at 50°, 75°, and 100°C, by feeding mixtures of 1-butene and hydrogen at different partial pressures. In Fig. 1 the hydrogenation conversions of 1-butene at 50°C are shown.

In double-bond migration the ratio *cis*-2-butene/*trans*-2-butene ($\simeq 0.5$)is near to equilibrium at 50°C and is independent of the contact time except at very low hydrogen pressures (see, for instance, the data of Fig. 2).

The reaction kinetics have been interpreted on the basis of the following scheme in which the half-hydrogenated compound has an important role:



where 1Δ, $2\Delta_c$, $2\Delta_t$ are the abbreviations for 1-butene, *cis*-2-butene, *trans*-2-butene respectively; ϑ_B and ϑ_A are the coverage of the two half-hydrogenated compounds; and ϑ_H is the coverage of hydrogen, b_H is the equilibrium constant of the dissociative adsorption of hydrogen.

In the previous mechanism the formation of the half-hydrogenated state occurs through the interaction of the olefin with a hydrogenated center, and this is in agreement with the known high activity of hydrogenated surfaces (*4*). In fact the kinetics of the reaction when performed in a static system is affected by the order of addition of the reactants to the catalyst. In any case it was observed that if hydrogen is admitted first the rate of hydrogenation is higher (*5*).

The formation of the half-hydrogenated compounds can happen either by a direct interaction of a physically adsorbed olefin with a hydrogen bound to a metal atom of the surface, or after a coordinative chemisorption of olefin on the hydrogenated metal atom. In fact, metal atoms in particular surface sites (edges, dislocations) are accessible to the coordination from many directions. The question as to which of the described processes actually occurs is less important, and it is difficult to answer it from a kinetic point of view.

The results of Fig. 2 and an analysis of the values of the ratio (1-butene/2-butenes) suggest that the isomerization reactions are faster than the hydrogenation ones. In a first approximation it seems justified to assume that the hydrogenation reaction of the half-hydrogenated species is the rate-limiting step, and therefore all the reversible reactions of scheme I are assumed to be at equilibrium. This is in agreement with the data obtained from the hydrogenation of 1-butene on nickel by which it appears that the slow step is the addition of hydrogen to the surface butyl radical (*6*).

It is also interesting to point out that the stability with respect to hydrogenation of

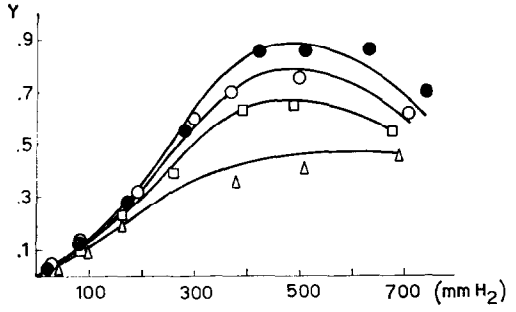


FIG. 1. Hydrogenation conversion of 1-butene at 50°C. The points correspond to different contact times W/F, where W is g Pd and F, moles/hr of 1-butene; ●, 3.392×10^{-3}; ○, 2.517×10^{-3}; □, 1.661×10^{-3}; △, 787×10^{-3}.

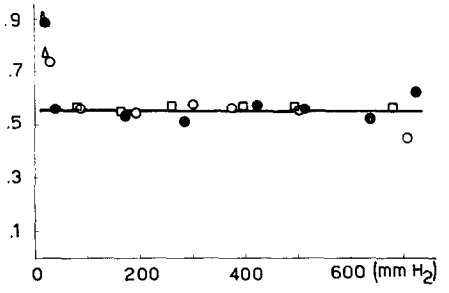


FIG. 2. Ratio (*cis*-2-butene/*trans*-2-butene) at 50°C vs. partial pressure of hydrogen. The points correspond to different contact times, W/F; ●, 3.392×10^{-3}; ○, 2.517×10^{-3}; □, 1.661×10^{-3}; △, 0.787×10^{-3}.

surface alkyl radicals is supported by the studies of butene deuteration (*7*). A random distribution of deuterium in hydrogenated products indicates a sufficiently long residence time of the alkyl radicals.

A straightforward derivation gives the following rate expression for the hydrogenation:

$$r = KP_{1\Delta}\frac{(b_H P_{H_2})^{1/2}}{1 + (b_H P_{H_2})^{1/2} + b_{1\Delta}P_{1\Delta}}P_{H_2} \quad (1)$$

where $K = [(k_1k_4/k_{-1}) + (k_6k_5/k_{-5})]$, $b_{1\Delta}$ is the equilibrium constant of the adsorption of olefin on active centers, $P_{1\Delta}$ and P_{H_2} are the partial pressures of 1-butene and hydrogen, respectively, and b_H is the dissociative adsorption constant of hydrogen on palladium.

Equation (1) takes into account the competitive adsorption of the olefin with respect to hydrogen on the surface atoms through the formation of π-complex associative adsorption. Nevertheless it is assumed that the formation of the half-hydrogenated compound should preferentially occur through the interaction of the olefin with a hydrogenated center (*5*) instead of hydrogenation of the adsorbed olefin. This fact is suggested by recent findings on the hydrogenation in solution catalyzed by the transition metal complexes (*8*).

The calculations were made by neglecting, to a first approximation the adsorption of the olefin. The satisfactory agreement reported in Fig. 1 could be due to the stronger ability of palladium to adsorb hydrogen. However, the nature of olefin is also important; in fact previous research (*9*) has confirmed that 1-butene is only weakly adsorbed. This could be due both to the steric repulsion between alkyl groups and to the low π-acceptor property of the olefin. Ethylene, which is adsorbed in a stronger way, can compete in adsorption with hydrogen, and this fact can justify, on the basis of Eq. (1), the lower reaction order found in the hydrogenation of ethylene with respect to 1-butene (*6*).

The hydrogenation conversions calculated by integration of Eq. (1) fit the experimental data satisfactorily (full lines in Fig. 1). The parameters of Eq. (1) are given in Table 1. The plot of log b_H vs. $1/T$ is given in Fig. 3. A value of the adsorption heat of hydrogen on palladium of about 19 kcal/mole was obtained, in nice agreement with the value obtained by calorimetry [about 20 kcal/mole at medium coverage (*6*)].

TABLE 1
KINETIC PARAMETERS OF EQ. (1)

Temperature (°C)	K (moles/hr g Pd mm²)	b_H (mm⁻¹)
50°	0.027	3.9×10^{-2}
75°	0.052	2.95×10^{-3}
100°	0.075	1.0×10^{-3}

A full description of the system can be given through a complete kinetic analysis based on the pseudo-stationary approximation for the half-hydrogenated compound. On the basis of scheme I the following rate equations were derived:

$$dX/dt = k_{-5}\vartheta_A + k_{-1}\vartheta_B - (k_1 + k_5)\vartheta_H P_{1\Delta}$$
$$dY/dt = k_4\vartheta_B P_{H_2} + k_6\vartheta_A P_{H_2} \quad (2)$$

where X and Y are the molar fractions of 1-butene and n-butane in hydrocarbon fraction. Besides,

$$\vartheta_B = \frac{k_{-2}}{k_2}P_{2\Delta_c}\vartheta_H$$
$$\vartheta_H = \frac{(b_H P_{H_2})^{1/2}}{1 + (b_H P_{H_2})^{1/2}}$$
$$\vartheta_A = \frac{k_5\vartheta_H P_{1\Delta}}{k_{-5} + k_6 P_{H_2}}$$

The ratio (*trans*-2-butene/*cis*-2-butene) is assumed to have an equilibrium value according to experimental data (Fig. 2).

The calculation of the degree of conversion at 75°C was performed by evaluating

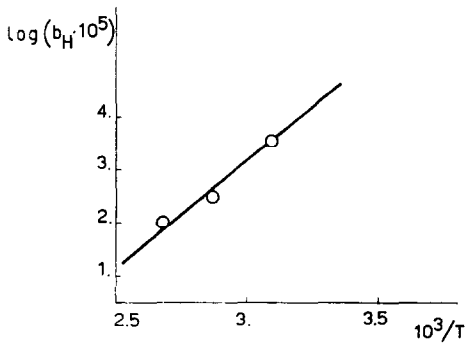


FIG. 3. Log b_H from Eq. (1) vs. 1/T.

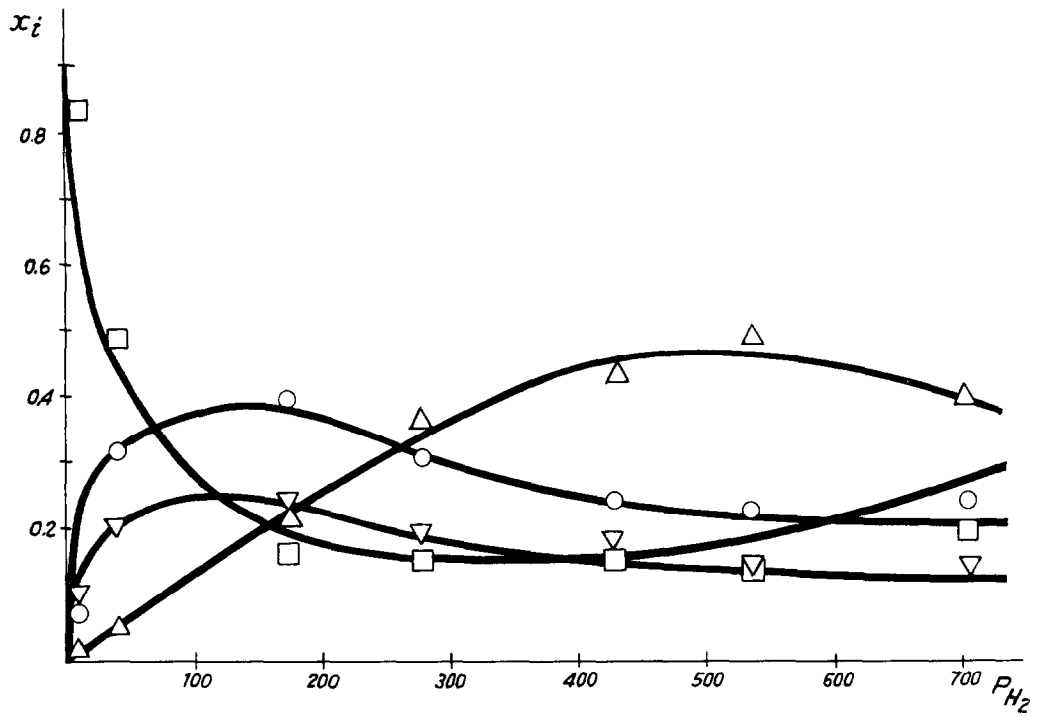


FIG. 4. Degrees of conversion at 75°C vs. hydrogen partial pressure. Contact time $W/F = 0.792 \times 10^{-3}$. Curves calculated by numerical integration of Eqs. (2); □, 1-butene; ▽, *cis*-2-butene; ○, *trans*-2-butene; △, *n*-butane.

through a nonlinear least-square analysis the kinetic parameters of Eq. (2), with the restriction that the expression $K = [(k_1k_4/k_{-1}) + (k_6k_5/k_{-5})]$ should be of the order of the value obtained with the simplified model. The parameters of Eqs. (2) are collected in Table 2. In Fig. 4 are reported (full lines) the calculated conversions of 1-butene, *cis*-2-butene, *trans*-2-butene, and *n*-butane. From the data of Table 2 it is possible to calculate a value of $K = 0.088$ close to that reported in Table 1 at 75°C. Therefore it appears that Eq. (1) is apt for the description of the hydrogenation reaction, at least at large contact times.

TABLE 2
KINETIC PARAMETERS OF EQ. (2) AT 75°C

b_H (mm^{-1})	$= 3.4 \times 10^{-3}$
k_1 (moles/hr g Pd mm)	$= 7.63$
k_4 (moles/hr g Pd mm)	$= 8.56 \times 10^{-3}$
k_5 (moles/hr g Pd mm)	$= 6.08$
k_6 (moles/hr g Pd mm)	$= 6.45 \times 10^{-3}$
k_{-1} (moles/hr g Pd)	$= 1.136$
k_{-5} (moles/hr g Pd)	$= 1.29$
$K_{2\,eq}$ (mm^{-1})	$= 2.90$

On the whole the proposed mechanism is consistent with the experimental data and it is interesting to point out that Eq. (1) is strictly related to the rate law for the hydrogenation in solution with Rh(I) complexes (*8*). This seems to support the increasing tendency to find an analogy between homogeneous and heterogeneous catalysis (*10*).

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