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KINETICS OF LIQUID PHASE HYDROGENATION OF BENZOIC ACID

By

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Abstract

The rate of hydrogenation on a palladium catalyst of benzoic acid dissolved in *n*-butyl alcohol is described by the equation $r = kPC/(1 + k'PC)$ where P is the hydrogen pressure and C is the concentration of benzoic acid. The equation corresponds to the intermediate formation on the catalyst surface of an adduct of an H_2 molecule and a molecule of C_6H_5COOH .

Reactions of liquid phase hydrogenation of unsaturated compounds on heterogeneous catalysts have been under active investigation. But in the majority of cases the authors did not compare quantitatively the experimental data on the reaction rate with the kinetic equations corresponding to definite reaction mechanisms. Such a comparison is not always possible even since the data are often complicated by the diffusion effects; it must be remembered that the diffusion coefficients in water and similar liquids are about 10^4 times lower than those in gaseous mixtures at 1 atm. Therefore, we expect the results given below to be of interest.

Hydrogenation of benzoic acid to cyclohexanecarboxylic acid



is a constituent part of industrial synthesis of caprolactam from toluene.¹⁾ The reaction is carried out in a liquid phase under elevated pressure with palladium supported on activated carbon as a catalyst. The kinetics of reaction (1) on palladium was the subject of the investigation by the research workers of *Snia Viscosa*.²⁾ In their experiments the reaction proceeded in mixtures of benzoic acid and the reaction product.

We used a solvent namely *n*-butyl alcohol. The steel reactor was supplied with propeller-type stirrer. The experiments were conducted at

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130°C (except those intended to determine the temperature dependence of constants) and at hydrogen pressures from 5 to 60 atm. The catalyst contained 5% of palladium on electrographite, the surface of palladium (measured by H₂ adsorption at 250°C) was 0.4 m² per gram of the catalyst. The size of the catalyst particles did not exceed 40 μm. A fresh portion of the catalyst was used in each run. The degree of conversion of benzoic acid did not exceed 5%. The reaction rate was determined from the rate of formation of cyclohexanecarboxylic acid; the concentration of the latter was found by gas chromatography. No other products of hydrogenation were formed. No esters were observed either.

A special attention was given to finding the conditions at which the reaction proceeds in the kinetic region. The rate of dissolution in water of spherical granules of oxalic acid was measured as a function of the rotation frequency of the stirrer and the coefficients of mass transfer β thus obtained were used to calculate β for diffusion of benzoic acid and hydrogen to the outer surface of the catalyst particles. It was done using the equation for mass transfer to particles suspended in a turbulent flow.²⁾ At a rotation frequency used in the experiments (1440 min⁻¹) the concentrations at the outer surface of catalyst particles and in the bulk of the solution were nearly the same. The estimation of the influence on the reaction rate of the diffusion in catalyst pores³⁾ showed that the efficiency factor was close to 1. The productivity of the reactor was found to be proportional to the catalyst charge which indicates that in the course of the reaction the solution was saturated with hydrogen. Because of this the hydrogen pressure P may be used in kinetic equations instead of the hydrogen concentration the solution.

We started with two series of kinetic measurements. In the first series the reaction rate r was determined at a constant concentration of benzoic acid C and different hydrogen pressures P ; in the second r was measured at constant P and different values of C . The results are presented in Tables 1 and 2. The following units are used throughout: P —atm, C —mol l^{-1} (the volume at room temperature), r —mmol hr⁻¹g⁻¹ (r is referred to the mass of the catalyst).

The experimental points of both series fall close to a straight line in the coordinates $(PC)/r$ against PC (Fig. 1) which means that the reaction rate is described by the equation

$$r = kPC/(1 + k'PC) \quad (2)$$

where k and k' are constants.

The straight line in Fig. 1 corresponds to $k=0.72 \text{ cm}^3 \text{ hr}^{-1} \text{ g}^{-1} \text{ atm}^{-1}$

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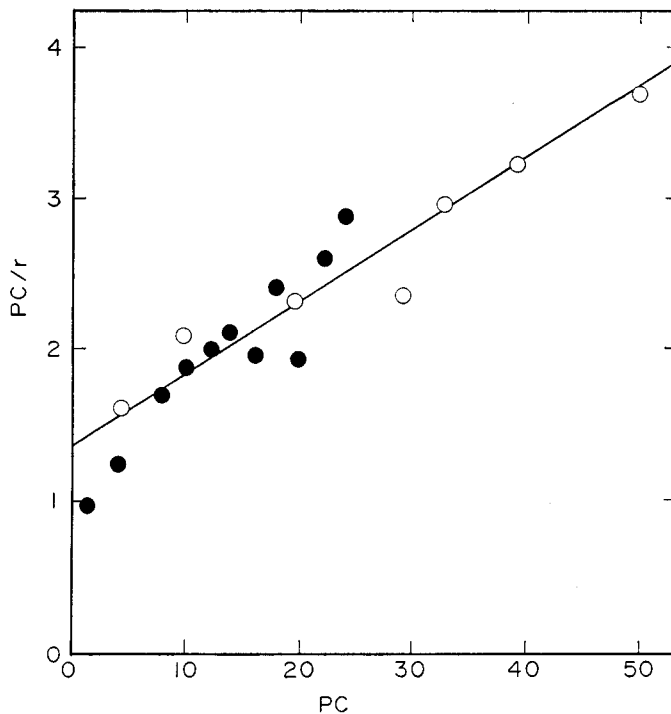


Fig. 1. Linear plot for Eq. (2).

●- $C=0.4$; ○- $P=50$.TABLE 1. $C=0.4$

| P | 10 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
|-----|------|------|------|------|------|------|------|-------|------|------|
| r | 3.12 | 4.72 | 5.34 | 6.00 | 6.72 | 8.16 | 7.50 | 10.36 | 8.50 | 8.16 |

and $k=0.0341 \text{ l mol}^{-1} \text{ atm}^{-1}$. These values are obtained from the data of the tables 1 and 2 by the least square method applied to the linearized eq. (2).

An additional series of the experiments confirmed the reaction rate to be independent of the concentration of cyclohexanecarboxylic acid C_B as is required by Eq. (2). This is seen from Table 3 (C_B is given in the same units as C).

TABLE 2. $P=50$

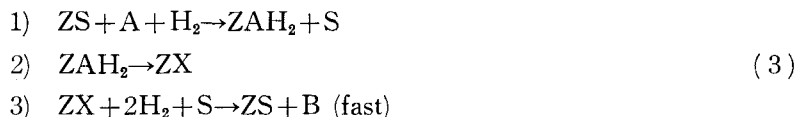
| C | 0.082 | 0.197 | 0.394 | 0.590 | 0.66 | 0.786 | 1.0 |
|-----|-------|-------|-------|-------|------|-------|------|
| r | 2.5 | 4.8 | 8.4 | 12.6 | 11.2 | 12.0 | 13.6 |

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TABLE 3. $P=50, C=0.1$

| C_B | 0 | 0.05 | 0.10 | 0.16 | 0.22 |
|-------|------|------|------|------|------|
| r | 4.78 | 4.81 | 4.95 | 4.39 | 4.75 |

Eq. (2) is explained if the existence is assumed of an intermediate AH_2 , formed from a molecule of benzoic acid A and a molecule of H_2 , which covers a considerable part of the catalyst surface. The intermediate isomerizes into cyclohexadienecarboxylic acid X which is then hydrogenated readily to cyclohexanecarboxylic acid B:



Here Z is a site on the surface, S is the solvent molecule; stage 3 is a sum of several elementary reactions. The covering of the surface with molecules of X is negligibly small since stage 3 is very fast. Let θ be the covering of the surface with AH_2 , then the covering with S is $1-\theta$. The rates of stage 1 and 2 are equal (it is the steady state condition):

$$k_1(1-\theta)CP = k_2\theta \quad (4)$$

where k_1 and k_2 are the rate constants of the stages. From Eq. (4) θ is found, and substitution in $r = k_2\theta$ gives Eq. (2) with $k = k_1$ and $k' = k_1/k_2$. If stage 1 is assumed to be reversible, Eq. (2) is obtained too, but with $k = k_1k_2/(k_{-1} + k_2)$ and $k' = k_1/(k_{-1} + k_2)$.

In the above derivation of Eq. (2) the surface is supposed to be homogeneous. But Eq. (2) holds true for a heterogeneous surface as well if the adsorption coefficients of AH_2 , S, and X on different surface sites are assumed to be mutually proportional.^{4,5)}

TABLE 4. $P=50$

| | | | | | | |
|----------|-----|------|------|-------|-------|-------|
| $C=0.2$ | °C | 100 | 112 | 130 | 139 | 150 |
| | r | 2.20 | 3.23 | 5.37 | 6.21 | 8.16 |
| $C=0.66$ | °C | 111 | 121 | 131 | 140 | 147 |
| | r | 5.70 | 7.80 | 11.20 | 12.84 | 15.48 |

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To determine the temperature dependence of k and k' , we measured the reaction rate under 50 atm of H_2 at two values of C and different temperatures.

Interpolation of the data of Table 4 gave the values of r at $C=0.2$ and $C=0.66$ and temperatures 100, 110, ... 150°C; then k and k' of Eq. (2) for each of the temperatures were found. From them the following equations were obtained by the least square method (k and k' in the same units as above; RT in cal.):

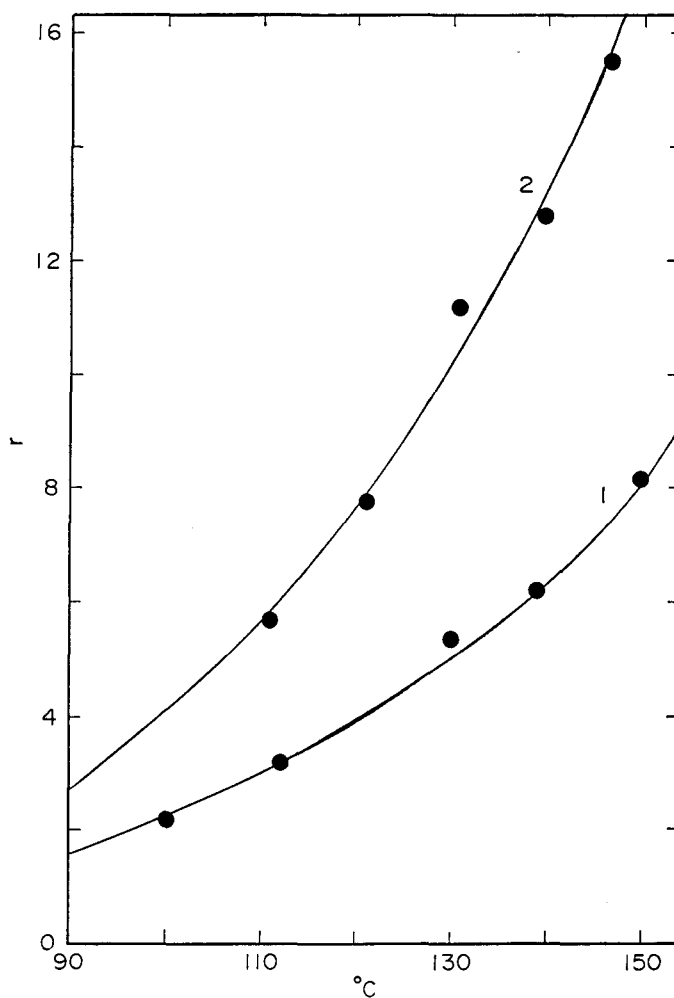


Fig. 2. Temperature dependence of the reaction rate. curve 1; $C=0.2$, curve 2; $C=0.66$.

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$$k = 3.8 \times 10^3 \exp(-6900/RT) \quad (5)$$

$$k' = 5.4 \times 10^{-4} \exp(3560/RT) \quad (6)$$

Fig. 2 shows that the curves plotted according to Eqs. (2), (5) and (6) agree with experimental data (shown by points). If stage 1 of the mechanism (3) is irreversible, then, according to (5) and (6), the activation energies of the stages $E_1=6.9$ kcal mol⁻¹ and $E_2=10.5$ kcal mol⁻¹.

The experimental results in Tables 1 and 2 can be, however, described not only with Eq. (2) but with other rate equations proposed for hydrogenation reactions. One of them is the equation

$$r = k_1 \frac{k_2 P}{1 + k_2 P} \frac{k_3 C}{1 + k_3 C} \quad (7)$$

suggested by Elovich and Zhabrova⁶ for the kinetics of ethylene hydrogenation on nickel. The authors derived Eq. (7) assuming two types of sites on the catalyst surface: the sites of the first type adsorb only ethylene and the sites of the second type—only hydrogen. An equation of the form of Eq. (7), but with an additional factor intended to account for a supposed decrease in catalytic activity with time during each run, was advanced¹⁰ also for the reaction (1). In Fig. 3 curve 1 corresponds to Eq. (2) with the above values of k and k' ; curves IIa and IIb correspond to the conditions of Tables 1 and 2, respectively, and to Eq. (7), with the following constants determined from the data of these Tables:

$$k_1 = 41 \text{ mmol hr}^{-1} \text{ g}^{-1}, \quad k_2 = 0.0278 \text{ atm}^{-1}, \quad k_3 = 1.35 \text{ l mol}^{-1}.$$

There are 2 separate curves IIa and IIb because Eq. (7) gives r as a function of C and P and not of their product CP . The curves agree sufficiently well with the experimental points from Tables 1 and 2.

The constants in Eq. (7) were obtained as follows. For the series with constant P the equation was written in the form

$$\frac{C}{r} = \left(\frac{1 + k_2 P}{k_1 k_2 k_3 P} \right) + \left(\frac{1 + k_2 P}{k_1 k_2 P} \right) C \quad (8)$$

and for the series with constant C in the form

$$\frac{P}{r} = \left(\frac{1 + k_3 C}{k_1 k_2 k_3 C} \right) + \left(\frac{1 + k_3 C}{k_1 k_3 C} \right) P \quad (9)$$

The least square method was used for determining the values in parentheses which are constant for each series. Then we found $k_2 = \left(\frac{1 + k_3 C}{k_1 k_3 C} \right) / \left(\frac{1 + k_3 C}{k_1 k_2 k_3 C} \right)$

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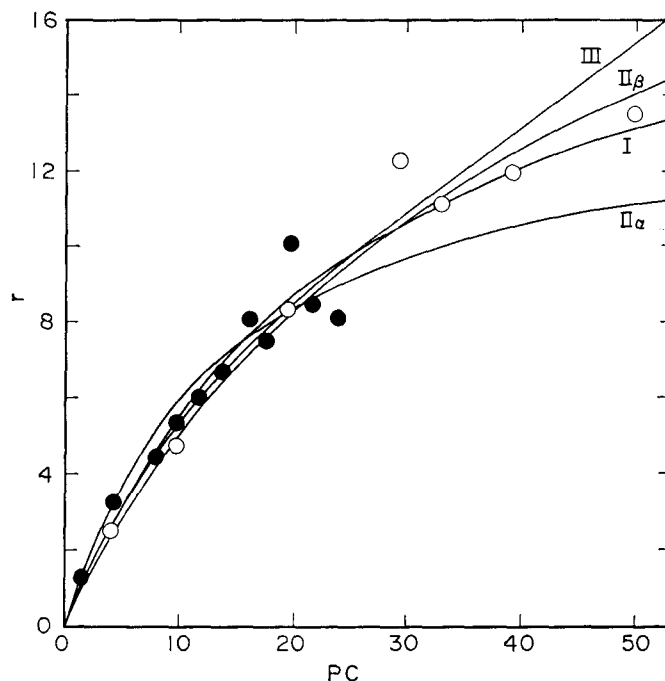


Fig. 3. Test of the rate equations.

I-Eq. (2); IIa-Eq. (7); $C=0.4$; IIb-Eq. (7); $P=50$; III-Eq. (10).

●- $C=0.4$; ○- $P=50$.

and $k_3 = \left(\frac{1+k_2P}{k_1k_2P} \right) \left(\frac{1+k_2P}{k_1k_2k_3P} \right)$. Substitution of the obtained values into $\left(\frac{1+k_2P}{k_1k_2k_3P} \right)$ and $\left(\frac{1+k_3C}{k_1k_2k_3C} \right)$, gave k_1 equal to 40 mmol hr⁻¹g⁻¹ and 42 mmol hr⁻¹g⁻¹ correspondingly. The closeness of these values indicates that Eq. (7) can be applied to the set of the data of Tables 1 and 2. A mean value of k_1 was accepted.

Kiperman⁷ considered three simplified schemes of the mechanism of hydrogenation in solutions which are constructed so as to make applicable the general rate equation for two-stage reactions on heterogeneous surfaces with one intermediate⁸: in the first scheme only the substrate is adsorbed, in the second — only hydrogen, and in the third the molecules of both are adsorbed on one site. The latter case is similar to mechanism (3) but in ref. 7 it did not result in Eq. (2) since adsorption of the solvent was not taken into account and the kinetics were treated as if the reaction proceeded in a gas phase. When the reaction rate is independent of the product con-

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centration as it is in our case, the equation obtained in ref. (7) is reduced to

$$r = k^*(PC)^n \quad (10)$$

where k^* and n are constants. With the data of Tables 1 and 2 the least square method applied to Eq. (10) (linearized by taking logarithms) gives $k^*=1.185$ and $n=0.654$. Curve III in Fig. 3 is plotted in accordance with Eq. (10) with these values of the constants. It is seen that experimental data presented in Tables 1 and 2 can be described with Eq. (10) about as well as with Eq. (2) or (7). To discriminate Eqs. (2), (7), and (10), we extrapolated r with these equations and the above values of the constants, and found such C and P at which r values expected from Eqs. (2) and (7), or (2) and (10) differ considerably (by factor about two). Additional experiments were conducted under these conditions. The results listed in Table 5 indicate that only Eq. (2) is confirmed but not (7) or (10). This increases the probability that the scheme (3) corresponds to the actual mechanism of the reaction.

TABLE 5. $C=4$
 r , calculated and experimental

| P | 5 | 10 | 40 | 60 |
|----------|------|------|------|------|
| Eq. (2) | 8.6 | 12.2 | 17.9 | 18.9 |
| Eq. (7) | 4.2 | 7.5 | — | — |
| Eq. (10) | — | — | 32.8 | 42.5 |
| Experim. | 10.0 | 13.5 | 15.8 | 18.0 |

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