

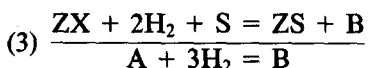
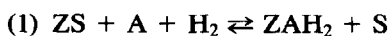
LETTERS TO THE EDITORS

On Kinetics of Hydrogenation of Benzene

Experimental data (1-3) on kinetics of hydrogenation of benzoic acid over palladium catalyst in *n*-butyl alcohol and other solvents agree with the equation

$$r = \frac{kP_H C}{1 + k'P_H C}, \quad (1)$$

where r is the reaction rate, P_H is the hydrogen pressure over solution saturated with hydrogen, C is the concentration of benzoic acid in the solution, and k and k' are constants. This result had been explained as follows. Reaction proceeds via the formation on the palladium surface of an intermediate adduct of H_2 to benzoic acid molecule A which isomerizes to cyclohexadienecarbonic acid and then is hydrogenated readily to cyclohexanecarbonic acid B :



Here Z is a surface site, S is the solvent molecule. Step (3) can be the sum of several fast steps. Only AH_2 particles are supposed to exist on the catalyst surface in essential amounts. Equation (1) follows from the Scheme (2) under the assumption that the surface is homogeneous. The constants are given by

$$k = \frac{k_1 k_2}{k_{-1} + k_2}, \quad k' = \frac{k_1}{k_{-1} + k_2}, \quad (3)$$

where k_1 and k_{-1} are the forward and backward rate constants of Step (1) and k_2 is the rate constant of Step (2). Scheme (2) takes into account that the addition of the first hydrogen molecule to the benzene ring is hindered because of the loss of aromaticity.

The addition of two other hydrogen molecules must be more rapid.

Equation (1) was found to be true also for kinetics of liquid-phase hydrogenation of phenol into cyclohexanol over nickel catalyst (4) (molar fraction being substituted for C). It is of interest to test the applicability of Eq. (1) to kinetics of hydrogenation of benzene. We shall use the recently reported experimental data (5). Benzene vapor was hydrogenized in a flow-circulation system over nickel catalyst at pressures up to 19 atm. The results are reported in Table 1 of Ref. (5). Partial pressure of benzene vapor P_b may be substituted for C in Eq. (1), then

$$r = \frac{kP_H P_B}{1 + k'P_H P_B}. \quad (4)$$

This equation can be obtained from a scheme analogous to (2) but without solvent S . Equation (4) is equivalent to

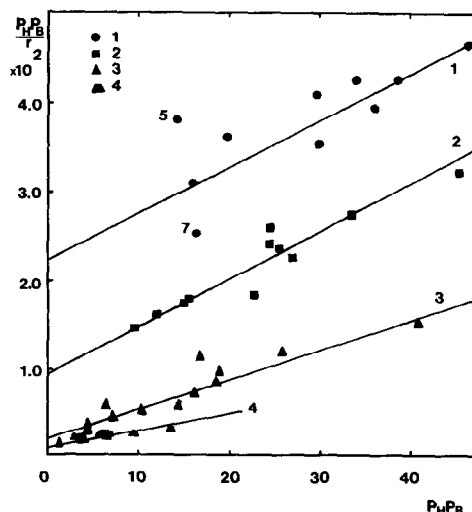


FIG. 1. Plot for Eq. (4): (1) 120°C, (2) 130°C, (3) 150°C, (4) 170°C.

TABLE 1
Constants of Eq. (4)

Temperature (°C)	$k \times 10^2$ (mol g ⁻¹ h ⁻¹ atm ⁻²)	$k' \times 10^2$ (atm ⁻²)
120	0.449	2.32
130	1.06	5.66
150	4.90	16.27
170	8.40	13.44

$$\frac{P_H P_B}{r} = \frac{1}{k} + \frac{k'}{k} P_H P_B. \quad (5)$$

The points in Fig. 1 show the data of (5) in coordinates of $P_H P_B / r$ and $P_H P_B$. Straight lines correspond to values of k and k' in Table 1, which were obtained by least-squares method from the data presented in the form of (5). Figure 1 demonstrates applicability of Eq. (4) to kinetics of hydrogenation of benzene over nickel catalyst. The points 5 and 7 which correspond to experiments No. 5 and 7 of Table 1 in Ref. (5) are exceptional and a similar discrepancy exists between values of r obtained from the experiment and those calculated from Eqs. (1)–(4) in Ref. (5), as shown in Table 2 (r in moles of C₆H₆ converted in 1 h per 1 g of catalyst).

This deviation of calculated rates from experimental ones is probably due to variation of catalyst activity.

According to Eq. (3), $k/k' = k_2$. In Arrhenius coordinates, $\ln k/k'$ vs $1/T$, the points must lie on a straight line. This is how it appears in Fig. 2. The least-squares method gives

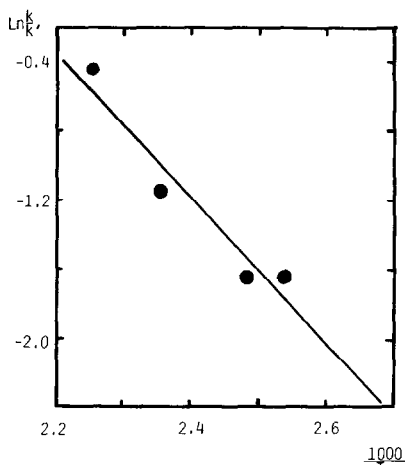


FIG. 2. Temperature dependence of k/k' .

$$\frac{k}{k'} = k_2 = 7.72 \times 10^3 \exp(-8410/RT), \quad (6)$$

where RT is in cal/mol. The value 8.41 kcal/mol is, according to our interpretation of the kinetics, the activation energy of Step (2).

Authors of Ref. (5) describe their result by equations equivalent to the following one

$$r = \frac{k_1 K_{B\pi/\sigma} P_B \sqrt{K_H P_H}}{(1 + \bar{K}_B P_B)(1 + \sqrt{K_H P_H})} + k_2 P_B \left[\frac{\sqrt{K_H P_H}}{1 + \sqrt{K_H P_H}} \right]^6, \quad (7)$$

where

$$\bar{K}_B = K_{B\pi/\sigma}(1 + K_{B\pi} + K_{B\sigma}/\sqrt{K_H P_H}). \quad (8)$$

Here k_1 , k_2 , $K_{B\pi/\sigma}$, K_H , $K_{B\pi}$, and $K_{B\sigma}$ are constants. In Fig. 3, which corresponds to the Fig. 2 calculated in Ref. (5), the experimental reaction rates, r_{obs} , are compared with the calculated ones, r_{cal} . In addition to the points calculated from Eq. (7), points calculated from Eq. (4) are also shown. Equation (4) agrees with the experiment no worse than Eq. (7), though there are only two adjustable parameters in Eq. (4) and six in Eq. (7). The correlation coefficient is 0.959 for (4) and 0.943 for (7) and the standard deviation is 19.2% for (4) and 20% for

TABLE 2
Exceptional Values of Reaction Rates

Experiment No.	r		
	Experimental	Eq. (4)	Eqs. (1)–(4) of Ref. (5)
5	3.78	4.86	5.95
7	6.62	5.37	5.53

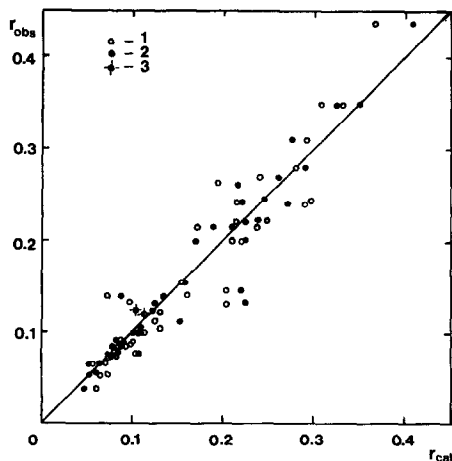


FIG. 3. Comparison of calculated and experimental rates. According to (●) Eq. (4), (○) Eq. (7), and (⊗) both Eqs. (4) and (7).

(7). Thus Eq. (1) describes the rate of vapor-phase hydrogenation of benzene over nickel catalyst.

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V. YU. KONYUKHOV
A. G. ZYSKIN

*Karpov Institute of Physical Chemistry
Ul Obukha 10, 107120
Moscow B-120, USSR*

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