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Abstract

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STUDY OF THE KINETICS OF BENZENE HYDROGENATION AT ATMOSPHERIC AND ELEVATED PRESSURES

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A review of the literature ([1–3]) on the hydrogenation of benzene showed that information on the kinetic regularities of this reaction is highly contradictory; this applies both to the values of the reaction order with respect to benzene, hydrogen, and cyclohexane, and to the values of the temperature coefficient, activation energy, and other characteristics.

Study of the published works led us to the conclusion that the contradictory nature of the experimental material and the variety of proposed kinetic rate equations for this reaction are due to the fact that the studies were carried out under different conditions, with imperfect research methods, usually in static or flow systems that did not ensure isothermal conditions of the process; one should also point to the insufficient substantiation of the proposed schemes for the mechanism of this reaction.

The use of the flow-circulation method for studying kinetics made it possible to investigate the reaction under isothermal conditions and to measure its rate directly at a constant composition of the reaction mixture in the catalyst bed.

Experiments on the hydrogenation of benzene over a nickel-on-chromium-oxide catalyst (as well as Raney nickel) were carried out on small catalyst grains in a flow-circulation glass apparatus at atmospheric pressure and in a metallic flow-circulation apparatus under elevated pressure, on whole catalyst pellets measuring 4×4 mm. Benzene was fed into the system by piston microdosers; the partial pressure of hydrogen was varied in the glass apparatus by diluting the reaction mixture with nitrogen or argon, and in the metallic apparatus by changing the total pressure. Variation of the catalyst grain size showed that experiments on small grains at temperatures of 85—185° belong to the kinetic region, whereas experiments carried out under elevated pressure on whole catalyst pellets belong to the region of internal diffusion. It turned out that the orders of this reaction are variable depending on the conditions under which it is conducted.

In the kinetic region, at temperatures up to 105° and degrees of conversion of benzene to cyclohexane up to 80%, the rate of the hydrogenation reaction has zero order with respect to benzene and half order with respect to hydrogen. When the temperature is raised from 105 to 185°, the order with respect to hydrogen increases from 0.5 to 1.2, and with respect to benzene increases from zero to 0.5.

In deriving the kinetic equations, the benzene hydrogenation reaction is considered as a process of successive addition of adsorbed hydrogen atoms to an adsorbed benzene molecule, with the formation of intermediate surface semihydrogenated compounds of composition C_6H_{6+n}, where n varies from 1 to 5. It is assumed that benzene and hydrogen are adsorbed on different centers and that hydrogen adsorption is small. The catalyst surface is regarded as effectively homogeneous.

The following two variants of the scheme of the process mechanism were investigated:

A. The rate of the process is determined by the rate of hydrogenation of one of the intermediate surface compounds C_6H_{6+n}. In this case the kine-

the kinetic equation has the following form:

$$W = kp_{\mathrm{H2}}^{1/2} \frac{Kp_{\mathrm{b}}p_{\mathrm{H2}}^{n/2}}{Kp_{\mathrm{b}}p_{\mathrm{H2}}^{n/2} + b_{\mathrm{b}}p_{\mathrm{b}} + b_{\mathrm{c}}p_{\mathrm{c}} + 1}, \tag{1}$$

where p_{H2}, p_{b}, and p_{c} are the partial pressures of hydrogen, benzene, and cyclohexane; k is the rate constant; $K = \mathcal{K} b_{\mathrm{H2}}^{n/2}$; $\mathcal{K}$ is the equilibrium constant for the formation of the surface compound C_6H_{6+n}, b_{H2} is the adsorption coefficient of hydrogen; b_{b}, b_{c} are the adsorption coefficients of benzene and cyclohexane.

B. According to this variant of the scheme, the rates of addition of all hydrogen atoms are close to one another. The rate of the process is determined by a group of six slow stages. The stages of adsorption of hydrogen, benzene, and cyclohexane are faster and are at equilibrium. In this case, to derive the kinetic equation, the method of M. I. Temkin [4] was applied. The following equation was obtained:

$$\begin{aligned} W = k\sqrt{p_{\mathrm{H2}}}\,&[b_{\mathrm{b}}p_{\mathrm{b}}(K\sqrt{p_{\mathrm{H2}}})^5(K\sqrt{p_{\mathrm{H2}}}-1)^2\times \\ &\times\{b_{\mathrm{b}}p_{\mathrm{b}}\{6(K\sqrt{p_{\mathrm{H2}}})^6(K\sqrt{p_{\mathrm{H2}}}-1)-[(K\sqrt{p_{\mathrm{H2}}})^6-1]\}+ \\ &+b_{\mathrm{c}}p_{\mathrm{c}}\{K\sqrt{p_{\mathrm{H2}}}[(K\sqrt{p_{\mathrm{H2}}})^6-1]-6(K\sqrt{p_{\mathrm{H2}}}-1)\}+ \\ &+(K\sqrt{p_{\mathrm{H2}}}-1)[(K\sqrt{p_{\mathrm{H2}}})^6-1]\}^{-1}, \end{aligned} \tag{2}$$

where $K = \mathcal{K} \cdot b_{\mathrm{H2}}^{1/2}$, $\mathcal{K}$ is the equilibrium constant of the stage

$$(C_6H_{6+n})_{\text{ads}} + (H)_{\text{ads}} \rightleftharpoons (C_6H_{7+n})_{\text{ads}},$$

where $n = 0, 1, 2, 3, 4, 5$. The remaining notation is the same as in equation (1).

Comparison of the experimental results with equations (1) and (2) was carried out with the aid of the Minsk-2 electronic digital computer, by gradient methods [5]. The constants of the equations were selected from the condition of the minimum of the function F:

$$F = \sum_{i=1}^{N} \left| \frac{W_\text{o}^i - W_\text{p}^i}{W_\text{o}^i} \right|^2, \tag{3}$$

where N is the number of experiments, and W_o^i and W_p^i are the experimental and calculated values of the reaction rate in the i-th experiment.

Construction of sections of the function F with respect to two variables showed that this function has "ravines," i.e., regions in which the function changes little when the variables are changed. Therefore, for solving problems of this type, programs were developed for searching for minima of functions of many variables that have "ravines." In determining the calculated values of the rates from equations (1) and (2), the constants were calculated by formulas taking into account their theoretical dependence on temperature. For the rate constant and the equilibrium constant of the surface hydrogenation stage, the following equations were used:

$$k = k_0 e^{-E/RT}; \qquad K = K_0 e^{Q_\text{r}/RT}, \tag{4}$$

where k_0 and K_0 are pre-exponential factors; E is the activation energy; Q_r is the heat of reaction. The adsorption coefficients for benzene and cyclohexane were calculated from the approximate Nernst formula:

$$\ln b = \frac{Q_\text{a}}{RT} - 1.75 \ln T - 2.3i, \tag{5}$$

where Q_a is the heat of adsorption, and i is the chemical constant; for all gases $i = 3$, and for hydrogen $i = 1.5$. The validity of this formula for adsorption equilibria was shown in one of the works of M. I. Temkin [6].

Thus, in searching for the minimum of the function F, the values of six variables were selected: k_0, E, K_0, Q_r, Q_b, and Q_c.

In processing the results of experiments carried out in the kinetic region, 117 experiments were calculated simultaneously. These experiments covered the following range of parameter variation: temperature from 85 to 185°, partial pressure of hydrogen from 0.2 to 1 atm, partial benzene pressure from 0.001 to 0.1 atm and partial pressure of cyclohexane from 0.07 to 0.14 atm. The calculated value of the rate was computed directly from equations (1) and (2).

The results of this treatment of 117 experiments are given in Table 1.

Table 1

Results of treatment of experiments belonging to the kinetic region (reaction rate expressed in mol/m^2 Ni per second, pressure in atm)

Constants	Equation (1), $n=2$	Equation (1), $n=3$	Equation (1), $n=4$	Equation (2)
$\ln k_0$	$-1,256$	$-1,135$	$-1,223$	$2,750$
E	10 760	10 910	10 870	12 430
$\ln K_0$	$-14,036$	$-21,843$	$-27,676$	$-8,126$
Q_r	16 590	24 180	30 180	7980
Q_b	17 020	16 770	16 670	18 650
Q_c	15 140	17 050	18 320	16 370
F	$7,036$	$5,629$	$6,445$	$4,973$
σ^*, %	$24,5$	$22,0$	$23,5$	$20,5$

* Root-mean-square relative deviation.

For the treatment of experiments carried out in the region of internal diffusion (i.d.), equations (1) and (2) were transformed ([7,8]) into the following equation:

$$W_{\text{i.d.}} = \frac{S}{\nu_i}\sqrt{2\nu_i \int_{C_i^n}^{C_i^\text{c}} D_i W_\text{kin}\, dC_i}\,, \tag{6}$$

where S is the external surface of the granule; ν_i is the stoichiometric coefficient; C_i^n is the concentration of the i-th component on the surface of the granule; C_i^c is the concentration of the i-th component at the center of the granule; W_kin is the reaction rate in the kinetic region.

To determine the limits of the diffusion region, the penetration depth of the reaction into the layer of porous material was estimated. According to the formula of D. A. Frank-Kamenetskii ([9]), for a reaction of n-th order we have:

$$L \approx \sqrt{\frac{D'}{k' C^{\,n-1}}}.$$

Here D' is the effective diffusion coefficient; k' is the rate constant of the chemical reaction referred to the catalyst volume; C is the concentration of the reacting substance at the catalyst surface.

As the lower boundary of the intradiffusion region, a value of 5 was chosen for the ratio of the radius of the catalyst granule R_0 to the penetration depth of the reaction into the layer L. It turned out that both at atmospheric pressure and at pressures of 10–50 atm on whole tablets of nickel-on-chromium-oxide catalyst ($R_0 = 0.2$ cm), the lower boundary of the intradiffusion region lies at temperatures of 100–150°. At elevated pressure this boundary can be refined from the change in the reaction order with respect to hydrogen.

The coefficient of molecular diffusion is inversely proportional to pressure; therefore, in the region of internal diffusion the reaction order with respect to hydrogen decreases sharply. If in the kinetic region it is equal to or greater than one half, then in the region of internal diffusion it is close to zero. Consideration of the experimental data showed that at a temperature of 130° and higher the reaction proceeds in the region of internal diffusion. In deriving

equation by formula (6), the inverse dependence of the diffusion coefficient on pressure was taken into account. The obtained dependence of the reaction rate on the hydrogen pressure coincided with the experimental one. Thus, the transition was made from equations for the rate of the benzene hydrogenation reaction in the kinetic region to equations for the reaction rate in the region of internal diffusion.

In calculations in the intradiffusion region, the results of 99 experiments were processed simultaneously; they covered the following ranges of parameter variation: temperature from 130 to 210°, hydrogen partial pressure from 10 to 50 atm, benzene partial pressure from 0.1 to 1.2 atm, and cyclohexane partial pressure from 0.2 to 1.9 atm. The results of the calculations are given in Table 2. As can be seen from Tables 1 and 2, equation (2) better

Table 2

Results of processing experiments relating to the region of internal diffusion
(reaction rate expressed in mol/ml of catalyst per hour, pressure in atm)

Constants	Equation (1), $n = 3$	Equation (2)	Constants	Equation (1), $n = 3$	Equation (2)
$\ln k_0$	3.683	5.104	Q_b	16 870	16 450
E	5580	5780	Q_c	17 520	16 630
$\ln K_0$	−25.350	−9.371	F	8.484	3.683
Q_g	21 060	7990	σ, %	29.2	19.3

describes the experimental results, especially in the intradiffusion region. Thus the mean errors σ when calculated by equation (2) are one and a half times smaller than when calculated by equation (1). The assumption underlying equation (2)—namely, the closeness of the rates of addition of all six hydrogen atoms to one another—is more plausible than the assumption of a limiting stage, since the compositions of the intermediate surface compounds C_6H_7, C_6H_8, C_6H_9, and the subsequent ones differ little from one another. The values of the constants of equation (2), found from data in the kinetic region and in the region of internal diffusion, are in good agreement. Thus, in accordance with equation (6), the activation energy of the reaction in the intradiffusion region is equal to half the value of the activation energy of the reaction in the kinetic region. Taking into account the value of the effective diffusion coefficient, the values of the pre-exponential factor of the rate constant agree well. The remaining constants have close values in both cases.

Thus, the kinetic equation derived from the assumption of similar rates of successive addition of six hydrogen atoms to the molecule of adsorbed benzene makes it possible successfully to describe the results of experiments both in the kinetic and in the intradiffusion regions of the reaction.

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