THE ELECTROCHEMICAL TREATMENT OF CATALYTIC HYDROGENATION OF ORGANIC COMPOUNDS ON METAL CATALYSTS IN ELECTROLYTE SOLUTIONS

A. V. Finkel'shtein

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Owing to the development and use of electrochemical methods for investigating heterogeneous catalytic processes by D. V. Sokol'skii and coworkers, a wealth of data concerning the change in the potentials of metal catalysts during liquid-phase catalytic hydrogenation of various organic compounds has been obtained, and a number of relations found between kinetic and electrochemical parameters of hydrogenation reactions (see, for example, [1-12]).

In the present paper we endeavor to show that the hypothesis according to which it is possible to realize hydrogenation via an electrochemical path is in good agreement with some experimental results obtained by D. V. Sokol'skii's school in hydrogenation studies on organic compounds. A special point must be made that it was L. V. Pisarzhevskii [13] who first pointed out the electrochemical character of some catalytic reactions, followed somewhat later by V. A. Roiter [14]. D. V. Sokol'skii does not discount this possibility either [4]. However, it appears that nobody has yet analyzed the electrochemical reaction scheme for the hydrogenation of organic compounds. Below we examine an electrochemical scheme for the catalytic hydrogenation of organic compounds on group VIII metals in electrolyte solutions.

When a metal catalyst placed into an electrolyte solution is treated with hydrogen, a potential drop (φ_0) corresponding to the equilibrium hydrogen potential under the given conditions is set up across the metal-electrolyte interface because the reactions

$$\begin{aligned} {}^1/_2H_2 &\xrightarrow{v_1} H^+ + e, \\ H^+ + e &\xrightarrow{v_2} {}^1/_2H_2 \end{aligned} \qquad (I)$$

take place.

When an organic substance is introduced into the equilibrium system indicated above, its molecules will be reduced as they get into the electric double layer if the potential for their electrochemical reduction, φ^*, on the given metal and under the given conditions is more positive than the equilibrium potential φ_0; i.e.,

$$\varphi^* > \varphi_0$$

will be a necessary condition for catalytic hydrogenation to occur via an electrochemical mechanism.

One can represent the reduction in this case schematically thus: in acidic media,

$$RY + e \xrightarrow{v_3} RY, \quad RY + H^+ \rightarrow RYH^+ \qquad (II)$$

or

$$RY^- + H^+ \rightarrow RYH, \quad RYH^+ + e \xrightarrow{v_3} RYH;$$

in alkaline and neutral media,

$$RY + e \xrightarrow{v_3} RY^- \quad RY^- + H_2O \rightarrow RYH + OH^-$$

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(protonation of the reaction center at the substrate can precede addition of the electron in acidic media).

The effect that the metal accelerates hydrogen addition to the substrate, i.e., its catalytic action, is imagined to occur on account of a lowering of the activation energy for the electron addition step under the influence of the electric double layer, in accordance with the widely known equation [15]

$$E = E_0 + \alpha F\varphi.$$

Here it is assumed, of course, that indeed electron addition to the substrate molecule is the limiting step in the reaction

$$RY + {}^1/_2H_2 \rightarrow RYH$$

when it proceeds via the electrochemical scheme proposed.

On account of reaction (II), the negative charge on the catalyst will begin to decrease, and its potential will shift to the anodic side, which causes the rates v_2 and v_3 to diminish and v_1 to increase. The exact variation of catalyst potential and rates will depend on the reaction order with respect to the substrate and on the regime in which it proceeds (diffusion or kinetic).

Consider the case of zeroth-order reactions with respect to the substance hydrogenated.

When the hydrogen pressure is kept constant during a hydrogenation reaction which is zeroth order with respect to the substrate, potential shift and rate changes must lead to the relation

$$v_1 = v_2 + v_3 \quad \text{or} \quad nFv_3 = i_1 - i_2; \tag{1}$$

once this has been established, reaction rates and catalyst potential will retain time-invariant values; i.e., a stationary state will be established in the system.

In Eq. (1), n is the number of electrons which are added to a substrate molecule during reduction, and i_1 and i_2 are the partial currents of the reactions (I).

We know that the quantities entering Eq. (1) can be represented in the following way:

$$i_1 = k_1[H^+]^{1/2} \exp(\Delta\varphi F / 2RT) = i_0 \exp(\Delta\varphi F / 2RT), \tag{2}$$

$$i_2 = k_2[H^+]^{1/2} \exp(-\Delta\varphi F / 2RT) = i_0 \exp(-\Delta\varphi F / 2RT), \tag{3}$$

$$nFv_3 = k_3 \exp(-n\alpha F\Delta\varphi / RT), \tag{4}$$

provided that the ψ_1 potential is taken into account in the k_i, the substrate surface concentration in k_3, and $\Delta\varphi = \varphi - \varphi_0$, where φ is the stationary value of the catalyst potential during the hydrogenation.

If $\varphi^* >> \varphi_0$, the stationary potential will turn out to be moved by a considerable amount from the equilibrium value into the anodic region, so that the relation $i_1 >> i_2$ will hold, and Eq. (1) assumes the form

$$nFv_3 = i_1. \tag{5}$$

In accordance with (2) one can rewrite this equation thus:

$$v_3 = (i_0 / nF) \exp(\Delta\varphi F / 2RT)$$

or

$$\ln v_3 = \ln(i_0 / nF) + F / 2RT\Delta\varphi, \tag{6}$$

which is in harmony with the formula found by D. V. Sokol'skii and coworkers,

$$\lg w = \lg k + b\Delta\varphi$$

(where w is the rate of substrate reduction; this is v_3 in the present work), and describing well the experimental data (see Fig. 1).

Substituting now (2) and (4) into (5) we shall obtain

$$k_3 \exp(-\alpha nF\Delta\varphi / RT) = k_1[H^+]^{1/2} \exp(\Delta\varphi F / 2RT),$$

whence

$$\Delta\varphi = \frac{2RT}{(2n\alpha + 1)F} \ln \frac{k_3}{k_1} + \frac{RT \cdot 2{,}303}{(2n\alpha + 1)F} \text{pH} \tag{7}$$

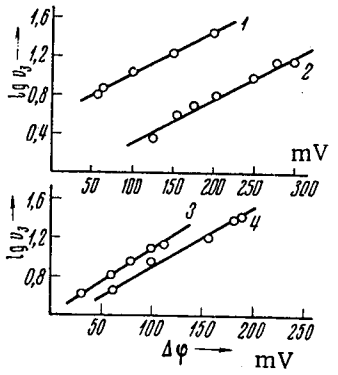


Fig. 1

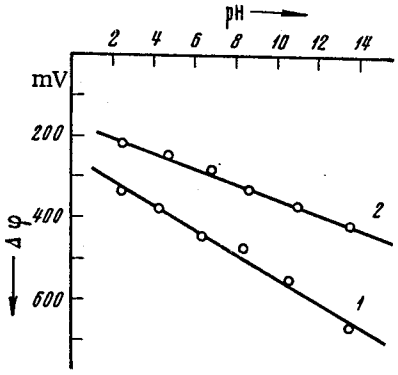


Fig. 2

Fig. 1. Relation between hydrogenation rate and catalyst-potential shift: 1) acrolein, $Pd/BaSO_4$; 2) acrolein, Raney nickel; 3) phenylacetylene, $Pd/BaSO_4$; 4) dimethylethynyl carbinol, Raney nickel.

Fig. 2. Dependence of catalyst-potential shift on reaction medium in phenylacetylene hydrogenation: 1) at 5°C; 2) at 30°C.

or

$$\Delta\varphi = C_1 + C_2\mathrm{pH} \tag{8}$$

(C_1 and C_2 are constants).

Equation (8) is in complete harmony, too, with the results on phenylacetylene and nitrobenzene hydrogenation with palladium catalysts [6], as shown in Fig. 2.

None of the quantities in (1) can be neglected when the reactivity of the substance being reduced is such that nFv_3 is commensurate with i_2. This will obviously be the case when φ^* is sufficiently close to φ_0. The potential shift $\Delta\varphi$ in the stationary state relative to the equilibrium value observed before introducing the substrate will be small under such conditions, and its relation to the hydrogenation rate will be represented in the following way, according to (1), (2), and (3):

$$nFv_3 = i_0[\exp(\Delta\varphi F / 2RT) - \exp(-\Delta\varphi F / 2RT)]. \tag{9}$$

Taking into account that $\Delta\varphi$ is small we obtain from (9), after series expansion,

$$v_3 = \Delta\varphi i_0 / nRT \tag{10}$$

or

$$v_3 = k\Delta\varphi, \tag{11}$$

in full harmony with [4, 5, 7-10].

In conclusion we believe that it ought to be noted that according to (6) and (10), the catalytic activity (in hydrogenation according to an electrochemical mechanism) will substantially depend on the exchange current density (i_0) of the reaction

$$H^+ + e \rightleftarrows {}^1/_2H_2,$$

which is realized on the catalyst in the same medium in which hydrogenation is supposed to be carried out. But inasmuch as the hydrogen overvoltage decreases with increasing i_0, Eqs. (6) and (10), and hence also the hydrogenation scheme set forth above, are supported by the well-known fact that hydrogen overpotential runs counter to catalytic activity during hydrogenation (see, for example, [16]).

Thus, the electrochemical treatment of catalytic hydrogenation leads to conclusions which are in good agreement with a number of experimental facts. Therefore, the possibility that hydrogenation proceeds via an electrochemical mechanism must be taken into consideration when results for liquid-phase catalytic hydrogenation of organic compounds on metal catalysts are examined.

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