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Abstract

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On the Nature of Catalytic Hydrogen Currents in Polarography

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The appearance of catalytic hydrogen waves ($^{1-5}$) is usually explained by a lowering of the activation energy of the discharge of hydrogen ions under the action of catalysts. In accordance with this, catalytic waves should have an irreversible character and their half-wave potentials should vary with the pH of the solution. This, however, is not consistent with experiment, at least in catalysis by organic bases. Thus, Kirkpatrick (^{3}) found that the potentials of waves caused by alkaloids are almost independent of pH; the same was observed by Kuta and Drabek (^{4}) for waves catalyzed by pyridine.

It is logical to suppose that the discharge of the pyridinium ion, which determines the catalytic wave, proceeds by the same mechanism as the discharge of N-substituted quaternary pyridinium salts (^{6}), i.e., that it is a reversible electrochemical process followed by rapid dimerization of the electrode products, leading, however, in contrast to N-substituted salts, not to a dimer (^{6}), but to the evolution of H_2 and regeneration of pyridine. In the present work the validity of this proposition is demonstrated, and, for one of the cases, values are also estimated for the rate constants of the reactions determining the catalytic wave.

The general scheme of the catalytic process may be represented as follows (^{5,7}):

$$\mathrm{B} + \mathrm{DH}^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{BH}^+ + \mathrm{D}, \qquad \text{(a)}$$

$$\mathrm{BH}^+ + e \overset{\mathrm{E}}{\rightleftarrows} \mathrm{BH}, \qquad \text{(b)}$$

$$2\mathrm{BH} \xrightarrow{k_3} 2\mathrm{B} + \mathrm{H}_2. \qquad \text{(c)}$$

The catalyst (which may exist in acid (BH^+) and basic (B) forms) is reversibly discharged at the cathode in the acid, cationic form BH^+, giving radicals BH. The radicals then rapidly dimerize, regenerating the catalyst in the basic form B and giving a hydrogen molecule. Next, the basic form, reacting with the proton donor DH^+ present at the electrode, passes into the acid form, and the whole cycle is repeated. Applying to this scheme the calculation method of Brdička and Wiesner ($^{8-10}$), we obtain for the material balance (^{5}):

$$i = \chi\left([\mathrm{BH}^+]_0 - [\mathrm{BH}^+]_s\right) + sF\mu_1\left(k_1[\mathrm{DH}^+]_s[\mathrm{B}]_s - k_2[\mathrm{BH}^+]_s[\mathrm{D}]_s\right), \qquad (1)$$

$$i = \chi\left([\mathrm{B}]_0 - [\mathrm{B}]_s\right) - sF\mu_1\left(k_1[\mathrm{DH}^+]_s[\mathrm{B}]_s - k_2[\mathrm{BH}^+]_s[\mathrm{D}]_s\right). \qquad (2)$$

$$sF\mu_3 k_3[\mathrm{BH}]_s^2 + \chi[\mathrm{BH}]_s = i. \qquad (3)$$

Here χ is the constant of the Ilkovič equation (assumed identical for all forms of the catalyst), s is the mean surface area of the dropping electrode, μ is the thickness of the reaction layer (^{8,9,11}), the subscript s refers to surface concentrations of substances, and 0 to bulk concentrations.

It follows from these equations that

$$i = \frac{\varkappa\left([\mathrm{BH}^+]_o - [\mathrm{BH}^+]_s\right) + P\varkappa[B]_o - R[\mathrm{BH}^+]_s}{1-P}, \qquad (4)$$

$$P = \frac{k_1 sF\mu_1[\mathrm{DH}^+]_s}{\varkappa + k_1 sF\mu_1[\mathrm{DH}^+]_s}, \qquad (5)$$

$$R = k_2 sF\mu_1[D]_s(1-P). \qquad (6)$$

In well-buffered solutions, at a constant height of the mercury column, $P = \mathrm{const}$, $R = \mathrm{const}$, $[\mathrm{DH}^+]_s = [\mathrm{DH}^+]_o$, and $[D]_s = [D]_o$.

For the limiting current ($[\mathrm{BH}^+]_s \to 0$), from (4) we obtain:

$$i_{\mathrm{pr}} = \frac{\varkappa\left([\mathrm{BH}^+]_o + P[B]_o\right)}{1-P} = \frac{\varkappa[B]_o}{1-P}\left(\frac{[\mathrm{BH}^+]_o}{[B]_o} + P\right). \qquad (7)$$

Comparing (4) and (7), we find that $[\mathrm{BH}^+]_s = (i_{\mathrm{pr}} - i)(1-P)/(\varkappa + R)$. We find $[\mathrm{BH}]_s$ in the following way. The second term on the left-hand side of equality (3) is usually several orders of magnitude smaller than the first; therefore, neglecting the small quantity $\varkappa[\mathrm{BH}]_s$ and taking into account (^{9,11}) that $\mu_3 = (D/k_3[\mathrm{BH}]_s)^{1/2}$, we obtain from (3): $[\mathrm{BH}]_s = (i/sFk_3^{1/2}D^{1/2})^{2/3}$, where D is the diffusion coefficient. Substituting the values of $[\mathrm{BH}^+]_s$ and $[\mathrm{BH}]_s$ into the Nernst relation, we obtain the general equation of the catalytic wave:

$$E = E_0 + \frac{RT}{F} \ln \frac{i_{\text{pr}} - i}{i^{2/3}} + \frac{RT}{F} \ln \frac{(1-P)(sF)^{2/3}(k_3 D)^{1/3}}{\varkappa + R} \tag{8}$$

or

$$E = \varepsilon_0 + \frac{RT}{F} \ln \frac{i_{\text{pr}} - i}{i^{2/3}}, \tag{9}$$

where ε_0 is a constant equal to the potential at $i^{2/3} = i_{\text{pr}} - i$; E_0 is the normal potential of the redox system. Let us consider particular cases of the catalytic currents of hydrogen in well-buffered solutions. At a very low rate k_1 of the catalytic process (a) and high $[\text{BH}^+]_o$, i.e., when $p \ll 1$ and $\varkappa \gg R$, the current, according to (4) and (7), is determined by the diffusion of BH^+ and, like the diffusion current, is proportional to $(h)^{1/2}$ or $t^{-1/2}$ (h is the height of the mercury column above the electrode, t is the drop period). In this case equation (8) becomes identical with the expression for the diffusion wave of a reversible process with rapid dimerization of the electrode products ([9,12]), studied using the reduction of N-alkylpyridinium salts as an example ([6]). The half-wave potential E_1 in this case becomes approximately 19 mV more negative upon a tenfold increase in t or C ($C = [\text{BH}^+]_o + [B]_o$ is the analytical concentration of the catalyst in solution).

At sufficiently high rates of the catalytic process and low $[\text{BH}^+]_o$ ($[\text{BH}^+]_o \ll [B]_o$), the current is determined mainly by the rate of the catalytic process (a) ([5]). Two cases may then occur.

1. If the rate of the reverse reaction (k_2) is also sufficiently high, then $R \gg \varkappa$ and $\mu_1 = (D/k_2[D]_s)^{1/2}$; in this case, if $p \ll 1$, then $\varkappa P$ and R, and hence also the catalytic current, do not depend on h or t ([5]). The quantity ε_0 in this case does not depend on C and t and is the characteristic electrochemical constant of the catalyst BH^+ at the given pH of the solution. The quantity $E_{1/2}$, as is seen from (5), (7), and (8), is determined by the expression:

$$E_{1/2} = E_0 + \frac{RT}{F} \ln \frac{(k_3 C)^{1/3} (\varkappa P)^{1/3}}{(k_2 [D]_o)^{1/2} [sF(1-P)]^{1/3} D^{1/6}}, \tag{10}$$

i.e., $E_{1/2}$ becomes approximately 19 mV more positive upon a tenfold increase in C and does not depend on t.

II. If the rate of the reverse reaction (a) is small, then μ_1 can extend to the dimensions of the diffusion layer and become equal to $0.233\sqrt{Dt}$ ([13]). In this case R, and for $P \ll 1$ also i_{lim}, increase as h decreases; moreover i_{lim} is proportional to $h^{-1/2}$ or $t^{1/2}$. Indeed, an increase in the catalytic current with decreasing h has been observed by a number of investigators ([4,14]); in this case, according to (8), ε_0 does not depend on C, but with

Figure 1 graph

Figure 1: Figure 1 graph

Figure 2 graph

Figure 2: Figure 2 graph

a change in t, depending on the ratio between the quantities $\varkappa$ and R, it can shift both toward positive and toward negative potentials. The $E_{1/2}$ of these waves is determined by the expression

Fig. 1. Dependence of $\lg i^{2/3}/(i_{\text{lim}} - i)$ on E for catalytic waves produced by pyridine in a 0.1 M borax solution

$$E_{1/2} = E_0 + \frac{RT}{F} \ln \frac{(1-P)^{2/3} sF(k_1k_3)^{1/2} C^{1/2} D^{1/2} (0.233\, t^{1/2})^{1/3}}{\varkappa + R}, \tag{11}$$

i.e., $E_{1/2}$, when C is increased tenfold, becomes $\sim$ 19 mV more positive, and when t is increased it becomes either more positive, at most by $\sim$ 38 mV (when $\varkappa \gg R$), or more negative–in the limiting case (when $\varkappa \ll R$) by $\sim$ 19 mV (since $\varkappa$ is proportional to $t^{-1/2}$, and R in this case to $\sim t^{1/2}$).

To verify the derived relationships, the catalytic hydrogen waves produced by pyridine in a 0.1 M borax solution and in reverse buffer solutions were investigated. The work was carried out at 25°. The capillary of the dropping electrode had a paddle for forced detachment of drops (^{15}); its m and t at $h = 50$ cm were, respectively, 3.82 mg/sec and 0.26 sec. The electrode potentials were measured potentiometrically relative to the saturated calomel electrode. A correction for iR_{om} in the cell was introduced into their values. $E_{1/2}$ was found by interpolation on rectilinear (in the middle portion) plots $(\lg i/(i_{\text{lim}} - i), E)$. The current intensity was corrected for the residual current. The solutions were freed from oxygen by purging with nitrogen.

Figure 1 shows the experimentally found dependence between $\lg i^{2/3}/(i_{\text{lim}} - i)$ and E; its rectilinear character and the magnitude of the slope correspond exactly to equation (8). The value ε_0, in accordance with (8), does not depend on C and at $h = 50$ cm in a 0.1 M borax solution is equal to -1.759 V. The value of i_{lim} of the waves in a 0.1 M borax solution increases with decreasing h almost proportionally to $h^{-1/2}$, which corresponds to a slow reverse reaction (a). In good quantitative agreement with the theory, for this case $\left([\text{BH}^+]_0 \ll [\text{B}]_0,\ \varkappa \ll R\right)$, $E_{1/2}$ becomes more positive with increasing C and more negative with increasing t (Fig. 2).

Fig. 2. Dependence of $E_{1/2}$ on the concentration C of pyridine (1) and on the drop time (2) in a 0.1 M borax solution

Fig. 3

Figure 3: Fig. 3

Since in alkaline solutions the proton donor DH^+ is water (^{4,5}) and D corresponds to OH^- ions, an increase in the pH of the solution should increase the rate of the reverse catalytic reaction and thereby decrease μ_1. At sufficiently high pH (for pyridine at pH > 10) μ_1 ceases to depend on t; a decrease in μ_1, in turn, leads to a decrease in P, and consequently also i_{lim}. For $P \ll 1$, it follows from (5) and (7) that

$$i_{\mathrm{lim}} = k_1 s F [\mathrm{H_2O}] \left(D / k_2 [\mathrm{OH}^-]_s \right)^{1/2},$$

i.e., i_{lim} at sufficiently high pH does not

depends on t and changes proportionally to $[\mathrm{OH}]^{-1/2}$. Experiment confirms this conclusion. The values of $E_{1/2}$ and ε_0, in accordance with (8), become more negative when the pH is increased (as a result of an increase in R).

Additional confirmation of the reversibility of the electrode process in the catalytic evolution of hydrogen may be provided by the intersection of catalytic waves with the so-called Fourier waves (Fig. 3), obtained when, in addition to a constant potential, a small sinusoidal voltage is also applied to the electrode ($^{16-18,6}$). It is interesting to note that, because of the influence of the preceding reaction, the potential of the intersection point E^* is situated considerably closer to $E_{1/2}$ in the case of catalytic waves than for a reversible process followed by dimerization (^{6}).

Fig. 3. Ordinary polarograms (2) and Fourier waves (3) with $E_\sim = 50$ mV, 100 Hz; background: 0.1 M borax solution (1). Pyridine concentration: a $-3.9 \cdot 10^{-4}$ M, b $-7.9 \cdot 10^{-4}$ M

An estimate of the rate constants of the reactions was made from the dependences for the catalytic current in a 0.1 M borax solution at 25°. The following data were used for the calculation: $\chi = 4.05$ $\mu\mathrm{a} \cdot \mathrm{l/m}M$ (accepted as equal to χ for N-methylpyridinium (^{6})), $s = 8.5 \cdot 10^{-3}$ cm^2, $\mu_1 = 5.7 \cdot 10^{-4}$ cm according to (^{13}) (at $t = 0.26$ sec), $[\mathrm{OH}^-] = 1.7 \cdot 10^{-5}$ mole/l (pH $= 9.24$). Since under these conditions $[\mathrm{BH}^+]_0 / [\mathrm{B}]_0 \ll P$ and $C \approx [\mathrm{B}]_0$, from the experimental value $i_{\mathrm{pr}}/C = 1.98$ $\mu\mathrm{a} \cdot \mathrm{l/m}M = \mathrm{const}$ (at $t = 0.26$) from (7) $P = 0.329$ was found, and from (5) $k_1 \cdot [\mathrm{H_2O}] = 4.3$ sec^{-1} ($k_1 = 7.8 \cdot 10^{-2}$ l/mole$\cdot$sec). From the value $K = k_1 [\mathrm{H_2O}] / k_2 = 1.7 \cdot 10^{-9}$, the value $k_2 = 2.5 \cdot 10^9$ l/mole$\cdot$sec was obtained. If one assumes that $E_0 \approx E^* = -1.778$ V ($^{6,16-18}$), then from the experimental value $\varepsilon_0 = -1.759$ V and $R = 13.3 \cdot 10^3$ $\mu\mathrm{a} \cdot \mathrm{l/m}M$ (according to (6)), from (8) the value 10^{14} l/mole$\cdot$sec was obtained for k_3. This value considerably exceeds the rate constant of dimerization of N-methylpyridinium radicals (^{6}).

In unbuffered solutions the reversibility of the electrode process is preserved;

however, owing to the change in pH in the near-electrode space, the i–E curves of the catalytic waves are stretched along the E axis. It may be assumed that an analogous mechanism of the catalytic process also takes place in catalysis by other catalysts with an onium structure ([7]); in any case, the catalytic waves are not connected with a lowering of the activation energy of the discharge of hydrogen ions, and their potentials are determined only by the electrochemical properties of the catalysts.

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