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Abstract

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CHANGE IN THE MECHANISM OF ELECTROCHEMICAL REACTIONS IN A NONPROTOGENIC MEDIUM UPON ADDITION OF A PROTON DONOR

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A polarographic study of conjugated hydrocarbons ([1]), quinones, and ketones ([2]) in media with low proton activity revealed a distinctive feature of the reduction mechanism in such media: the two-electron wave observed in protonic solvents splits into two waves, the ratio of the heights of which may vary. Kheytnik ([1]) proposed a scheme that satisfactorily explains the qualitative aspect of the phenomena observed. The scheme is based on the assumption that, when the availability of the proton is low, the protonation of either the intermediate radical R^- or the product of two-electron reduction R^{2-} is slowed down (in particular, interrupted).

We have shown ([3]) that the nitro group in the nonprotogenic solvent dimethylformamide is reduced by a similar mechanism, with the four-electron wave splitting into one- and three-electron waves. It then proved that addition of weakly active proton donors (water, ethanol) affects the quinone and nitro-group waves in a similar manner: the ratio of the wave heights is preserved, the position of the first wave changes comparatively little, while the second wave shifts strongly in the positive direction (Fig. 1). The invariance (to a first approximation) of the parameters of the first wave shows that protonation of R^- has not accelerated appreciably. On the other hand, the large shift of the second wave cannot be explained solely by a change in solvation and in the structure of the double layer. It remains to assume that the effect is caused by an increase in the rate of protonation of the anion R^{2-}, which is the final product in the reduction of a quinone and an intermediate product in the reduction of the nitro group. In order to make a quantitative test of this hypothesis possible, the corresponding wave equation is derived here.

Fig. 1. Polarograms of nitrobenzene in dimethylformamide; supporting electrolyte–0.1 M $N(C_2H_5)_4J$. Water added: 1–0%; 2–6.0%; 3–21.7%.

Koutecký ([4]) solved this problem for the case expressed by the scheme

$$A \xrightarrow{ne} B \underset{\rho\sigma}{\overset{\rho}{\rightleftarrows}} C,$$

where ρ and $\rho\sigma$ are the rate constants of the chemical reaction deactivating the depolarization product and of the reverse reaction. The derivation is, of course, applicable

and to the case of a bimolecular deactivating reaction, in particular, the protolytic one

$$\mathrm{B} + \mathrm{DH} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{BH}^+ + \mathrm{D}^-,$$

but under the condition of buffering of the medium; then

$$\rho = k_1 C_{\mathrm{DH}} = \text{const}, \tag{1a}$$

$$\rho\sigma = k_2 C_{\mathrm{D}} = \text{const}. \tag{1b}$$

Solving the problem by Koutecký' s method for an unbuffered medium proved to be excessively complicated; therefore the steady-state method was applied, and, for simplicity, the electrode reaction was assumed to be reversible. First the case will be considered in which the rate of the reaction

$$\mathrm{R}^{2-} + \mathrm{DH} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{RH}^- + \mathrm{D}^- \tag{1}$$

is appreciable, while the addition of the second proton may be neglected. Let us introduce the notation: i is the current at any point of the second wave, C is the concentration, χ is the Il' kovich equation constant ($\chi = i_d/C$); lower indices denote the type of particles (R^- is replaced by R', etc.), and the upper index s denotes the concentration at the electrode surface. For convenience the coefficient

$$\chi = qF\mu\rho, \tag{2}$$

is also introduced, where q is the mean surface area of the mercury drop, and μ is the thickness of the reaction layer for the deactivating reaction. In the present problem ρ is constant, while $C^s_{\mathrm{D}'}$ and σ are functions of the current. The initial equations will be

$$i = \chi_{\mathrm{R}} C_{\mathrm{R}} - \chi_{\mathrm{R}'} C^s_{\mathrm{R}'}, \tag{3}$$

$$\chi_{\mathrm{R}} C_{\mathrm{R}} = \chi_{\mathrm{R}'} C^s_{\mathrm{R}'} + \chi_{\mathrm{R}''} C^s_{\mathrm{R}''} + \chi \left(C^s_{\mathrm{R}''} - \sigma^s_{\mathrm{RH}} \right), \tag{4}$$

$$\chi C^s_{\mathrm{R}''} = (\chi\sigma + \chi_{\mathrm{RH}'}) C^s_{\mathrm{RH}'}. \tag{5}$$

From these, expressions are found for $C^s_{\mathrm{R}'}$, $C^s_{\mathrm{R}''}$, and $C^s_{\mathrm{RH}'}$. In doing so it may be assumed that $\chi_{\mathrm{R}'} = \chi_{\mathrm{R}''} = \chi_{\mathrm{RH}'} = \chi_{\mathrm{R}}$. From the expression for $C^s_{\mathrm{RH}'}$ one obtains

$$C^s_{\mathrm{D}'} = \chi i / \chi_{\mathrm{D}'} [\chi(\sigma + 1) + \chi_{\mathrm{R}}]. \tag{6}$$

Substituting this into (1b) and solving with respect to σ, we obtain

$$\sigma = [A^{1/2} - \chi_{\mathrm{D}'}(\chi + \chi_{\mathrm{R}})] / 2\chi_{\mathrm{D}'}\chi\rho, \tag{7}$$

where

$$A = [\chi_{\mathrm{D}'}(\chi + \chi_{\mathrm{R}})\rho]^2 + 4\chi_{\mathrm{D}'}\chi^2\rho k_2 i.$$

Substituting $C^s_{\mathrm{R}'}$ and $C^s_{\mathrm{R}''}$ into the Nernst equation and using (7), we obtain the wave equation (φ is the r.c.e. potential)

$$\varphi = \varphi^0 + \frac{RT}{F} \ln \frac{A^{1/2} + \chi_{\mathrm{D}'}(\chi + \chi_{\mathrm{R}})\rho}{A^{1/2} - \chi_{\mathrm{D}'}(\chi - \chi_{\mathrm{R}})\rho}. \tag{8}$$

In such a general form the equation is inconvenient for analysis, but it is simplified under certain particular assumptions. First of all, only the case in which ρ is large is of interest. If in (2) one substitutes $\mu = \sqrt{D(1+\sigma)/\rho}$ [5] (D is the diffusion coefficient) and uses the Il' kovich equation, then one obtains (t_1 is the drop time)

$$\chi = 0.81\, \chi_{\mathrm{R}} \sqrt{\rho(1+\sigma)t_1}. \tag{9}$$

Thus, if ρ is large, then $\chi \gg \chi_{\mathrm{R}}$.

To estimate σ, let us note that $k_2/k_1 = K/K_{\mathrm{D}}$, where K and K_{D} are the dissociation constants, respectively, of the acids RH^- and DH in the given medium. But $\sigma_d = k_2(C_{\mathrm{D}'})_d / k_1 C_{\mathrm{DH}}$ (σ_d and $(C_{\mathrm{D}'})_d$ are the values at $i = i_d$); hence, with weak proton donors σ may be of the order of unity or higher, whereas in the case of active donors $\sigma \ll 1$.

In the first case, in (8) one must set $\chi_R = 0$, and one obtains

$$\varphi = \varphi^0 + \frac{RT}{F} \ln \frac{(4k_2 i + \rho\chi_{D'})^{1/2} + (\rho\chi_{D'})^{1/2}}{(4k_2 i + \rho\chi_{D'})^{1/2} - (\rho\chi_{D'})^{1/2}} - \frac{RT}{F} \ln \frac{i}{c_d - i}, \qquad (10)$$

$$\varphi_{1/2} = \varphi^0 + \frac{RT}{F} \ln \frac{(2k_2 i_d + \rho\chi_{D'})^{1/2} + (\rho\chi_{D'})^{1/2}}{(2k_2 i_d + \rho\chi_{D'})^{1/2} - (\rho\chi_{D'})^{1/2}}. \qquad (11)$$

Equation (10) represents a wave whose shape differs from a reversible one. Differentiation of (11) gives

$$\frac{d\varphi_{1/2}}{d \ln C_{\mathrm{DH}}} = \frac{RT}{F} \left(\frac{\rho}{\rho + 2k_2 i_d / \chi_{D'}} \right)^{1/2}. \qquad (12)$$

But from equation (7), $k_2 i / \chi_{D'} = \sigma(\sigma + 1)\rho$, whence

$$\frac{d\varphi_{1/2}}{d \ln C_{\mathrm{DH}}} = \frac{RT}{F} \left(\frac{1}{1 + 2\sigma_d(\sigma_d + 1)} \right)^{1/2}. \qquad (13)$$

Thus, the magnitude of the shift of $\varphi_{1/2}$ with increasing C_{DH} depends only on the "constant" of the protolytic equilibrium σ, with $d\varphi_{1/2}/d \ln C_{\mathrm{DH}} \leq RT/F$.

The transition to the case $\sigma \ll 1$ can be carried out by writing (8) in the form

$$\varphi = \varphi^0 - \frac{RT}{F} \ln \frac{(1 + Q)^{1/2} - 1 + \chi_R/\chi}{(1 + Q)^{1/2} + 1 + \chi_R/\chi},$$

where $Q = 2(2\chi k_2 i + \chi_D \chi_D \rho)/\chi_D \chi \rho$ is a small quantity. Using the relation $(1 + Q)^{1/2} \simeq 1 + Q/2$, we obtain

$$\varphi = \varphi^0 = \frac{RT}{F} \ln \frac{\chi k_2 i + \chi_D \chi_R \rho}{\chi \chi_D \rho} - \frac{RT}{F} \ln \frac{i}{i_d - i}$$

and, taking equation (9) into account,

$$\varphi = \varphi^0 + \frac{RT}{F} \ln 0.81 \sqrt{\rho t_1} - \frac{RT}{F} \ln \left(1 + 0.81 \frac{k_2 i}{\chi_{D'}} \sqrt{t_1/\rho} \right) - \frac{RT}{F} \ln \frac{i}{i_d - i}. \qquad (14)$$

Koutecký' s equation [4] can also be brought to a practically identical form. In the original, the key is the differential equation

$$\frac{\partial^2 \psi}{\partial x^2} - \frac{\rho + k_2 C_{D'}}{D} \psi = 0.$$

In our case $C_{D'}$ depends on x; if, however, proceeding from the assumption that $k_2 C_{D'} \ll \rho$, one sets $\rho + k_2 C_{D'} \simeq \text{const}$, then the equation is integrated, and nothing changes in the course of Koutecký' s reasoning. After the corresponding substitutions, equation (14) is obtained, in which only the coefficient 0.81 is replaced by 0.87. However, this method cannot be regarded as satisfactory, since the error cannot be estimated.

From equation (14) it follows that

$$\varphi_{1/2} = \varphi^{0'} + \frac{RT}{F} \ln \sqrt{\rho t_1} - \frac{RT}{F} \ln \left(1 + 0.81 \frac{k_2 i_d}{2\chi_{D'}} \sqrt{t_1/\rho} \right), \tag{15}$$

$$\frac{d\varphi_{1/2}}{d \ln C_{\mathrm{DH}}} = \frac{RT}{2F} \frac{1 + 0.81\sigma_d \sqrt{\rho t_1}}{1 + 0.405\sigma_d \sqrt{\rho t_0}}, \tag{16}$$

whence $RT/2F \leq d\varphi_{1/2}/d \ln C_{\mathrm{DH}} < RT/F$, with the smallest value corresponding to $\sigma_d = 0$ (DH is a strong acid!).

To determine the form of the wave, let us consider two limiting cases:

1. $k_2 = 0$, i.e., the reverse reaction may be neglected. Then

$$\varphi = \text{const} - \frac{RT}{F} \ln \frac{i}{i_d - i}. \tag{17}$$

This is the equation of an ordinary reversible wave.

2. $\frac{k_2 i_d}{\chi_D} \sqrt{t_1/\rho} \gg 1$, or, equivalently, $\sigma_d \sqrt{\rho t_1} \gg 1$. In view of the assumption that $\sigma_d \ll 1$, this condition requires very large values of ρ and k_1. Then

$$\varphi = \text{const} - \frac{RT}{F} \ln \frac{i^2}{i_d - i}. \tag{18}$$

In this case the plot of φ against $\log[i/(i_d - i)]$ is not rectilinear, and the slope at the half-wave point is reduced to 2/3 of the value characteristic of a reversible wave. It is evident that, in the intermediate case as well, the wave will have a reduced slope.

It remains to consider the case in which the rate of the reaction

$$\mathrm{RH}^- + \mathrm{DH} \underset{k_2'}{\overset{k_1'}{\rightleftarrows}} \mathrm{RH}_2 + \mathrm{D}^- \tag{II}$$

can no longer be neglected. Let us introduce the notation: $\rho' = k_1' C_{\mathrm{DH}}$, $\rho'\sigma' = k_2' C_{\mathrm{D}}^s$, $\chi' = qF\mu\rho'$. We note that if k_1' is very large ($\chi' \gg \chi_R$), then the

reverse reaction (I) may be neglected, and the case expressed by equation (17) is realized. Similarly, if it is assumed that in reaction (I) σ is comparable with unity, then $C^s_{\mathrm{RH}'}$ becomes small, and reaction (II) loses significance: the wave is again represented by equation (10). Therefore only the case expressed by the conditions $\chi \gg \chi_R$, $\sigma \ll 1$, $\sigma' \ll 1$, with χ' comparable to χ_R, is distinctive. To the equations of the first problem the following are added:

$$\chi C^s_{R''} + (\chi' - \chi\sigma) C^s_{\mathrm{RH}'} - \chi'\sigma' C^s_{\mathrm{RH2}} = \chi_D C^s_{\mathrm{D}'}; \tag{19}$$

$$\chi' C^s_{\mathrm{RH}'} = (\chi'\sigma' + \chi_R) C^s_{\mathrm{RH2}}. \tag{20}$$

From this system the wave equation is derived:

$$\varphi = \varphi^0 + \frac{RT}{F} \ln 0.81\sqrt{\rho t_1}\,(1 + 0.81\sqrt{\rho' t_1}) -$$

$$-\frac{RT}{F} \ln\left(1 + 0.81\, P\, \frac{k_{2i}}{\chi_D}\sqrt{t_1/\rho} + 0.81\sqrt{\rho' t_1}\right) - \frac{RT}{F} \ln \frac{i}{i_d - i}, \tag{21}$$

where

$$P = (1 + 1.62\sqrt{\rho' t_1})/(1 + 0.81\rho' t_1).$$

Investigation of this equation shows that addition of the second proton does not substantially change the character of the overall process: as before, $RT/2F \leq d\varphi_{1/2}/d \ln C_{\mathrm{DH}} < RT/F$, and the slope of the wave is less than that of a reversible one.

The conclusions of the theory are qualitatively justified by experiment both in the case of quinones, to which the theory is directly applicable, and in the case of nitro compounds, which give an irreversible three-electron second wave; however, $d\varphi_{1/2}/d \log C_{\mathrm{DH}}$ always considerably exceeds the limits indicated by the theory. It is possible that the discrepancy is only apparent and is caused by substituting concentration values for activities, as the theory in fact requires, but there are not enough data to verify this assumption.

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CITED LITERATURE

1. G. J. Hoijtink et al., *Rec. trav. chim. Pays-Bas*, **73**, 355 (1954).

2. P. H. Given, M. E. Peover, *J. Chem. Soc.*, **1958**, 2674; **1960**, 385.

3. E. S. Levin, Z. I. Fodiman, Abstracts of Reports, First Conference on Organic Analysis, Moscow State University Press, 1961, p. 108.

4. J. Koutecky, Collection of Czechoslovak Chemical Papers, **20**, 116 (1955).

5. J. Koutecky, ibid., **18**, 597 (1953).

Note: Figure translations are in progress. See original paper for figures.