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Abstract

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DEPENDENCE OF POLAROGRAPHIC CATALYTIC WAVES OF HYDROGEN ON THE STRUCTURE OF ORGANIC CATALYSTS

(Presented by Academician A. N. Frumkin, 13 XI 1961)

Knobloch (^1) was the first to point out that the lowering of the hydrogen overvoltage on a mercury dropping electrode in the presence of a number of heterocyclic catalysts is the greater, the higher the acidity of the catalyst. Facilitation, in many cases, of the catalytic evolution of hydrogen with decreasing pK_A in a series of structurally similar catalysts is also indicated by the data of Stakelberg and co-workers (^2), obtained for various classes of organic substances—catalysts. Qualitatively this is readily explained on the basis of the previously proposed (^3) scheme for the occurrence of a catalytic wave: the discharge of the electrochemically active acidic form of the catalyst proceeds, according to the Shikata-Tachi rule (^4), the more easily the more electronegative the residue is that is bonded to the reducible group (^5); the introduction of a negative group into an acid molecule, as is known, lowers its pK_A. The height of the catalytic wave, on the contrary, is usually greater for catalysts with a higher pK_A ([1],6). This is connected, roughly speaking, with the fact that, other conditions being equal, as the pK_A of the catalyst increases, the protolytic equilibrium between its forms (see the scheme, process (I)) is shifted toward its electrochemically active (acidic) form.

The present communication is devoted to consideration of the factors that determine the relation between the structure of the catalyst and the character of the wave caused by it. Quantitatively, this dependence is most conveniently followed using the example of "bulk" (^7) reversible catalytic waves, when adsorption phenomena that complicate the picture are absent. For this purpose catalytic waves caused by pyridine, picolines, and α, α'-lutidine were studied; as was shown (^8), these waves are determined by bulk chemical reactions.

The experimental procedure was the same as in (^9). Polarograms were recorded at 25°, in solutions with catalyst concentrations of $\sim$ 0.5 mM. Borate and veronal buffer solutions with ionic strength 0.5 (addition of KCl), containing only K^+ cations, were used. In each series of experiments, at strictly constant pH and ionic strength, only the buffer capacity of the solutions was varied. The dropping electrode with forced detachment of drops had the characteristics: $m = 1.95$ mg/sec; $t = 0.26$ sec. After recording each catalytic wave, the dropping electrode was washed externally with nitric acid to remove catalytically active reduction products (⁀8). The pK_A values (Table 1) were found potentiometrically by titration of ~ 0.05 M solution of the catalyst-base in 0.5 M KCl with 0.05 M HCl solution in 0.45 M KCl at 25°.

The catalytic process for the case under consideration is described by the scheme (⁀3):

$$\mathrm{B} + \mathrm{DH}^+ \underset{\rho\sigma}{\overset{\rho}{\rightleftarrows}} \mathrm{BH}^+ + \mathrm{D}, \tag{I}$$

$$\mathrm{BH}^+ + e \overset{\mathrm{el}}{\rightleftarrows} \mathrm{BH}, \tag{II}$$

$$2\mathrm{BH} \xrightarrow{k} 2\mathrm{B} + \mathrm{H}_2, \tag{III}$$

where B and BH^+ are the basic and ⋯

the acidic (electrochemically active) form of the catalyst, DH^+ and D—proton donors in solution and the conjugate bases corresponding to them, BH—a particle formed upon discharge of BH^+ and having the character of a free radical.

Properties of pyridine and its methyl derivatives
Table 1

Catalyst	Pyridine	α-Picoline	β-Picoline	γ-Picoline	α,α'-Lutidine
pK_A (25°, 0.5 M KCl)	5.50	6.15	5.90	6.19	6.83
k (l/mol · sec)	$5.0 \cdot 10^8$	$3.8 \cdot 10^7$	$1.4 \cdot 10^8$	$\sim 3 \cdot 10^5$	$1.5 \cdot 10^6$
E_0 (V relative to sat. cal. el.)	−1.632	−1.670	−1.655	−1.673	−1.710
$k_{\mathrm{H_3BO_3}}$ (l/mol · sec)	$7 \cdot 10^3$	$1.5\text{-}2 \cdot 10^3$	$7\text{-}10 \cdot 10^3$	$1\text{-}2 \cdot 10^4$	~ 100

Fig. 1

Figure 1: Fig. 1

Catalyst	Pyridine	α-Picoline	β-Picoline	γ-Picoline	α, α'-Lutidine
k_{ver} (l/mol · sec) N-methyliodides in 0.5 M KCl	$1.3 \cdot 10^5$	$4 \cdot 10^4$	1-2 $\cdot 10^5$	3-6 $\cdot 10^5$	$\sim 8 \cdot 10^3$
$E_{1/2}$ ($\sim$ 0.5 mM solutions)	−1.522	−1.620	−1.560	−1.671	−1.698
D, (cm^2/sec$\cdot 10^{-5}$)	1.05	1.05	0.95	1.00	1.10

The exact solution of the depolarization problem gives, for the half-wave potential (see equation (61) in $^{(10)}$):

$$E_{1/2} = E_0 + \frac{RT}{3F} \ln \frac{k\alpha}{3\rho\sigma^2}, \tag{1}$$

where E_0 is the normal redox potential of system (II), α is the analytical concentration of the catalyst, ρ is the total rate constant of protonation of the catalyst (first order):

$$\rho = k_1[DH^+]_1 + k_2[DH^+]_2 + \dots, \quad \sigma = K_A/[H^+]$$

—the equilibrium constant between B and BH^+, k is the rate constant of bimolecular regeneration (i.e., process (III)).

Fig. 1. Dependence of $(i_{\text{pr}}/i_{\text{d}})^2$ on the concentration of undissociated H_3BO_3 in borate buffer at pH 8.40 (ionic strength 0.5 M) for catalytic hydrogen waves produced by $\sim$ 0.5 mM solutions: 1—pyridine, 2—α-picoline, 3—β-picoline, 4—γ-picoline, 5—α, α'-lutidine.

The height of the catalytic wave i_{pr} is determined by expression (52) in $^{(10)}$:

$$\frac{i_{\text{d}}}{i_{\text{pr}}} = \left[\frac{3}{2 \cdot 0.81^2 k\alpha t}\right]^{1/3} \left(\frac{i_{\text{d}}}{i_{\text{pr}}}\right)^{1/3} + \frac{1}{0.81}\sqrt{\frac{\sigma}{\rho t}}. \tag{2}$$

Figure 2

Figure 2: Figure 2

In the present case, the diffusion currents of the corresponding iodide methylates in 0.5 M KCl solution were taken as i_d. The calculated from i_d values of the diffusion coefficients, as well as the $E_{1/2}$ values of the reduction waves of the iodide methylates at their concentration of $\sim$ 0.5 mM, are given in Table 1. Under the conditions of our experiments, the magnitude of the second term on the right-hand side of (2) usually considerably exceeds the first term; therefore, at pH = const (i.e., σ = const), i_pr should vary proportionally to $\sqrt{\rho}$, i.e., should vary linearly with the buffer capacity to the power 1/2. As an example, Fig. 1 shows the dependence of $(i_\mathrm{pr}/i_\mathrm{d})^2$ on the concentration of undissociated boric acid in solution at $pH = \text{const} = 8.40$.

As can be seen from Fig. 1, $(i_\mathrm{pr}/i_\mathrm{d})^2$ indeed varies linearly with $[\mathrm{H_3BO_3}]$, and the slope of the straight lines obtained, determined by the rate of protonation, depends on the nature of the catalyst. Calculation by (2) of the values of ρ

(on the estimation of the values k needed for calculating ρ by (2), see below) and plotting them against the concentration of the acidic component of the buffer at pH = const gave straight lines (see, for example, ([9])), from whose slopes the values of the partial protonation rate constants k'_A of the catalyst with the given proton donor were found. As in the case of pyridine ([9]), k'_A also increases for other catalysts with increasing pH of the solution, owing to the increasing influence of the structure of the double layer ([9]). Therefore i_pr of the catalytic waves decreases with increasing pH more slowly than it should according to (2). Plotting k'_A against $1/[\mathrm{H}^+]$ and extrapolating to $1/[\mathrm{H}^+] \to 0$ gives the true values k_A. The slope of the extrapolation straight lines for waves of homologues is almost the same as in the case of pyridine:

$$\frac{\Delta k'_A}{k_A \cdot \Delta(1/[\mathrm{H}^+])} = 6\text{—}10 \cdot 10^{-9}\ M.$$

In the case of lutidine at high pH, the values of k'_A increase somewhat faster than $1/[\mathrm{H}^+]$ increases. This is apparently connected with a certain adsorbability of α, α'-lutidine, as a result of which, when the pH is raised (i.e., when the thickness of the reaction layer is decreased), the surface component of the current begins to show itself (cf. ([11])).

Fig. 2. Dependence of $E_{1/2}$ of the catalytic waves on the pH of the solution at a catalyst concentration of $\sim$ 0.5 mM and $\rho \approx 1500\ \mathrm{sec}^{-1}$. Catalyst: 1—pyridine, 2—α-picoline, 3—β-picoline, 4—γ-picoline, 5—α, α'-lutidine. Symbols without circles—borate buffer solutions; circled symbols—veronal solutions.

Because the background discharge current is superimposed on the catalytic waves, especially in solutions of γ-picoline, the errors in determining their i_pr increase and, consequently, the accuracy of the values k_A is considerably reduced (see Table 1). For a series of similarly constructed catalysts, the protonation rate constants with one and the same acid k_A, in accordance with the Brønsted relation, should increase with increasing pK_A of the catalyst. A linear dependence was indeed found between pK_A and the logarithm of the protonation rate constant of pyridine and its methyl derivatives in interaction with water k_{H_2O} (^{11}). In the case of protonation under the action of H_3BO_3 and veronal, k_{ver} and $k_{H_3BO_3}$ for the α-methyl derivatives (see Table 1), because of steric hindrance (^{12}), are considerably lower than follows from the Brønsted relation. Steric factors can thus have a substantial influence on the heights of catalytic waves.

With increasing buffer capacity at pH = const, the $E_{1/2}$ values of the bulk catalytic waves become more negative; in the cases studied by us, in accordance with (1), $\Delta E_{1/2}/\Delta\rho \approx -20$ mV. With increasing pH, the $E_{1/2}$ values of the waves become more negative. Figure 2 gives the $E_{1/2}$ values of the waves in $\sim 0.5\ mM$ solutions of the substances studied, referred to one and the same $\rho \approx 1500\ \text{sec}^{-1}$. It follows from Fig. 2 that at pH < 8.8, $(\Delta E_{1/2}/\Delta\text{pH})_{\rho,\alpha} \approx -40$ mV, as is also required by (1). The deviations of $E_{1/2}$ from the theoretical straight line at high pH are connected with the increased influence of the structure of the double layer when the thickness of the reaction space decreases (^{9}).

Equation (1) makes it possible to find the values of the normal redox potentials E_0 for reactions (II). Substitution into (1) of the values k for pyridine and α,α'-lutidine, found earlier (^{9}), gives for E_0 of the discharge of their ions the values -1.626 and -1.715 V (sat. calomel electrode). The values of E_0 are related to pK_A by the relation

$$E_0 = \text{const} - \frac{2.3RT}{F}\,pK_A. \tag{3}$$

Substitution into (3) of the values for pyridine and α,α'-lutidine gives for const the values -1.302 and -1.312, respectively. Taking into account the low accuracy of the determination of k $^{(9)}$, the discrepancy in const should be considered insignificant, and the values of k found in $^{(9)}$ correct in order of magnitude. From (1) and (3), with const = 1.307, the values of k for the picolines (Table 1) used to calculate ρ by (2) were found. As noted in $^{(9)}$, even a comparatively large error in k has almost no effect on the values of ρ found by (2). From equations (1) and (3) the relationship of $E_{1/2}$ of the catalytic waves with the pK_A of the catalysts is evident.

Attention is drawn to the appreciable negative value of $E_{1/2}$ of the catalytic wave in a solution of γ-picoline (Fig. 2), as well as $E_{1/2}$ of the wave of reduction of its N-methyl derivative (Table 1). This is explained by the relatively low values of the rate constant k for the bimolecular interaction of radicals (according to scheme III) in the case of γ-picoline derivatives (see $^{(1)}$, and also $^{(13)}$). The lower values of k for the γ-derivatives as compared with the α-derivatives indicate that the radicals formed upon discharge of pyridine derivatives interact with the formation of hydrodipyridyls (which decompose rapidly in the case of catalytic waves (5)) chiefly in the γ-, and not in the α-position. Direct estimation of k for γ-picoline, as was done for pyridine and α, α'-lutidine (9), proved impossible because of the very negative potentials at which the catalytic wave is observed in solutions of γ-picoline.

The surface activity of many organic substances leads to the fact that the hydrogen catalytic waves caused by them are determined by surface processes and have an irreversible electrochemical stage. The change in the adsorbability of the catalyst with potential determines the characteristic shape of surface waves (14). The magnitude of the surface catalytic current is determined not only by the rate constant for protonation of the catalyst, which depends on its pK_A, but also by the adsorbability of the catalyst (14): an increase in the latter leads to a significant increase in the catalytic current.

The "half-peak" potentials of surface catalytic waves (finding their true $E_{1/2}$ is difficult (14)) depend on the pK_A of the catalyst in accordance with one of the modified Hammett equations (see, for example, (15)); however, the potentials must also be affected by the adsorbability of the catalyst. Surface catalytic waves are very sensitive to subtle changes in the structure of the catalyst. Thus, Zuman found (16) that the second wave on the polarograms of erythrophenylcysteine in an ammoniacal solution of $CoCl_2$ is almost twice as high as that for threo-phenylcysteine. This is connected with the difference in the adsorption and catalytic properties of the complexes of the indicated substances with Co^{2+} (17).

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REFERENCES

[1] E. Knobloch, *Coll. Czechoslov. Chem. Commun.*, **12**, 407 (1947).
[2] M. Stackelberg, W. Hans, W. Jensch, *Zs. Elektrochem.*, **62**, 834 (1958).
[3] S. G. Mairanovskii, *DAN*, **114**, 1272 (1957).
[4] M. Shikata, I. Tachi, *Coll. Czechoslov. Chem. Commun.*, **10**, 368 (1938).
[5] S. G. Mairanovskii, N. V. Barashkova, F. D. Alasheeva, *ZhFKh*, **35**, 435 (1961).
[6] M. Strier, J. Cavagnol, *J. Am. Chem. Soc.*, **80**, 1565 (1958).
[7] S. G. Mairanovskii, *DAN*, **132**, 1352 (1960).
[8] G. A. Tedoradze, S. G. Mairanovskii, L. D. Klyukina, *Izv. AN SSSR, OKhN*, **1961**, No. 7, 1352.
[9] S. G. Mairanovskii, L. I. Lishcheta, *Izv. AN SSSR, OKhN*, **1962**, No. 2; S. G. Mairanovskii, Ya. Koutecký, V. Hanuš, *ZhFKh*, **36** (1962).
[10] Ya. Koutecký, V. Hanuš, S. G. Mairanovskii, *ZhFKh*, **34**, 651 (1960).

[11] S. G. Mairanovskii, *Izv. AN SSSR, OKhN*, **1962**, No. 5.
[12] H. C. Brown, R. R. Holmes, *J. Am. Chem. Soc.*, **77**, 1727 (1955).
[13] J. Koutecký, V. Hanuš, *Coll. Czechoslov. Chem. Commun.*, **20**, 124 (1955).
[14] S. G. Mairanovskii, *DAN*, **133**, 162 (1960).
[15] P. Zuman, *Coll. Czechoslov. Chem. Commun.*, **25**, 3225 (1960).
[16] P. Zuman, *Chem. Listy*, **52**, 1349 (1958).
[17] S. G. Mairanovskii, E. F. Mairanovskaya, *Izv. AN SSSR, OKhN*, **1961**, 922.

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