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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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ON KINETIC CURRENTS IN THE REDUCTION OF NAPHTHALENESULFONIC ACIDS

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In general terms, the picture of the reduction of naphthalenesulfonic acids at the mercury dropping electrode may be characterized as follows (1):

1. The reduction reaction is reduced to cleavage of the C–S bond with formation of the sulfite ion

$$\mathrm{R{-}SO_3^- + 2e + H^+ \rightarrow RH + SO_3^{2-}}.$$

2. In the presence of several sulfo groups, their cleavage occurs, generally speaking, stepwise; moreover, upon accumulation of sulfo groups, the first wave shifts in the positive direction.

Basically the picture is analogous to that observed in the reduction of aromatic compounds with other negative substituents, for example halides or the group $-SO_2-R$ (2). However, a more detailed study of polarograms reveals a number of anomalies (Fig. 1) that require explanation:

Fig. 1. Polarization curves of naphthalenesulfonic acids: (abscissa–potential relative to the saturated calomel electrode; ordinate–current strength): 1–1-sulfonic acid; 2–1,5-disulfonic acid; 3–1,3,6-trisulfonic acid; 4–1,3,5,7-tetrasulfonic acid.

1. In the case of multistep reduction, the heights of the successive waves are usually unequal and are not in a simple ratio. In the case of the tri- and tetrasulfonic acids, the wave corresponding to cleavage of the last sulfo group is altogether absent.

Table 1

	1-sulfonic acid	2-sulfonic acid	1,3,6-trisulfonic acid	1,3,5,7-tetrasulfonic acid*
β, %	1.57	1.24	1.86	1.87
$(i_l)_{2H}/(i_l)_H$	1.41	–	1.42	1.39

	1-sulfonic acid	2-sulfonic acid	1,3,6-trisulfonic acid	1,3,5,7-tetrasulfonic acid*

* Sum of the heights of two waves.

2. In some cases the limiting current does not follow the laws of diffusion limitation.

It is significant that the limiting current (i_l) of the first wave in magnitude corresponds to a two-electron process and behaves like a normal diffusion current. Sometimes the second wave has the same character, and then the total height of both waves corresponds to 4 electrons (1,5- and 1,3,5,7-sulfonic acids). The diffusion nature of the corresponding limiting currents is illustrated by the data in Table 1 (β—temperature coefficient, H—height of the mercury column),

Conversely, the second wave of 1,3,6-trisulfonic acid has characteristics typical of a kinetic wave: the number of electrons $n < 2$, $\beta \simeq 7\%$, $(i_l)_{2H}/(i_l)_H \simeq 1$; moreover, the limiting current decreases noticeably with increasing pH. The third wave of 1,3,5,7-tetrasulfonic acid behaves analogously.

A quantitative theory of the phenomena described can be constructed on the assumption that, in the multistep reduction of sulfonic acids, the slow step is the intermediate addition of a proton to the carbanion. For the first waves of all sulfonic acids there is no reason to expect any chemical reaction preceding the electrode reaction, and, consequently, kinetic limitations are absent. The situation is different in the case of the subsequent waves; for definiteness, the second wave of 1,3,6-trisulfonic acid is considered here.

At a potential in the region of the second wave, a rapid transfer of two electrons first occurs $(X = \mathrm{SO_3})^*$

$$(\mathrm{R})^{\mathrm{CX}}_{\mathrm{CX}} + 2e \rightarrow (\mathrm{R})^{\mathrm{C}^-}_{\mathrm{CX}} + \mathrm{X}^-. \tag{I}$$

It is further assumed: a) that transfer of the next electron to the carbanion does not proceed at a measurable rate, but becomes possible after the reaction

$$(\mathrm{R})^{\mathrm{C}^-}_{\mathrm{CX}} + \mathrm{H}^+ \xrightarrow{k} (\mathrm{R})^{\mathrm{CH}}_{\mathrm{CX}}; \tag{II}$$

b) that the rate of this irreversible reaction is comparable with the rate of diffusion; c) that the slow transfer of the third electron is followed by rapid transfer of the fourth,

$$(\mathrm{R})^{\mathrm{CH}}_{\mathrm{CX}} + e \xrightarrow{k_e} (\mathrm{R})^{\mathrm{CH}}_{\mathrm{C}\bullet} + \mathrm{X}^-; \tag{III}$$

$$(\mathrm{R})^{\mathrm{CH}}_{\mathrm{C}^{\bullet}} + e \rightarrow (\mathrm{R})^{\mathrm{CH}}_{\mathrm{C}^{-}}. \tag{IV}$$

To derive the kinetic equations, the approximate method of the steady state is used and, hence, mean values are taken for all quantities depending on time. The solution is assumed to be buffered with respect to proton donors and acceptors, as a result of which reaction (II) becomes pseudomonomolecular; it is characterized by the heterogeneous rate constant k. Concentrations are denoted by c_A, where A is the kind of molecule, with the indices on c abbreviated as follows: $\mathrm{RX}_2 = (\mathrm{R})^{\mathrm{CX}}_{\mathrm{CX}}$, $\mathrm{RX}^- = (\mathrm{R})^{\mathrm{C}^-}_{\mathrm{CX}}$, $\mathrm{RHX} = (\mathrm{R})^{\mathrm{CH}}_{\mathrm{CX}}$; the superscript s denotes the concentration near the electrode surface. k_{RX2}, etc., are Ilkovič-equation constants for the corresponding species. Instead of k, $k' = Fqk$ has been introduced, where q is the surface area of the cathode; the constants k', $k_{\mathrm{RX2}}, \ldots$ have the same dimension. i denotes the kinetic current at any point of the second wave; i_k is the limiting kinetic current; i_d is the limiting diffusion current, which for the first and second waves is determined by one and the same equation

$$i_d = nk_{\mathrm{RX2}}c_{\mathrm{RX2}} \quad (n = 2). \tag{1}$$

Under the assumptions made, the currents are expressed as follows:

$$i_d = 2\left(k' + k_{\mathrm{RX}^-}\right) c^s_{\mathrm{RX}^-}; \tag{2}$$

$$i = 2\left(k' c^s_{\mathrm{RX}^-} + k_{\mathrm{RHX}} c^s_{\mathrm{RHX}}\right). \tag{3}$$

From equations (2) and (3) one obtains

$$i = \frac{k'}{k' + k_{\mathrm{RX}^-}}\, i_d - 2k_{\mathrm{RHX}} c^s_{\mathrm{RHX}}. \tag{4}$$

In the limiting-current region of the second wave $c_{\mathrm{RHX}} = 0$, and

$$i_k = i_d \frac{k'}{k' + k_{\mathrm{RX}^-}}. \tag{5}$$

Substituting here $k' = Fqk$ and $k_{\mathrm{RX}_-} \simeq k_{\mathrm{RX2}} = \dfrac{i_d}{nc_{\mathrm{RX2}}}$, and denoting c_{RX2} simply by c, we obtain

$$i_k = i_d \frac{k}{k + i_d/nFqc}. \tag{6}$$

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* Here and below, (R) denotes the part of the molecule (which may also include sulfo groups) not participating in the reactions under discussion.

The Ilković equation for the mean current can be written as follows (t_1 is the drop time):

$$i_d = \frac{10}{7}\sqrt{\frac{7}{3\pi}}\, nFqD^{1/2}ct_1^{-1/2} \simeq 1.23\, nFqD^{1/2}ct_1^{-1/2},$$

by virtue of which equation (6) takes the form

$$i_k = i_d \frac{k}{k + 1.23\sqrt{D/t_1}}. \tag{7}$$

It is of interest to compare the expression obtained with that given by a more exact theory. There is no direct solution in the literature for the problem posed here, but Kern (^{3}), developing Koutecký' s considerations, found that for all polarographic processes involving only one slow stage, the expression for the current can be written in one and the same form—the only thing that changes is the meaning of the heterogeneous rate constant entering the equation. It is clear that the case discussed here, if only the limiting kinetic current is considered, satisfies Kern' s condition. On the other hand, Koutecký (^{4}) derived the most exact equation for the mean current in the case of a slow electrode reaction and found that it is well approximated by the simple expression

Table 2

c, mmol/l	i_d, μA	i_d/c	i_k, μA	γ
0.41	1.32	3.20	0.30	0.23
0.86	2.84	3.29	0.625	0.22
1.30	4.15	3.18	0.96	0.23

$$i = i_d \frac{0.87\chi}{1 + 0.87\chi}, \tag{8}$$

where, in the case of a completely irreversible reaction, $\chi = k_e\sqrt{t_1/D}$. Replacing i by i_k, and k_e by k, we obtain

$$i_k = i_d \frac{0.87k\sqrt{t_1/D}}{1 + 0.87k\sqrt{t_1/D}} = i_d \frac{k}{k + 1.15\sqrt{D/t_1}}. \tag{9}$$

Equations (7) and (9), obtained in substantially different ways, coincide in form; the small difference in the coefficient is insignificant in the present case, since the accuracy of measurement of i_k is not high.

To test the theory, the polarization curves of 1,3,6-trisulfonic acid were recorded in buffer solutions composed of N $(C_2H_5)_4OH$ and H_3BO_3 or H_3PO_4, and in solutions of N $(C_2H_5)_4OH$; N $(C_2H_5)_4J$ was always added at a concentration of 0.05-0.1 M; the pH was varied in the range 9-13: in more acidic solutions the second wave of the sulfonic acid is overlapped by the hydrogen-discharge wave. The background curve was always recorded in parallel, and the true value of the current was determined from the difference: $i_{\text{true}} = i - i_\phi$. The values of the limiting current were read at -1.97 V for the first and at -2.19 V for the second wave (relative to the saturated calomel electrode). In calculating $i_{1/2}(= i_k)$, the fall of $i_{1/1}(= i_d)$ due to the decrease in drop time at more negative potential was taken into account. The capillary had the following parameters: at $H_{\text{Hg}} = 400$ mm, $m = 1.06$ mg/sec, $t_0 = 3.6$ sec.

The accuracy of measuring i_k is strongly limited by two circumstances: the considerable magnitude of the residual current in the region of the second wave and the appearance, in some experiments, of a catalytic current of unknown nature.

First of all it was established that i_k and i_d are proportional to the concentration c and, consequently, $\gamma = i_k/i_d$ does not depend on c (Table 2).

Table 3

pH	γ, H_1	γ, H_2	k', H_1	k', H_2	pH	γ, H_1	γ, H_2	k', H_1	k', H_2
9.16	–	0.55	–	2.17	10.85	0.31	0.22	0.57	0.51
9.30	0.62	0.52	2.11	1.96	11.82	0.30	0.24	0.56	0.58
9.68	–	0.27	–	0.67	12.0	$\geq$ 0.28	0.22	0.52*	0.48*
9.88	0.33	0.25	0.63	0.62					

* Average from several experiments in 0.01-0.05 M $N(C_2H_5)_4OH$.

For what follows it is convenient to use equation (5), writing it in the form

$$k' = \frac{\gamma}{1-\gamma} k_{\mathrm{RX}^-}. \qquad (10)$$

Here $k_{\mathrm{RX}^-} \simeq \dfrac{i_d}{nc_{\mathrm{RX}2}}$, and thus all quantities on the right-hand side are known from experiment. The results of the calculation are presented in Table 3, for heights of the mercury column H_1 and $H_2 = 2H_1$.

The most direct confirmation of the theory is the satisfactory agreement of the values of k', calculated for different heights of the mercury column. The course of the change in k' with increasing pH also agrees with expectations. At pH > 10, k' depends little on pH because the source of protons is not the H_3O^+ ion, but other donors (mainly, probably, H_2O).

Very indicative are the polarograms of the same sulfonic acid dissolved in dimethylformamide (supporting electrolyte–0.1 M $N(C_2H_5)_4J$), i.e., in a medium containing no proton donors. As was to be expected, in this case only one wave is observed.

The theory developed above also makes it possible to interpret all other features of the polarization curves of sulfonic acids. Thus, in the case of 1,3,6-tri- and 1,3,5,7-tetrasulfonic acids, the absence of the wave corresponding to cleavage of the last sulfo group can be explained by the very small value of the constant k. The 1,5-disulfonic acid behaves in a peculiar way. The sum of the heights of the two waves corresponds to the transfer of 4 electrons, and the total limiting current is controlled by diffusion; however, the ratio $i_{l_2}/i_{l_1} \simeq$ 0.65-0.80 and decreases with increasing H_{Hg}. Thus, the second sulfo group is partially cleaved already in the region of the first wave. Such a picture can be explained by assuming that transfer of the second pair of electrons is possible already in the potential region of the first wave, but only after a proton has added to the carbanion. Since, in total, $n = 4$, it must be assumed that in the region of the second wave the direct transfer of an electron to the carbanion occurs sufficiently rapidly.

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