Fundamental Studies on the Current-Voltage Curve in Polarography. IV. On the Reduction Wave of Organic Compounds——Especially on the Wave which Involves the "Kinetic Current"

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There exist many possible types of the redox reaction of organic compounds at the dropping mercury electrode surface, and the formulae of the polarographic current-voltage curve will take various forms according to the type of the reaction. In the present paper, the case in which the undissociated molecule of an organic acid is reduced at the more positive potential than the corresponding dissociated anion has been investigated. After deriving the general formulae for the current-voltage curve, the special case which involves the "kinetic current" has been considered, and the discussions on some properties of the polarographic waves of pyruvic acid(1) have been carried out.

Derivation of the General Formulae

Let us consider that in the body of the solution the equilibrium between the dissociated

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(1) R. Brdička, *Collection Czechoslov. Chem. Communs.*, **12**, 212 (1947).

anion, A′, and the undissociated molecule, HA, is kept according to the following equation:

$$\mathrm{A}' + \mathrm{H}^+ \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{HA} \tag{1}$$

On the other hand, at the electrode surface the undissociated molecule combines with the electrons and then the reduced ion, $\mathrm{R}^=$, reacts with the hydrogen ions getting the reduced molecule, $\mathrm{RH_2}$.

$$\mathrm{HA} + 2\varepsilon \underset{\kappa_2E_2}{\overset{\kappa_1E_1}{\rightleftharpoons}} \mathrm{R}^= \tag{2}$$

$$\mathrm{R}^= + 2\mathrm{H}^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{RH_2} \tag{3}$$

It is assumed that the equilibrium concentration of the undissociated molecule at the electrode surface is maintained by the diffusion process from the interior of the solution and by the recombination reaction at the electrode surface (the forward reaction of process (1)). Furthermore, accompanying these processes at the electrode surface, the diffusion process of the hydrogen ion between the body of the solution and the electrode surface comes into cosideration. Under these conditions the current flowing at the electrode surface can be represented by the following equations:

$$\begin{aligned} I &= 2\varepsilon K_{HA}([C_{HA}]^\circ-[C_{HA}]) \\ &\quad +2\varepsilon K_A([C_A]^\circ-[C_A]) \\ &= 2\varepsilon K_{HA}'([A_{HA}]^\circ-[A_{HA}]) \\ &\quad +2\varepsilon K_A'([A_A]^\circ-[A_A]) \\ &=I_{HA}+I_k{}^{(2)} \end{aligned} \tag{4}$$

$$I = 2\varepsilon(\kappa_1E_1[A_{HA}]-\kappa_2E_2[A_{R^=}]) \tag{5}$$

$$\begin{aligned} I_k &= 2\varepsilon\sigma(k_3[A_{H^+}][A_A]-k_4[A_{HA}]) \\ &=2\varepsilon(k_3'[A_A]-k_4'[A_{HA}]), \\ &k_3'\equiv\sigma k_3[A_{H^+}],\ k_4'\equiv\sigma k_4 \end{aligned} \tag{6}$$

$$\begin{aligned} I &= 2\varepsilon\sigma(k_1[A_{H^+}]^2[A_{R^=}]-k_2[A_{RH_2}]) \\ &=2\varepsilon(k_1'[A_{R^=}]-k_2'[A_{RH_2}]), \\ &k_1'\equiv\sigma k_1[A_{H^+}]^2,\ k_2'\equiv\sigma k_2 \end{aligned} \tag{7}$$

$$\begin{aligned} I &= 2\varepsilon K_{RH_2}([C_{RH_2}]-[C_{RH_2}]^\circ) \\ &=2\varepsilon K_{RH_2}'([A_{RH_2}]-[A_{RH_2}]^\circ) \end{aligned} \tag{8}$$

$$\begin{aligned} I &= 2\varepsilon K_{H^+}([C_{H^+}]^\circ-[C_{H^+}]) \\ &=2\varepsilon K_{H^+}'([A_{H^+}]^\circ-[A_{H^+}]) \end{aligned} \tag{9}$$

σ: the constant concerning the nature of the electrode.

$[C]^\circ$, $[C]$: concentrations in the body of the solution and at the electrode surface.

$[A]^\circ$, $[A]$: activities in the body of the solution and at the electrode surface.

K: the constant concerning the diffusion process.

$K'\equiv K/f$, f is the activity-coefficient.

$k_1'\sim k_4'$, κ_1E_1, κ_2E_2: the terms concerning the reaction rates of the corresponding processes.(3)

If the solution is well buffered, however, the diffusion process of the hydrogen ion can be neglected and $[A_{H^+}]$ is considered to be equal to $[A_{H^+}]^\circ$. In this paper such a case only has been dealt with.

Generally, the two constants, K_{HA} and K_A, concerning the diffusion coefficients of the undissociated molecule and the dissociated anion, are nearly the same, and can be written as K_O, so that Eq. (4) is reduced to

$$\begin{aligned} I &= 2\varepsilon K_O([C_O]^\circ-[C_O]) \\ &= 2\varepsilon K_O'([A_O]^\circ-[A_O]), \end{aligned} \tag{10}$$

where $[C_O]^\circ$ and $[C_O]$ are the analytical concentrations of the oxidized form in the body of the solution and at the electrode surface, which can be represented by the relations

$$\begin{aligned} [C_O]^\circ &= [C_{HA}]^\circ+[C_A]^\circ, \\ [C_O] &= [C_{HA}]+[C_A]. \end{aligned}$$

$[A_O]^\circ$ and $[A_O]$ are the activities of the corresponding terms. By eliminating $[A_{RH_2}]$, $[A_{R^=}]$ and $[A_{HA}]$ from these equations the formula

$$\begin{aligned} I/2\varepsilon &= \kappa_1E_1\frac{k_3'(K_O'[A_O]^\circ-I)-K_O'I_k}{K_O'(k_3'+k_4')} \\ &\quad -\kappa_2E_2\frac{k_2'(K_R'[A_R]^\circ+I)+K_R'I}{K_R'k_1'} \end{aligned}$$

is obtained. Now, let us introduce the relation

$$I_k = \rho I \tag{11}$$

where ρ is a proportional constant. Then the relation between the current and the electrode potential can be written as follows:

$$I/2\varepsilon = \frac{[A_O]^\circ-[E][A_{RH_2}]^\circ}{\frac{1}{[\kappa_1E_1]}+\left(\frac{1}{K_O'}+\frac{\rho}{k_3'}\right)+[E]\left(\frac{1}{K_R'}+\frac{1}{k_4'}\right)} \tag{12}$$

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(2) R. Brdička and K. Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 138 (1947).

(3) The explanations for κ_1E_1 and κ_2E_2 were set down in the previous papers (N. Tanaka and R. Tamamushi, *Bull. Chem. Soc. Japan*, **22**, 187 (1949), *etc.*).

$$=\frac{[E]'[A_O]^\circ-[A_{RH_2}]^\circ}{\dfrac{1}{[\kappa_2E_2]}+\left(\dfrac{1}{K_R'}+\dfrac{1}{k_2'}\right)+[E]'\left(\dfrac{1}{K_O'}+\dfrac{\rho}{k_3'}\right)} \tag{12'}$$

where

$$[\kappa_1E_1]\equiv\frac{k_3'}{k_3'+k_4'}\kappa_1E_1,\quad [\kappa_2E_2]\equiv\frac{k_2'}{k_1'}\kappa_2E_2 \tag{13}$$

$$[E]\equiv\frac{[\kappa_2E_2]}{[\kappa_1E_1]},\qquad [E]'\equiv\frac{[\kappa_1E_1]}{[\kappa_2E_2]}$$

Eqs. (12) and (12′) are the general formulae of the oxidation-reduction wave which appears according to the electrode processes (1)-(3).

The formulae for the various conditions can be derived by the same method as mentioned in the previous papers, because general formulae (12) and (12′) are quite analogous with those of the complex metal ion.(4) In the following section, the theoretical analysis of the wave will be set down under the condition that the terms k_2' and k_3' are comparable with K_O' and K_R'.

The Case When k_2' and k_3' are Comparable with K_O' and K_R'

Now, two special cases can be considered according to the relative magnitudes of the terms, k_2', k_3', K_O', K_R', $[\kappa_1E_1]$ and $[\kappa_2E_2]$. One of them is the case when k_2', k_3', K_O', and K_R' are much smaller than $[\kappa_1E_1]$ and $[\kappa_2E_2]$ at the electrode potential where $[\kappa_1E_1]$ is nearly equal to $[\kappa_2E_2]$, and the other case is that in which the relation between these terms is reverse. The latter corresponds to the activation-controlled one, and only the discussion on the reduction wave obtained in such a case is carried out in the present paper.

If the rate-determining step of the over-all electrode process is the activation process which contains the transfer of the electrons, the condition that $1/[\kappa_1E_1]$ is much larger than both of $1/K_O'+\rho/k_3'$ and $1/K_R'+1/k_2'$ is satisfied at the electrode potential where $[\kappa_1E_1]$ is nearly equal to $[\kappa_2E_2]$. According to the value of the electrode potential the following three cases are considered, *i. e.*, $[\kappa_1E_1]\cong[\kappa_2E_2]$ (Part A), $[\kappa_1E_1]\gg[\kappa_2E_2]$ (Part B), and $[\kappa_1E_1]\ll[\kappa_2E_2]$ (Part C).(4), (5)

Part A. $[\kappa_1E_1]\cong[\kappa_2E_2]$

In this potential region the current flowing is represented as follows:

$$I/2\mathcal{E}=[\kappa_1E_1][A_O]^\circ-[\kappa_2E_2][A_{RH_2}]^\circ, \tag{14}$$

and the current is completely defined by the activation process. The equation for the potential where the current flowing is zero can be derived from the above equation.

Part B. $[\kappa_1E_1]\gg[\kappa_2E_2]$

(1) $1/[\kappa_1E_1]\cong 1/K_O'+\rho/k_3'$

In this case the equations for the reduction wave,

$$I/2\mathcal{E}=\frac{[A_O]^\circ}{\dfrac{1}{[\kappa_1E_1]}+\left(\dfrac{1}{K_O'}+\dfrac{\rho}{k_3'}\right)}$$

or (15)

$$[\kappa_1E_1]=K_O'\frac{(I_l)_O}{(I_d)_O}\frac{I}{(I_l)_O-I}$$

are derived, where $(I_d)_O$ equals $2\mathcal{E}K_O'[A_O]^\circ$ and $(I_l)_O$ represents the limiting current of the wave. The detailed discussion of the limiting current, $(I_l)_O$, will be carried out in the following.

(2) $1/[\kappa_1E_1]\ll 1/K_O'+\rho/k_3'$

Now, the limiting current is obtained, and it is represented as follows:

$$(I_l)_O=\frac{1}{K_O'}\frac{(I_d)_O}{\dfrac{1}{K_O'}+\dfrac{\rho}{k_3'}}=\frac{k_3'(I_d)_O}{k_3'+\rho K_O'}$$

Part C. $[\kappa_1E_1]\ll[\kappa_2E_2]$

This is the potential region for the oxidation wave,(5) but all discussions on this part are omitted in this paper.

In the following section some discussions will be made on the properties of the reduction wave by means of the equations derived above.

Analysis of the Limiting Current.—It can be considered that the limiting current, (I_l), is the sum of the term $(I_d)_{HA}$ due to the diffusion process of the undissociated molecule HA and the term I_k which is attributed to the recombination reaction (3), *i. e.*,

$$(I_l)_O=(I_d)_{HA}+I_k. \tag{17}$$

By the definition of ρ, previously mentioned, the relation

$$\rho=\frac{I_k}{(I_l)_O}=\frac{(I_l)_O-(I_d)_{HA}}{(I_l)_O}$$

is derived, and if $[A_{HA}]^\circ$ is the activity of the undissociated molecule in the body of the solution the term $(I_d)_{HA}$ can be written as follows:

$$(I_d)_{HA}=2\mathcal{E}K_O'[A_{HA}]^\circ$$

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(4) R. Tamamushi and N. Tanaka, *Bull. Chem. Soc. Japan*, **23**, 110 (1950).

(5) R. Tamamushi and N. Tanaka, *ibid.*, **22**, 227 (1949).

Moreover, as it can be considered that in the body of the solution the dissociation equilibrium is maintained, ρ can be represented as below by means of the relations cited above.

$$\rho = \frac{(I_l)_O - 2\varepsilon K_O'[A_O]^{\circ}\dfrac{[A_H{}^+]}{[A_H{}^+]+\Gamma}}{(I_l)_O}$$

$$= \frac{(I_l)_O - (I_d)_O\dfrac{[A_H{}^+]}{[A_H{}^+]+\Gamma}}{(I_l)_O} \qquad (18)$$

Γ means the dissociation constant of the molecule, HA, and is equal to k_4/k_3. When the terms $(I_d)_O$, Γ and $[A_H{}^+]$ are known, the value of ρ can be calculated by Eq. (18). By introducing this relation into Eq. (16) we can write $(I_l)_O$ in terms of $(I_d)_O$, Γ and $[A_H{}^+]$, *i. e.*,

$$(I_l)_O = (I_d)_O\frac{k_3'(\Gamma+[A_H{}^+])+K_O'[A_H{}^+]}{(k_3'+K_O')([A_H{}^+]+\Gamma)}$$

$$= 2\varepsilon\frac{K_O'[A_O]^{\circ}[A_H{}^+]}{\Gamma+[A_H{}^+]}\;\frac{\sigma k_2(\Gamma+[A_H{}^+])+K_O'}{K_O'+\sigma k_3[A_H{}^+]} \qquad (19)$$

This formula is quite the same as has been set down by R. Brdička for the "kinetic current."(2) Furthermore, if we take into account the relation obtained by Brdička, the constant σ can be written as follows: (2)

$$\sigma = q\cdot\mu\cdot 10^{-3}\ {}^{(6)} \qquad (20)$$

q: the surface area of the dropping mercury electrode in cm.^{2}

μ: the thickness of the reaction layer at the electrode surface in cm.

On the Rate of the Recombination Reaction.—The following relation for k_3' is easily obtained from Eq. (16)

$$k_3' = \sigma k_3[A_H{}^+] = \frac{K_O'\rho(I_l)_O}{(I_d)_O-(I_l)_O} \qquad (21)$$

Therefore, if $(I_d)_O$, $(I_l)_O$, K_O', and ρ are known from the experimental data and others, the terms k_3', σk_3, and μk_3 can be calculated from Eqs. (20) and (21). If we use the theoretical expression for μ obtained by J. Koutecky and R. Brdička(7)

$$\mu = \sqrt{\frac{D}{k_3\Gamma}}$$

the equation for k_3,

$$k_3 = \frac{(\mu k_3)^2\Gamma}{D} \quad \text{sec.}^{-1}(\text{mol/liter})^{-1}, \qquad (22)$$

is obtained, where D is the diffusion constant of the depolarizer. Hence the value of k_3 can be determined from the experiments.

Moreover, by means of the ratio, $(I_l)/_O(I_d)_O = T$, the equation

$$k_3' = \frac{K_O'[T\Gamma-[A_H{}^+](1-T)]}{(\Gamma+[A_H{}^+])(1-T)} \qquad (23)$$

is derived.

The Relation between V and $\log I/((I_l)_O-I)$.—This relation is a straight line whose tangent is $0.059/2\alpha$ volt at 25°, if the value of α is constant. From this tangent the value of α can be calculated.

Half-wave Potential.—By introducing the relation, $I=(I_l)_O/2$, for the current at the half-wave potential, the equation

$$[\kappa_1 E_1]_{1/2} = \frac{k_3'K_O'}{k_3'+\rho K_O'} \qquad (24)$$

is obtained from Eq. (15), and, furthermore, this formula can be written as follows by means of relation (13) and the definition of Γ,

$$V_{1/2} = \frac{RT}{2\alpha F}\left(\ln s\frac{kT}{h} - \ln K_O'\right) - \frac{RT}{2\alpha F}\ln\frac{\sigma k_3([A_H{}^+]+\Gamma)}{\sigma k_3[A_H{}^+]+\rho K_O'} - \frac{\varDelta F_1}{2\alpha F}$$

$$= \text{const.} - \frac{RT}{2\alpha F}\ln\frac{\sigma k_3([A_H{}^+]+\Gamma)}{\sigma k_3[A_H{}^+]+\rho K_O'} \qquad (24')$$

s: the constant concerning the nature of the electrode.

It can be said that $V_{1/2}$ is constant and independent of the activity of the substance concerned, if pH, α and the ionic strength of the solution remain constant. If the values of K_O', k_3', Γ, ρ, α, and others are known, the free energy of the activation, $\varDelta F_1$, can be calculated from the formula mentioned above.

Now, let us consider the relation between $V_{1/2}$ and pH. Representing the half-wave potentials corresponding to the hydrogen ion concentrations $[A_H{}^+]_a$ and $[A_H{}^+]_b$ by $(V_{1/2})_a$ and $(V_{1/2})_b$, respectively, then for the shift of the half-wave potential with respect to the change of pH the following relation is obtained:

$$(V_{1/2})_a - (V_{1/2})_b = \varDelta V_{1/2}$$

$$= \frac{RT}{2\alpha F}\ln\frac{([A_H{}^+]_b+\Gamma)\,(\sigma k_3[A_H{}^+]_a+K_O'\rho_a)}{([A_H{}^+]_a+\Gamma)\,(\sigma k_3[A_H{}^+]_b+K_O'\rho_b)} \qquad (25)$$

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(6) In this case the unit of the concentration is mol per liter.

(7) J. Koutecky and R. Brdička, *Collection Czechoslov. Chem. Communs.*, **12**, 337 (1947).

It is found from Eqs. (24′) and (25) that when the value of pH is large the value of $V_{1/2}$ becomes independent of pH and reaches a constant value, and this can be thought as a special character of the reduction wave which is obtained under the condition mentioned above (Fig. 1).

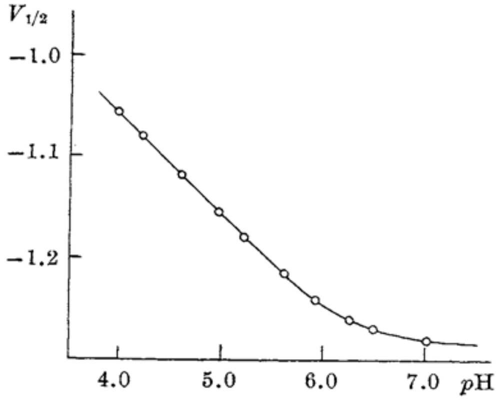

Fig. 1.

Hitherto, the case, in which K_O', K_R', k_2' and k_3' have the values nearly of the same order, has been discussed. The important character in such a case is that the limiting current is not represented only by the rate of the diffusion process but also by the term concerning the reaction rate such as k_3'. For such a limiting current, it is obvious that the application of the Ilkovič' equation fails, and the "kinetic current" mentioned by Brdička corresponds to this current. We can distinguish the "kinetic current" from the ordinary "diffusion current" by its dependence on the nature of the electrode, temperature and so forth.(1), (2)

As for the example of the application of the theoretical results obtained above, the shift of the half-wave potential and the calculation of the free enery of the activation, ΔF_1, of the reduction process of pyruvic acid are discussed in the following section.

Discussion on the Properties of the Reduction Wave of Pyruvic Acid(1)

The polarographic study on the pyruvic and phenylglyoxylic acids was carried out, at first, by O. H. Müller,(8) and recently by R. Brdička.(1) The latter has explained the appearance of the double-wave by introducing the conception of the "kinetic current." However, the shift of the half-wave potential accompanying the change of pH has not yet been interpreted.

By means of the theoretical equations described above, the discussion on the half-wave potential and the calculation of the value of ΔF_1 can be carried out. The experimental data obtained by Brdička have been used for the present calculation.

Calculation of the Shift of the Half-wave Potential.—First, the linear relations have been found between V and $\log I/(I_l-I)$ for the actual polarograms of pyruvic and phenylglyoxylic acids. From these relations the value of α for each case has been calculated. While the value of α for pyruvic acid has been nearly constant and equal to 0.28, on the other hand, that of phenylglyoxylic acid varied from 0.54 to 0.34 according to the change of pH. Unless the value of α remains constant, it is quite doubtful whether Eqs. (24′) and (25) can be applicable or not for the present purpose, so only the calculation for pyruvic acid will be carried out in the following.

After having been determined the value of α, the term μk_3 has been calculated from Eqs. (20) and (21), the mean value of which over the range of pH 4.95-6.81 is 3.2×10^3. The terms ρ, K_O' and $m^{2/3}\,t^{1/6}$ (the capillary constant) have been obtained from the polarograms observed by Brdička, and for the value of Γ, 4×10^{-3} has been used. Then, the shift of the half-wave potential with the change of pH has been calculated from Eq. (25), and the results have been compared with the experimental data obtained by Brdička (Table 1). The half-wave potential of the wave at pH$=5.20$ (−1.180 volts) has been taken as the standard for the present calculation. It has been shown by the experimental results that half-wave potential of such a wave tends to reach the constant value when pH increases. This property can be completely interpreted by Eq. (25), and the calculated limiting value of the half-wave potential for pyruvic acid is obtained to be −1.287 volts. From this result it can be said that the theoretical treatement mentioned above can interpret the properties of the wave of pyruvic acid at least qualitatively.

Table 1

pH	$\Delta V_{1/2}$ *calc.*, mV.	$\Delta V_{1/2}$ *obs.*, mV.	pH	$\Delta V_{1/2}$ *calc.*, mV.	$\Delta V_{1/2}$ *obs.*, mV.
3.95	127	114	5.59	−35	−35
4.19	102	90	5.91	−60	−60
4.58	61	65	6.24	−79	−80
4.95	24	28	6.48	−89	−80
5.20	—	—	6.64	−93	—

Calculation of ΔF_1.—Introducing the values

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(8) O. H. Müller, *J. Am. Chem. Soc.*, **61**, 590 (1939).

of α, σk_3, ρ, and others to Eq. (24′) the value of the free energy of the activation for the forward reaction of the process (2), ΔF_1, can be calculated.[9] In the case of pyruvic acid the results obtained over the range of pH 4.95-6.48 are shown in Table 2.

Table 2

pH	$V_{1/2}$, volt	ΔF_1, joule
4.95	−1.152	9.5×10^4
5.20	−1.180	9.5×10^4
5.59	−1.215	9.6×10^4
5.91	−1.240	9.6×10^4
6.24	−1.260	9.6×10^4
6.49	−1.260	9.5×10^4
		mean value......9.6×10^4

Summary

Of the oxidation-reduction reaction of organic compounds, the case, in which the undissociated molecule of an organic acid is reduced at the more positive potential than the corresponding dissociated anion and the equilibrium concentration of the reducible form at the electrode surface is kept by the diffusion process and the recombination reaction at the electrode surface, has been taken into consideration. Under such conditions, the general formulae for the polarographic current-voltage curve have been derived, and the special case which involves the "kinetic current" has been investigated. The theoretical discussions on the limiting current and the shift of the half-wave potential with the change of pH have been carried out. Moreover, the results obtained have been applied to interpret the properties of the wave of pyruvic acid observed by R. Brdička. A considerably good agreement between the experimental data and the theoretical results has been obtained, and it is probably said that the properties of the various polarographic waves and the mechanism of the electrode process can be investigated by the analogous treatment mentioned above.

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[9] The constant s in Eq. (24′) is assumed to be equal to the constant σ.