[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

Polarographic Reduction of Carbon Dioxide. II. Polymerization and Adsorption at the Dropping Mercury Cathode[1]

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In a recent brief note[1a] we have reported certain observations made on polarographic reduction waves obtained with solutions of carbon dioxide in 0.1 molar tetramethylammonium chloride. The slopes of the waves were found to differ appreciably from those obtained in the ordinary reversible reductions involving two hydrogen ions and two electrons per molecule reduced. This feature of the carbon dioxide waves is shared by many other polarographic waves on record for which no entirely satisfactory interpretation has so far been advanced. In the present paper we develop, for those cases (including carbon dioxide) where the influence of temperature on the half-wave potential and the slope indicates no irreversibility on account of rate complications, an interpretation based upon consideration of polymerization and adsorption at the dropping mercury cathode.

In general polarographic reduction waves follow equations of the type[2]

$$E = E_{1/2} + \frac{RT}{\alpha F} \ln \frac{i}{i_d - i} \qquad (1)$$

(E = absolute value of the cathode potential, $E_{1/2}$ = absolute value of the half-wave potential, R = molar gas constant, T = absolute temperature, α = parameter, F = one faraday, ln = symbol of natural logarithms, i = reduction current, i_d = limiting diffusion current). When α is a small integer it represents the number of electrons involved in the reduction of one ion or one molecule. There are, however, many cases on record for which α is smaller than one. Carbon dioxide is one more case of this type. This situation is particularly frequent with organic reductions and is then often ascribed to one or more of a variety of factors causing irreversibility. Since in many of these cases the reduction products cannot be isolated it is impossible to establish whether the polarographic half-wave potential coincides with a potentiometrically determined reversible oxidation–reduction potential[3] or not. In other words, in such cases, the actual proof of irreversibility is lacking, and it is reasonable to develop interpretations of these waves on the basis of the theory of electrochemical equilibrium which is the foundation of the interpretation of the great majority of polarographic waves. Such a procedure is particularly indicated when the variation of the half-wave potential with temperature is small enough to preclude rate complications and therefore real irreversibility.[4] As a matter of fact a rather larger variation with temperature than is usually accepted is still compatible with reversibility when, as is the case with the following treatment, adsorption equilibrium constants are incorporated into the half-wave potentials. Irreversibility should also manifest itself through a temperature variation of α in equation (1). The closeness of equation (1), even with α smaller than one or different from some simple integer, to the ordinary Nernst-type of equation strongly suggests that similar interpretations apply to all these cases. In the present paper we show that an equation of type (1), with α smaller than one, corresponds to the reversible reduction of neutral molecules (carbon dioxide for instance) when several of these molecules, adsorbed at the surface of the mercury drop, share two hydrogen ions and two electrons, and when the reduction product is adsorbed at the mercury surface but in equilibrium with some dissolved reduction product in accordance with a Freundlich adsorption isotherm. By "reversible" reduction we mean a reduction following a potential concentration equation of the Nernst type derived on the basis of the general condition of electrochemical equilibrium.

We shall divide our discussion into two parts, according to whether the solutions considered are buffered or not. We shall introduce the following two notations

$$1/\alpha = x/2 \qquad (2)$$

and

$$i/i_d = u \qquad (3)$$

Equation (1) is thus transformed into

$$E = E_{1/2} + \frac{xRT}{2F} \ln \frac{u}{1 - u} \qquad (4)$$

Case I: The Solution is Buffered

Let us consider the reaction

$$x\mathrm{R} + 2\mathrm{H}^+ + 2\mathrm{e}^- \longrightarrow \mathrm{R}_x\mathrm{H}_2 \qquad (5)$$

in which R represents some reducible substance. We refer the number x of molecules reduced to two electrons rather than to one because, if one electron were involved, free radicals would be formed and there would in general be association of these radicals two by two. If reaction (5) occurs reversibly at the dropping mercury cathode the reduction potential E would be of the form[5]

(1) Presented as part of a paper entitled "Polarographic Studies on Carbon Dioxide and Chlorophyll," by P. Van Rysselberghe and J. M. McGee at the Pacific Northwest Regional Meeting of the American Chemical Society in Seattle, October 20, 1945.

(1a) P. Van Rysselberghe and G. J. Alkire, THIS JOURNAL, **66**, 1801 (1944). Henceforth referred to as Paper I of this series.

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 194–195.

(3) O. H. Müller, *Cold Spring Harbor Symposia Quant. Biol.*, **7**, 59 (1939).

(4) I. M. Kolthoff and J. J. Lingane, reference 2, pp. 153–154, 182–183.

(5) I. M. Kolthoff and J. J. Lingane, reference 2, p. 184.

$$E = E_0 + \frac{RT}{2F} \ln \frac{C_X}{C_R^x a_{H^+}^2} \quad (6)$$

in which C is the symbol for molar concentration, X designates the reduction product R_xH_2, a_{H^+} the activity of the hydrogen ion. The activity coefficients of the neutral species are taken equal to unity. The x molecules of R reacting are regarded as adsorbed on the mercury surface in some sort of geometrical pattern: polygons with an R molecule at each corner, for instance. The hydrogen ions and electrons react with two of these molecules forming two HR-radicals and forcing in the $(x-2)$ other molecules of R rearrangements of electronic pairs with the resulting formation of a reduced polymer R_xH_2.

The solution being buffered we can write

$$E = E_0' + \frac{RT}{2F} \ln \frac{C_X}{C_R^x} \quad (7)$$

Then, in accordance with well-known steps in polarographic theory, we have

$$i = k (C_R^0 - C_R) \quad (8)$$

$$i_d = k C_R^0 \quad (9)$$

and

$$C_R = \frac{1}{k} (i_d - i) \quad (10)$$

in which C_R^0 designates the bulk concentration of R, C_R the concentration in immediate contact with the surface of the mercury drop. Turning now to the reduction product X we shall consider it as formed and present for the major part in an adsorbed state at the surface of the mercury drops, the concentration C_X in the solution near the drops being in equilibrium with a surface concentration C_{Xs} in accordance with a Freundlich adsorption isotherm

$$C_X = K C_{Xs}^z \quad (11)$$

in which z is a parameter having some value larger than one. The surface concentration C_{Xs} will be proportional to the current i

$$C_{Xs} = k' i \quad (12)$$

Replacing C_R and C_{Xs} by their values (10) and (12) in (7) we get

$$E = E_0'' + \frac{RT}{2F} \ln \frac{i^z}{(i_d - i)^x} \quad (13)$$

with

$$E_0'' = E_0 - \frac{RT}{F} \ln a_{H^+} + \frac{RT}{2F} \ln (K k'^z k^x) \quad (14)$$

Introducing the ratio $i/i_d = u$ we find

$$E = E_0'' + \frac{RT}{2F} \ln i_d^{z-x} + \frac{RT}{2F} \ln \frac{u^z}{(1-u)^x} \quad (15)$$

The half-wave potential corresponds to $u = 1/2$

$$E_{1/2} = E_0'' + \frac{RT}{2F} \ln \left(\frac{i_d}{2}\right)^{z-x} \quad (16)$$

In case the half-wave potential is independent of i_d, and hence of the concentration of the reducible substance, we should have $z = x$, and formula (15) becomes

$$E = E_{1/2} + \frac{xRT}{2F} \ln \frac{u}{1-u} \quad (17)$$

a formula identical with the empirical formula (4). A wave of this type has a slope dE/du given by

$$\frac{dE}{du} = E' = \frac{xRT}{2F} \left(\frac{1}{u} + \frac{1}{1-u}\right) \quad (18)$$

which at the half-wave gives, for 25°

$$E'_{1/2} = 2x \frac{RT}{F} = 0.051\, x \quad (19)$$

One should also note that the half-wave is then a point of inflection

$$\frac{d^2E}{du^2} = E'' = \frac{xRT}{2F} \left(-\frac{1}{u^2} + \frac{1}{(1-u)^2}\right) \quad (20)$$

$$E''_{1/2} = 0 \quad (21)$$

Waves for which $E_{1/2}$ is not independent of i_d may be interpreted on the basis of values of x and z different from each other. For such waves the slope E' derived from (15) is

$$\frac{dE}{du} = E' = \frac{RT}{2F} \left(\frac{z}{u} + \frac{x}{1-u}\right) \quad (22)$$

and

$$E'_{1/2} = (z + x) \frac{RT}{F} = 0.051 \frac{z+x}{2} \quad (23)$$

The point of inflection is not at the half-wave, but is such that

$$\frac{d^2E}{du^2} = E'' = \frac{RT}{2F} \left(-\frac{z}{u^2} + \frac{x}{(1-u)^2}\right) = 0 \quad (24)$$

or

$$\frac{x}{z} = \left(\frac{1-u}{u}\right)^2 \quad (25)$$

When the point of inflection is located on the experimental wave the corresponding value of u can be introduced in (25) which thus gives the ratio x/z, while the sum $x + z$ can be obtained from the slope at the half-wave according to (23).

Case II: The Solution is Not Buffered

In many cases (that of carbon dioxide for instance) special conditions prevent the use of buffered solutions. This case divides itself into two sub-cases: a. The reducible substance R has no acid properties and the original solution is neutral. b. The reducible substance R is an acid and there is immediate adjustment of the equilibrium between R and H^+.

Sub-Case a.—Reaction (5) should be rewritten as

$$xR + 2H_2O + 2e^- \longrightarrow R_xH_2 + 2OH^- \quad (26)$$

The concentration of OH^- is thus (see equation (8))

$$C_{OH^-} = \frac{2}{x} (C_R^0 - C_R) = \frac{2i}{kx} \quad (27)$$

and, at 25°

$$C_{H^+} = 10^{-14} kx/2i \quad (28)$$

This value of C_{H^+} can then be introduced into (6) and the resulting formula can be transformed in a manner similar to that of Case I.

Sub-Case b.—Whether the reducible acid substance R yields one or more protons to the solvent the acidity of the solution will usually depend on the first dissociation constant only. The supporting electrolyte is usually a neutral salt. We have therefore

$$C_{H^+}^2 = K_a C_R \tag{29}$$

and formula (6) becomes

$$E = E_0' + \frac{RT}{2F} \ln \frac{C_X}{C_R^{x+1}} \tag{30}$$

which can then be transformed into a formula of the same type as (15)

$$E = E_0^* + \frac{RT}{2F} \ln i_d^{x-z-1} + \frac{RT}{2F} \ln \frac{u^z}{(1-u)^{z+1}} \tag{31}$$

with

$$E_0^* = E_0 + \frac{RT}{2F} \ln \frac{Kk'^z k^{z+1}}{K_a} \tag{32}$$

All the subsequent developments of Case I apply here with the difference that x is now replaced by $x + 1$. In particular, if it is found experimentally that the half-wave potential is independent of i_d, we have, in place of (19), at 25°

$$E_{1/2}' = 2(x+1)\frac{RT}{F} = 0.051(x+1) \tag{33}$$

and, as in (21)

$$E_{1/2}'' = 0 \tag{34}$$

If, on the other hand, $E_{1/2}$ varies with i_d, we have, in place of (23)

$$E_{1/2}' = (z+x+1)\frac{RT}{F} \tag{35}$$

and, at the point of inflection, in place of (25)

$$\frac{x+1}{z} = \left(\frac{1-u}{u}\right)^2 \tag{36}$$

It will be shown in the following paper[6] that the reduction waves of carbon dioxide are logically and simply interpreted as belonging to this subcase b of Case II.

Free Energy Changes Involved in the Reduction Process

In this part of the discussion we shall restrict ourselves to Case II, sub-case b, which is the one upon which the interpretation of our results on carbon dioxide is based. Making $z = x + 1$ in (31) and (32) and multiplying by $2F$ we get, for $u = 1/2$

$$2FE_{1/2} = 2FE_0^* = 2FE_0 + RT \ln \frac{K(k'k)^{x+1}}{K_a} \tag{37}$$

The standard free energy change for the reaction

$$xR + 2H^+ + 2e^- \longrightarrow R_xH_2 \tag{38}$$

or

$$xR + H_2 \longrightarrow R_xH_2 \tag{39}$$

is (our E_0, $E_{1/2}$, etc., are absolute values of cathodic potentials)

$$\Delta F^0 = 2FE_0 \tag{40}$$

which can be obtained from $2FE_0^*$ (with $E_0^* = E_{1/2}$ referred to the standard hydrogen electrode) by the formula

$$\Delta F^0 = 2FE_0 = 2FE_0^* - RT \ln \frac{K(k'k)^{x+1}}{K_a} \tag{41}$$

Formulas (10) and (12) show that k and $1/k'$ are of the same order of magnitude. The term $(x + 1)\ln(k'k)$ will thus be of a smaller order of magnitude than the term $\ln(K/K_a)$. The ionization constant K_a will in general be known, E_0^* is an experimentally determined quantity, while ΔF^0 may in many cases be estimated from free energy tables such as that established by Parks and Huffman.[7] It is then possible to obtain at least an approximation for the adsorption equilibrium constant K. The method of calculation here outlined will be applied to the case of carbon dioxide in the following paper of this series.[5]

Summary

An interpretation of certain polarographic waves is provided by a theory based upon:

1. The sharing of two hydrogen ions and of two electrons by more than one molecule of the reducible substance.
2. The establishment of an adsorption equilibrium of the reduction product between the dropping mercury cathode and the solution.

Two main cases are considered: buffered and unbuffered solutions. The latter case is divided into two sub-cases according to whether the reducible substance is an acid or not.

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(6) P. Van Rysselberghe, G. J. Alkire and J. M. McGee, THIS JOURNAL, **68**, 2050 (1946).

(7) G. S. Parks and H. M. Huffman, "The Free Energy of Some Organic Compounds," Chemical Catalog Co., New York, N. Y., 1932, see Table 40, pp. 210–211.