tion of the bound cation on the polyion coil[6] seems to be valid for the sodium polymetaphosphate solutions. This probably is partly due to the fact that the polymetaphosphates have a lower degree of polymerization than the organic polymers which were investigated. In any event, the average polymetaphosphate k values are of the same order of magnitude as the k values found for many of the other polymers. The exchange rates at 0 and 25° are not very different, showing that the energy of activation for exchange is low.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

Electrophilic Displacement Reactions. III. Kinetics of the Reaction between Hydrogen Peroxide and Benzeneboronic Acid[1]

BY HENRY G. KUIVILA

RECEIVED SEPTEMBER 28, 1953

A study of the kinetics of the reaction between hydrogen peroxide and benzeneboronic acid at values of pH between 2 and 6 has been made. Two ionic mechanisms are distinguishable; each is first order in peroxide; one is first order and the other is second order in boronic acid. The rates of both reactions increase with pH but are independent of buffer concentration in the case of phthalate buffers. In acetate and chloroacetate buffers the same specific rate constants are observed as in phthalate. Specific catalytic effects are exhibited by boric acid, zinc perchlorate, citrate and tartrate. The mechanisms of the reactions are discussed in the light of these experimental facts.

Among the reactions of benzeneboronic acid that with hydrogen peroxide is particularly interesting.[2] It is the only reaction involving replacement of the boronic acid function which both aromatic and

$$C_6H_5B(OH)_2 + HOOH \longrightarrow C_6H_5OH + B(OH)_3$$

aliphatic[3] boronic acids are known to undergo under comparable conditions. A second point of interest involves the relative ease of replacement of hydrogen and the boronic acid function in aromatic compounds. Both are replaced with comparable ease by halogens.[3,4] Replacement of hydrogen by hydroxyl, however, is not nearly as facile as replacement of the boronic acid group. The former requires either a strongly basic medium and the presence of hydroxyl groups in the ring[5] or catalysis by iron salts[6] in which case a free radical mechanism is clearly indicated.

An investigation of the kinetics of the reaction between benzeneboronic acid and hydrogen peroxide is repeated herein. The results obtained to date suggest mechanisms which render the above observations reasonable.

Experimental

Materials.—Benzeneboronic acid was prepared as described by Bean and Johnson[7] and stored as the anhydride, m.p. 214–216°.[1] Chloroacetic acid (Matheson) was recrystallized from benzene and the sodium salt prepared by addition of the acid to sodium methoxide in anhydrous methanol. All other reagents were the purest grade available commercially and were used without further purification. Sodium perchlorate was used in adjusting ionic strengths.

Stoichiometry of the Reaction.—A solution at pH 5.6, 0.0500 M in boronic acid and 0.64 M in hydrogen peroxide was allowed to stand three hours. From previous rate measurements this period was known to be long enough for greater than 99% consumption of boronic acid. Titration of an aliquot showed a change of 0.0504 M in peroxide concentration. At this time another aliquot (5 ml.) was removed. To this were added 1 ml. of concd. hydrochloric acid, 10 ml. of water, 0.5 g. of sodium bromide and 0.5 ml. of 0.5 M ammonium molybdate. The bromine thus formed could brominate the phenol present. After 15 min. potassium iodide was added and the iodine titrated with thiosulfate. The difference between this last titer and the preceding one indicated a change of 0.146 M in bromine concentration as compared with 0.150 M required on the basis of boronic acid originally present.

A similar determination on a reaction in 4.12 M perchloric acid showed consumption by the phenol produced in the reaction of 0.0742 M bromine *vs.* 0.0750 M calculated.

This procedure for quantitative estimation of phenol is a modification of that given by Siggia.[8]

Rate Measurements.—A flask containing appropriate concentrations of boronic acid, buffer and sodium perchlorate was placed in a bath at 25.10 ± 0.02°. After at least 15 minutes an aliquot of hydrogen peroxide solution at the same temperature was added. Aliquots were removed at intervals and transferred to flasks containing 5 ml. of 4 M sulfuric acid, 5 ml. of 5% potassium iodide solution and 5 drops of 0.5 M ammonium molybdate.[9] The resulting iodine was titrated with freshly standardized sodium thiosulfate, 0.01 N or 0.02 N. When runs were made in acid solutions the sulfuric acid was omitted from the quenching solution.

In the presence of chelating agents the catalytic effect of molybdate on the iodine–peroxide reaction is negligible and therefore the iodometric analysis is unreliable. The colorimetric method involving titanium(IV)[10] was used. Measurements were made with a Bausch and Lomb photoelectric colorimeter, Model 35. At 415 mμ Beer's law is obeyed in the concentration range 1 × 10^{-4} to 8 × 10^{-4} mole per liter (13-mm. cuvettes). The optical density was not affected by any of the solutes. A slow decrease in absorption occurred with time when boronic acid and tartrate or citrate were present, but readings were always completed within two minutes so that the error introduced was never as much as 0.5% in the peroxide concentration.

Determinations of pH were made with a Beckman model H2 pH meter.

Results

Preliminary experiments showed that the reaction proceeds at a conveniently measurable rate

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(1) For preceding paper in this series see H. G. Kuivila and A. R. Hendrickson, THIS JOURNAL, **74**, 5068 (1952).

(2) A. D. Ainley and F. Challenger, *J. Chem. Soc.*, 2171 (1930).

(3) H. R. Snyder, J. A. Kuck and J. R. Johnson, THIS JOURNAL, **60**, 105 (1938).

(4) N. N. Melnikov, *J. Gen. Chem.* (*U.S.S.R.*), **6**, 636 (1931); *C. A.*, **30**, 5571 (1936).

(5) R. G. Jones and H. A. Shonle, THIS JOURNAL, **67**, 1034 (1945).

(6) A. Chwala and M. Pailar, *J. prakt. Chem.*, **152**, 45 (1939); H. Goldhammer, *Biochem. Z.*, **189**, 81 (1927).

(7) F. R. Bean and J. R. Johnson, THIS JOURNAL, **54**, 4415 (1932).

(8) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 111.

(9) I. M. Kolthoff and N. H. Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1929, p. 392.

(10) G. M. Eisenberg, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 327 (1943).

at 25° in water. In the absence of other substances the kinetics is complex. This is shown in Fig. 1 which represents the conventional second-order plot for three reactions in which the hydrogen peroxide concentration was varied. The increase in initial slope with decreasing concentration indicates an order of less than one for peroxide and suggests that dissociation is involved. That this is an acid–base dissociation is shown in Fig. 2. Here it is seen that the initial slopes for the two different peroxide concentrations are the same in a buffered solution. Added phenol, acetanilide or boric acid in 0.02 *M* concentration at *p*H 4.44 did not alter the rate.

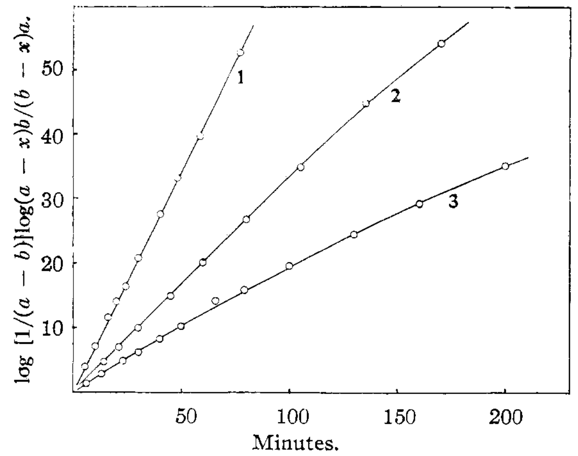

Fig. 1.—Effect of varying initial peroxide concentration on apparent second-order rate in unbuffered solution: curve 1, 0.00510 *M* H_2O_2; 2, 0.0205 *M* H_2O_2; 3, 0.0414 *M* H_2O_2; $[C_6H_5B(OH)_2]_0$ 0.025 *M*, μ 0.02.

The decrease in the apparent second-order rate constants observed in Fig. 2 is evidently due to the presence of a reaction second order in boronic acid. At the higher peroxide concentration a sufficiently large change in boronic acid concentration occurs to be easily manifested in the rate plot as a decrease in slope. To test this a series of runs with different initial boronic acid concentrations was made. The apparent initial second-order rate constants proved to be linear functions of boronic acid concentration. Several such plots at different values of the *p*H are shown in Fig. 3. The observed rate constant at a given *p*H can thus be represented by equation 1. Logarithms of the

$$k_{\text{obsd}} = k_1 + k_2[C_6H_5B(OH)_2] \quad (1)$$

values of k_1 and k_2 evaluated by the method of least squares are plotted as a function of *p*H in Fig. 4. Each pair of points was obtained from a set of at least five runs made at different boronic acid

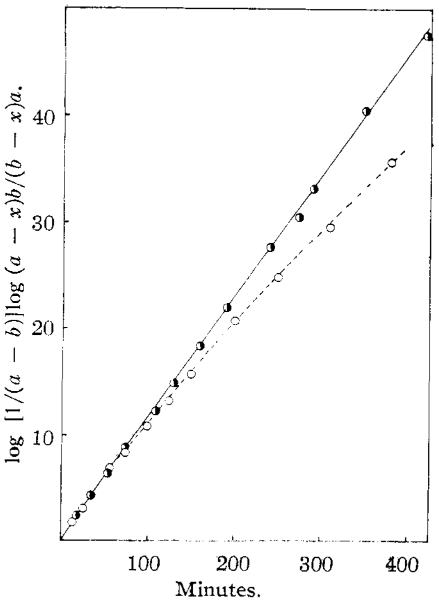

Fig. 2.—Effect of varying initial peroxide concentration on apparent second-order rate in phthalate buffer: ◑, 0.00988 *M* H_2O_2; ○, 0.0398 *M* H_2O_2; $[C_6H_5B(OH)_2]_0$ 0.025 *M*, *p*H 4.44, μ 0.20.

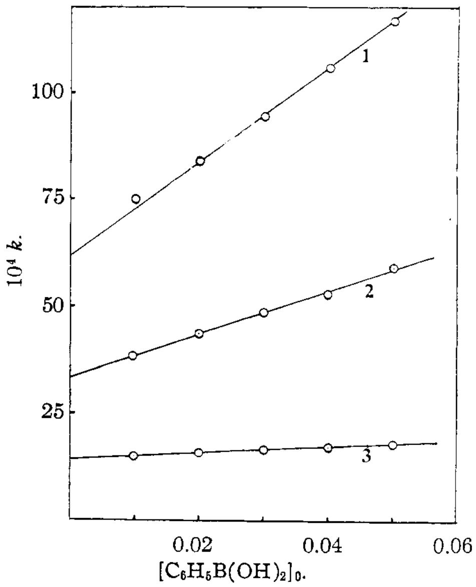

Fig. 3.—Effect of initial boronic acid concentration on apparent second-order rate constant: curve 1, *p*H 4.82; 2, *p*H 4.44; 3, *p*H 3.76.

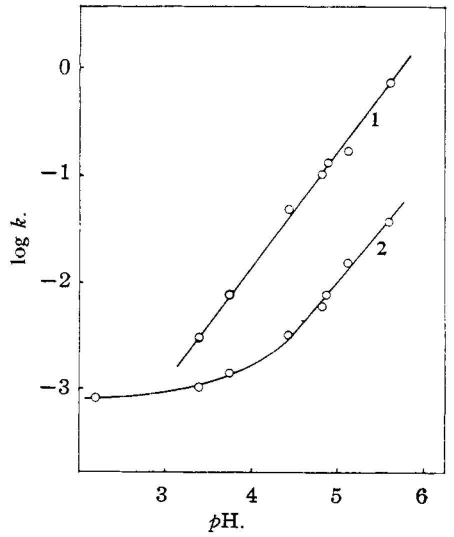

Fig. 4.—Effect of *p*H on k_1 and k_2: curve 1, k_2; 2, k_1.

concentrations. The least squares slope of the k_2 plot is 1.10 in fair agreement with the theoretical value of unit for base catalysis. The terminal slope of the k_1 plot as drawn is unity.

The figures in Table I show that k_1 and k_2 are independent of buffer concentration. Thus each reaction has the characteristics of first-order specific lyate ion[11] catalysis. This is confirmed by the data in Table II involving acetate and chloroacetate, respectively, as buffers. In Table II $k_{\text{calcd.}}$ was computed for the boronic acid concentration given from values of k_1 and k_2 taken from Fig. 4.

TABLE I

VALUES OF k_1 AND k_2 AT DIFFERENT BUFFER CONCENTRATIONS, PHTHALATE BUFFER AT *p*H 4.44

Buffer concn. mole/l.	10^3k_1, l mole^{-1} sec.$^{-1}$	10^3k_2, l.^{2} mole^{-2} sec.$^{-1}$
0.02	3.32	50.6
.05	3.01	51.3
.10	3.38	47.0

TABLE II

VALUES OF k_{obsd} FOR ACETATE AND CHLOROACETATE BUFFERS

Buffer	Buffer concn. mole/l.	*p*H	$[C_6H_5B(OH)_2]^0$ moles/l. × 10^3	$10^3k_{\text{obsd.}}$	$10^3k_{\text{calcd.}}$
Acetate	0.05	4.88	20.0	9.92	9.9
	.05	4.88	40.0	12.6	12.4
	.05	5.24	10.0	19.8	20.2
	.05	5.24	20.0	22.8	23.4
Chloro-acetate	0.22	3.75	40.0	1.73	1.66
	.22	3.75	20.0	1.58	1.51
	.055	3.67	40.0	1.61	1.54
	.055	3.67	20.0	1.45	1.42

A test of the validity of equation 1 for the runs in Fig. 2 is shown in Fig. 5. The left side of equation 2 where a and b are initial concentrations of

$$\frac{dx}{(a - x)(b - x)\{k_1 + k_2(a - x)\}} = dt \qquad (2)$$

boronic acid and hydrogen peroxide, respectively, and x represents the concentration of the products, was evaluated by graphical integration. Values of k_1 and k_2 from Fig. 4 were used. Values of the integral agree with the time for each point within 3% over 90% consumption of the reactant in lowest initial concentration. The line in Fig. 5 is drawn with unit slope.

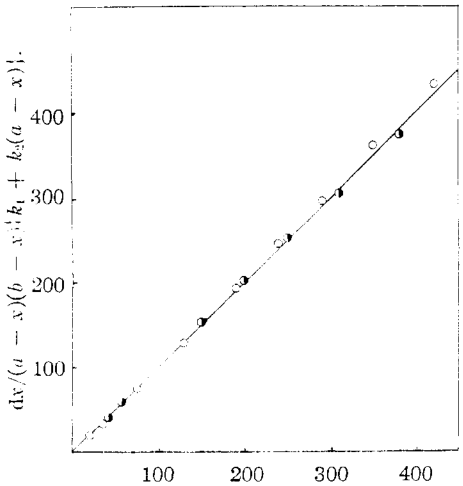

Fig. 5.—Graphical test of equation 2: ○, 0.00988 M H_2O_2: ◑, 0.0398 M H_2O_2.

Since one molecule of boronic acid functions as a catalyst for the reaction of a second with hydrogen peroxide it was of interest to determine whether boric acid could act in the same way. At *p*H 4.44, 0.02 M boric acid did not affect the rate perceptibly. However, as shown by the figures in Table III, catalysis by boric acid is unmistakable at *p*H 5.24. At this *p*H (equation 1) k_2 is 0.32 l.^{2} mole^{-2} sec.$^{-1}$, whereas k_c for boric acid catalysis would be 0.054 l.^{2} mole^{-2} sec.$^{-1}$ so that the boronic acid is the better catalyst by a factor of about six. Zinc perchlorate increases the rate markedly, whereas magnesium perchlorate has a negligible effect. A positive salt effect is also indicated by the data in the table.

TABLE III

EFFECT OF ADDED SUBSTANCES ON RATE OF REACTION (ACETATE BUFFER, 0.01 M BORONIC ACID IN ALL RUNS)

Buffer, mole/l.	*p*H	Added substance	Concn., moles/l.	μ	$10^3k_{\text{obsd.}}$ l. mole^{-1} sec.$^{-1}$
0.05	5.24			0.20	20.1
.05	5.24	H_3BO_3	0.05	.20	22.8
.20	4.71			.50	9.13
.20	4.71			.53	9.30
.20	4.69			.60	9.84
.20	4.62	$Zn(ClO_4)_2$	0.02	[a]	11.0
.20	4.71	$Mg(ClO_4)_2$	0.02	[a]	9.38

[a] μ = 0.50 if perchlorate is undissociated and μ = 0.53 if it is completely dissociated.

Both citrate and tartrate function as specific catalysts but differ from each other in their detailed behavior. From Fig. 6 it follows that tartrate catalyzes both reactions giving an observed k_1 of 0.0116 l. mole^{-1} sec.$^{-1}$ and k_2 of 0.445 l.^{2} mole^{-2} sec.$^{-1}$ as compared with 0.00105 l. mole^{-1} sec.$^{-1}$ and 0.00240 l.^{2} mole^{-2} sec.$^{-1}$, respectively, for the uncatalyzed reactions. Citrate behaves quite differently. At *p*H 4.60 in 0.05 M concentration no reaction second order in boronic acid can be detected. Figure 7 represents the effect of citrate concentration at two different boronic acid concentrations. The observed rate constants appear to be approaching a constant value

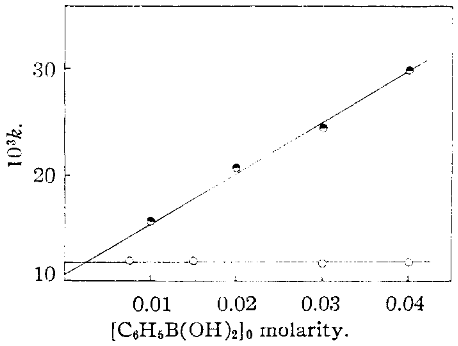

Fig. 6.—Effect of boronic acid concentration on $k_{\text{obsd.}}$ in ●, tartrate (*p*H 3.30), and ○, citrate (*p*H 4.60) buffers.

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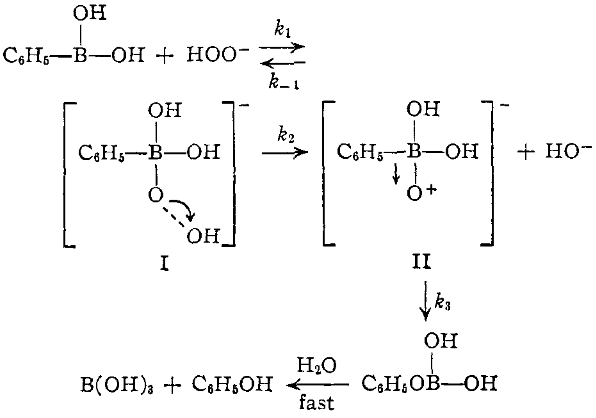
(11) N. Bjerrum, *Chem. Revs.*, **16**, 287 (1935).

with increasing citrate concentration. It appears, therefore, that under the conditions studied 0.05 *M* citrate ties up most of the boronic acid, preventing it from functioning as a catalyst. Tartrate, on the other hand, ties up only a small fraction as a complex which reacts much more readily with peroxide than either the free boronic acid or the citrate complex.

Discussion

The Base Catalysis.—The specific lyate ion catalysis means that the rate is proportional to some species whose concentration depends only on *p*H. From the results represented in Figs. 1 and 2 it is clear that this species must be the hydroperoxide ion. On the basis of this fact the following mechanism for the reaction seems to be reasonable.



The data presented do not permit definite assignment of relative values to the rate constants. However, on the basis of the fact that esters of boronic acids appear to form and hydrolyze rapidly, it may be assumed that k_1 and k_{-1} are large compared with k_2. Steps 2 and 3 may be entirely distinct as one possible extreme or simultaneous as another. The positive salt effect indicates that a charge separation as in step 2 is a part of the rate-determining step.

This mechanism is analogous to those generally written for the reactions of Caro acids and percarboxylic acids with ketones to produce esters.[12] The epoxidation of α,β-unsaturated ketones involves attack by hydroperoxide ion on the β-carbon followed by loss of hydroxide ion and formation of the oxide.[13] This reaction does not occur with simple olefins in which polarization of the double bond by the carbonyl group is absent.

The fact that the slope of the log k_1–*p*H plot approaches zero as the *p*H decreases suggests the possibility that a mechanism involving molecular hydrogen peroxide becomes important in this range. Actually, below *p*H 1 in solutions of perchloric and sulfuric acids the rate increases rapidly with acidity. However, a simple correlation between acidity and rate remains to be found.

The Third-order Reaction.—The intermediate in the third-order reaction must be derived from two molecules of boronic acid and a hydroperoxide ion. An intermediate such as III may be reasonable. Cleavage at b would result in II and benzeneboronate anion. Thus the function of the second molecule of acid is to promote the ionic cleavage of the peroxide bond as a result of the electron-attracting character of the boron atom. This picture receives added support from the fact that boric acid and zinc salts also catalyze the reaction. Both can function in a manner analogous to the second benzeneboronic acid molecule. The fact that magnesium is ineffective may be attributed to its relatively lower electrophilic activity. Similarly, boric acid (pK_a 9.2) is less effective than benzeneboronic acid (pK_a 8.7).

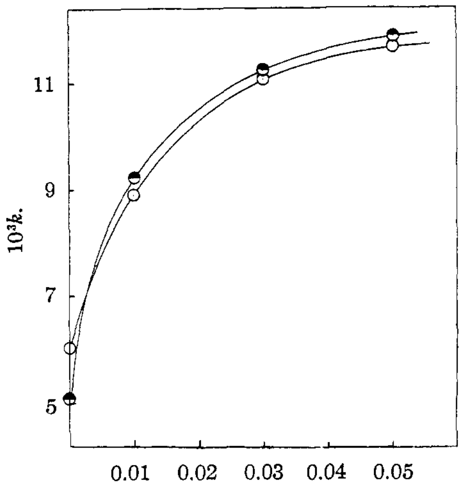
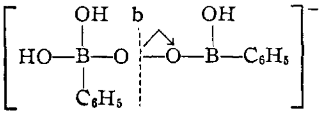
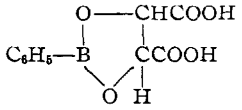


Fig. 7.—Effect of citrate buffer concentration on $k_{\text{obsd.}}$: ●, $[C_6H_5B(OH)_2]_0$, 0.15 *M*, ○, $[C_6H_5B(OH)_2]_0$, 0.030 *M*.

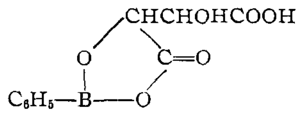


III

The Catalysis by Chelating Agents.—It is well known that certain polyhydroxy compounds increase the acidity of solutions of boric acid[14] and boronic acids.[15] This is attributed, in the case of boric acid, to the formation of quadricovalent chelate complexes involving one or two molecules of chelating agent. In the case of boronic acids only single chelation is possible because of the organic group attached to the boron. Formation of an intermediate, such as IV or V with tartaric acid, leads to a decrease in the O-B-O bond angle



IV



V

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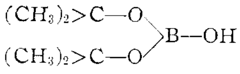
[12] A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1574 (1948); R. Criegee, *Ann.*, **560**, 127 (1948); S. L. Friess, THIS JOURNAL, **71**, 2571 (1949).

[13] C. A. Bunton and G. J. Minton, *J. Chem. Soc.*, 665 (1949).

[14] J. Böeseken, N. Vermaas and A. Th. Kuchlin, *Rec. trav. chim.*, **49**, 711 (1930).

[15] G. E. K. Branch, D. L. Yabroff and B. Bettman, THIS JOURNAL, **56**, 1865 (1934).

from 120° to one approaching the 108° of a regular pentagon. This provides a driving force for the addition of hydroperoxide ion leading to an intermediate analogous to I with tetrahedral boron.[16]



VI

Thus the concentration of this type of intermediate would be increased, resulting in a greater rate of reaction if the rate of the subsequent slow step is comparable to that involving I.

A systematic investigation of the effects of various chelating agents on the rate of the reaction is now in progress.

Acknowledgment.—It is a pleasure to acknowledge substantial support of this work by the Office of Naval Research under contract Nonr 806(01).

DURHAM, NEW HAMPSHIRE

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(16) *Cf.* N. Vermaas, *Rec. trav. chim.*, **51**, 67 (1932). A limitation in this postulate is implicit in the data and discussion of Vermaas in the fact that some mono-1,2-diol borates (*e.g.*, that from pinacol, VI) are not strong acids, *i.e.*, the boron in these esters does not show a great tendency to assume the tetrahedral configuration.

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Theory of Electrolysis at Constant Current in Unstirred Solution. III. Experimental Study of Potential–Time Curves

BY PAUL DELAHAY AND CALVIN C. MATTAX

RECEIVED JUNE 29, 1953

Experimental methods for the precise recording of potential–time curves are described and applied to various electrode processes. The theoretical treatment of reversible electrode processes is verified in the cases of the reduction of ferricyanide, thallous and cadmium ions. The properties of potential–time curves obtained by reversing the current at the transition time are also in good agreement with theory. The features of experimental potential–time curves for the irreversible reduction of oxygen, nickel(II) and cobalt(II) in various electrolytes also agree well with theory. The analysis of potential–time curves for the reduction of chromate ion in 1 molar sodium hydroxide indicates the occurrence of a stepwise process. Potentialities of the constant current method in the study of electrode processes are discussed, and the possible application to analytical determinations is mentioned. Experimental data determined by the present method are used in the verification of the theory of irreversible polarographic waves previously developed.

Theoretical treatments of potential–time curves were developed in two previous publications.[1,2] It is the purpose of the present paper[3] to determine experimentally the validity of some of the conclusions previously reported. A detailed description of a convenient apparatus for the precise recording of potential–time curves also will be given.

Experimental

Electrolytic Cell.—Electrolytic cells were designed to reproduce as well as possible the conditions of semi-infinite linear diffusion at the polarizable electrode. Solid electrodes (platinum) and mercury pool electrodes were used. The cells designed for the latter type of electrode will be first described. A mercury pool electrode was used previously,[1,2] but various modifications in design were introduced, and the two types of cell represented in Fig. 1 finally were adopted.

The cells were composed of three electrodes: the mercury pool, the auxiliary platinum electrode and the reference electrode. The first two electrodes were connected to the constant current power supply, and the voltage between the mercury pool and the reference electrode was recorded. The mercury pool was renewed before each recording. In the case of cell A, one arm of the three-way stopcock was connected to a mercury reservoir of 200 ml. A constant level was thus obtained. The stopcock was closed to avoid contamination of the mercury in the reservoir. A mercury pool of reproducible area was obtained in cell B by introducing a known volume of mercury in the cell. The diameter of the mercury pool in cell A was 1.4 cm., but even larger diameters are advisable in order to minimize the effect of the mercury meniscus. The area of the mercury pool varies with potential, because the interfacial tension mercury–solution—and consequently the curvature of the meniscus—depend on the potential of the mercury pool. The movement of the surface of the pool causes a slight stirring of the solution, and a departure from conditions of mass transfer under the sole influence of diffusion. In cell B the diameter of the mercury pool was approximately 2.5 cm.

A commercial saturated calomel electrode (Beckman industrial model) was used. To avoid errors resulting from the ohmic drop in the solution the reference electrode was immersed in a sleeve whose tip (outside diameter 1 mm.) was very close (0.5 mm. or less) to the surface of the mercury pool. Since the value of the potential of the auxiliary platinum electrode was unimportant, both compartments of the cell were filled with the solution being electrolyzed. Diffusion from one compartment to the other was practically prevented by a disk of fritted glass as in H cells used in polarography. No plug of agar agar as customarily used in polarography was needed.

Cell A is somewhat more convenient to use than cell B because of the ease of renewing the mercury pool and the simplicity of design. This cell thus can be recommended for exploratory work or for analytical determinations. It has, however, the disadvantage of not providing for a uniform distribution of current density (asymmetric position of the auxiliary electrode with respect to the mercury pool). This disadvantage is eliminated in cell B of Fig. 1. The results reported below were obtained with cell A, but it was verified that the operation of cell B is entirely satisfactory.

The platinum electrode used in the reduction of ferricyanide was constructed by sealing a platinum disk (approximately 0.8 cm.^{2}) in a glass sleeve in the form of a U-tube. The platinum disk was horizontal, and the lid of the sleeve extended approximately 0.5 cm. above the disk.[4]

The temperature of the electrolyzed solution was 30 ± 2°.

Recorder and Related Equipment.—The electrolytic cell in series with resistance R_1 (Fig. 2) was connected to a commercial power supply with electronic regulation of the output voltage (200–300 v.).[5] The current intensity was determined from the ohmic drop in a calibrated resistance R_2, the

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(1) P. Delahay and T. Berzins, THIS JOURNAL, **75**, 2486 (1953).

(2) T. Berzins and P. Delahay, *ibid.*, **75**, 4205 (1953).

(3) For a brief survey of literature see ref. 1 and 2.

(4) H. A. Laitinen and I. M. Kolthoff, THIS JOURNAL, **61**, 3344 (1939).

(5) Even better regulation of the current could be obtained by using automatic regulation of the current as in coulometric titrations. See, for example, D. D. De Ford, C. J. Johns and J. N. Pitts, *Anal. Chem.*, **23**, 941 (1951); C. N. Reilley, R. H. Adams and N. H. Furman, *ibid.*, **24**, 1044 (1952).