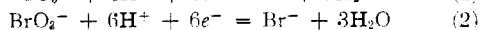
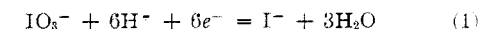


[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reduction of Iodate and Bromate in Acid Medium at the Dropping Mercury Electrode¹

BY E. F. ORLEMANN² AND I. M. KOLTHOFF

The reduction of iodate and bromate ions at the dropping mercury electrode has been investigated by Rylich³ who concluded that the total diffusion current observed corresponds to one of the following net electrode reactions



A more exact investigation in this Laboratory⁴ confirmed Rylich's conclusion that the number of electrons involved in the reduction of iodate is equal to six.

In "neutral" (unbuffered) and in alkaline media Rylich found a single continuous wave on the c. v. (current-voltage) curves of iodate and bromate. The decomposition potentials of iodate and bromate in the above media were found to be independent of the *pH*, but greatly dependent upon the kind and concentration of cations present in the solution. In the presence of a sufficient amount of sulfuric acid, Rylich also found a single continuous wave on the c. v. curve of iodate and bromate. The decomposition potentials in the acid solutions were much more positive than those in neutral or alkaline media. Rylich's study of the "acid" waves was carried out in unbuffered media. Since there is a depletion of hydrogen ions at the electrode during the reduction of iodate and bromate ions (see Eqs. 1 and 2) if the solution is unbuffered, the effect of *pH* on the "acid" wave was not clear in Rylich's work.

In the present study c. v. curves of iodate and bromate have been obtained in buffered and unbuffered acid solutions and a mechanism for these reductions has been developed which accounts for most of the observed phenomena. In a subsequent communication the results of a study of the "neutral" and "alkaline" waves of iodate and bromate will be presented.

(1) From a thesis submitted by Edwin F. Orlemann to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.

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(3) A. Rylich, *Collection Czechoslov. Chem. Commun.*, **7**, 288 (1935).

(4) J. J. Lingane and I. M. Kolthoff, *THIS JOURNAL*, **61**, 825 (1939).

Experimental

Apparatus.—The manual apparatus described in a previous paper⁴ from this Laboratory was used in all the experiments. The saturated calomel electrode (hereafter abbreviated S. C. E.) at 25° was the reference electrode for all the potentials reported in this paper. All experiments were carried out in a thermostat at 25.00 ± 0.05°. Three capillaries with the following characteristics were used: Capillary 1, pressure, 28 cm. of mercury; *m* (mass of mercury flowing per second) at -0.6 v., 3.05 mg. sec.⁻¹; *t* (drop time) at -0.6 v. 3.58 sec.—Capillary 2, pressure 90 cm. of mercury; *m* = 1.93, *t* = 3.60—Capillary 3, pressure 80 cm. of mercury; *m* = 1.80; *t* = 3.52. When diffusion currents (hereafter abbreviated *i*_d) obtained at different potentials are compared (as in Table I) proper correction has been made for the effect of a change in *m*²/*t*^{3/2} on *i*_d.⁵ The c. v. curves shown in the figures have been plotted without making any correction for the residual current but all values of the current given in the tables and used in analyzing the waves have been properly corrected for the residual current.

The *pH* values for the buffers used were determined with a quinhydrone electrode, in the absence of iodate, when the *pH* was less than eight. When the *pH* of the medium was greater than eight, the hydrogen ion exponent was calculated from the composition of the medium. Since the c. v. curves are not affected by the hydrogen ion concentration if the *pH* is greater than eight, an exact knowledge of the *pH* in these cases was not necessary. In solutions of strong acids where the concentration was greater than 0.1 *N*, interaction between the mercury and the iodate or bromate was prevented by using an external anode and collecting the mercury drops in a special container.⁴

Current-Voltage Curves of Iodate in Buffered Solutions.—Figure 1 shows the c. v. curves of iodate in well-buffered solutions at various values of the *pH*. Different capillaries were used and the concentration of iodate was varied from 0.500 to 1.00 × 10⁻³ *M*. The actual experimental conditions are given in Table I. It is seen in Fig. 1 that the waves of iodate shift to more negative potentials with increasing *pH*. When the *pH* becomes equal to 9, a further increase in *pH* has no effect on the location of the wave. The half-wave potentials (*π*_{1/2}) found at various values of the *pH* are given in the last column of Table I. The diffusion currents of iodate at the potentials indicated in Table I were calculated by means of the

(5) C. I. M. Kolthoff and E. F. Orlemann, *ibid.*, **63**, 2085 (1941).

TABLE I
CHARACTERISTICS OF C. V. CURVES OF IODATE AT VARIOUS VALUES OF THE pH IN BUFFERED SOLUTIONS AT 25°

Curve in Fig. 1	Capillary	Concn. of salt added	Buffer	pH	Concn. $\text{KIO}_3 \times 10^3 \text{ M}$	$i_d \times 10^6 \text{ amp.}$	$\pi^c \text{ vs. S. C. E.}$	$K_{\text{obs.}}$	$K_{\text{calcd. (eq. 3)}}$	Dev. in %	Value of $a \text{ (eq. 4)}$	$\pi_{1/2} \text{ vs. S. C. E.}$
1	3	1.2 M HClO ₄	0.2	0.500	11.0	-0.50	22.0	21.5	2	...	+0.040
...	3	1.0 M HNO ₃	.55	.500	11.0	-.50	22.0	21.5	2	...	0.000
...	3	0.12 M HClO ₄	.90	.525	11.5	-.60	22.0	21.5	2	125	-.050
2	2	0.2 M KNO ₃	.1 M H ₂ SO ₄	1.10	.500	11.7	-.60	23.4	22.9	2	115	-.080
3	1	.12 M KCl	.1 M biphthalate	3.20	1.00	31.5	-.60	31.5	31.4	0	120	-.305
...	1	.12 M KCl	.1 M acetate ^b	4.20	1.00	30.7	-.60	30.7	31.4	-2	120	-.425
4	1	.12 M KCl	.1 M acetate ^b	4.90	1.00	30.6	-.90	30.6	31.4	-2	120	-.500
...	2	1.5 M acetate ^b	6.10	0.500	10.0	-1.30	20.0	22.2	-10	...	-.640
5	2	0.1 M citrate	5.95	.500	11.2	-1.30	22.4	22.2	1	220	-.650
...	22 M phosphate	6.40	.500	11.3	-1.30	22.6	22.2	2	235	-.790
6	22 M phosphate	7.10	.500	11.2	-1.30	22.4	22.2	1	...	-1.050
...	2	.2 M KCl ^a	1.00	22.4	-1.50	22.4	21.8	3	90	-1.240
7	1	.2 M KNO ₃	.50 M borax	9.2	1.00	29.7	-1.50	29.7	29.7	0	95	-1.200
8	1	.12 M KCl	.1 M NaOH	12.7	1.00	30.0	-1.50	30.0	29.7	1	85	-1.210

^a Solution unbuffered, pH around electrode increases with increasing current. ^b Acetic acid-sodium acetate buffer. ^c π = potential at which i_d was measured.

Ilkovic⁶ equation

$$i_d/C = K = 605nD^{1/2}m^{2/3}t^{1/6} \quad (3)$$

The value of n (the number of electrons transferred per molecule of iodate) was taken as six. A value of $1.09 \times 10^{-6} \text{ cm.}^2 \text{ sec.}^{-1}$ for D (the diffusion coefficient of iodate ions) was calculated from the equivalent conductance of iodate ions at infinite dilution at 25°. Using the characteristics of the capillaries previously listed, values of $m^{2/3}t^{1/6}$ at the indicated potentials were calculated by means of the data in a previous paper.⁵ A comparison of the calculated and observed values of K (Eq. 3) in Table I shows that the number of electrons involved in the iodate reduction at all values of the pH is equal to six and that the Ilkovic equation is valid for the reduction of iodate at the dropping mercury electrode. The discrepancy of 10% between the calculated and observed values of K in the acetate buffer containing 1.5 M sodium acetate was found to be due to the presence of a trace of an oxidizable impurity in the sodium acetate used.

From an analysis of the waves it is found that at most values of the pH there is a linear relation between $\log(i_d - i)/i$ and the potential, π . As an example, a few of the analyses of the waves are shown in Fig. 2. Proper corrections for the iR drop have been applied. When such a linear relation is found the equation for the wave is of the type

$$\pi = \pi_{1/2} + a \log(i_d - i)/i \quad (4)$$

Values of a , in millivolts, at various values of the

(6) D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934).

(7) Cf. I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

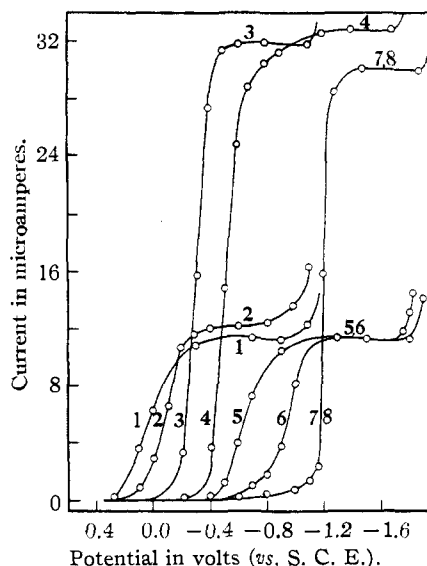


Fig. 1.—Current-voltage curves of iodate solutions of varying concentration in buffered solutions of the following pH: curve 1, pH 0.2; curve 2, pH 1.10; curve 3, pH 3.2; curve 4, pH 4.9; curve 5, pH 5.95; curve 6, pH 7.10; curve 7, pH 9.2; curve 8, pH 12.7. The experimental details are given in Table I.

pH were found from the slopes of the linear $\log(i_d - i)/i$ versus potential plots. These values of a are reported in Table I. From the results in Table I it appears that the diffusion coefficient of iodate is independent of the pH and that the diffusion current is proportional to the concentration of iodate. At a constant pH, the half-wave potential was found to be independent of the concentration of iodate between 10^{-4} and 10^{-3} M .

The relation between the half-wave potentials and the pH is shown in Fig. 3. From this graph

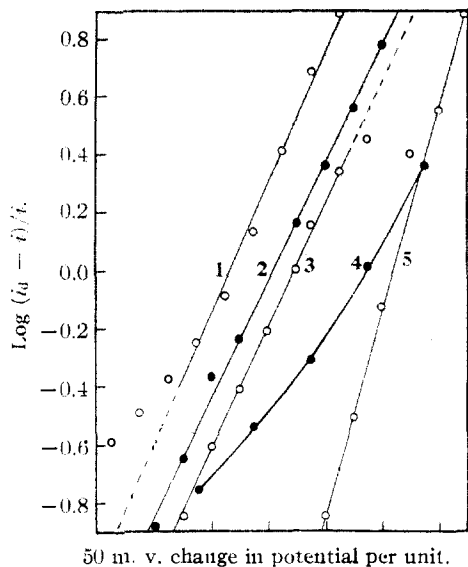


Fig. 2.—Typical analyses of the iodate waves obtained in buffered solutions: curve 1, pH 1.1; curve 2, pH 3.2; curve 3, pH 4.9; curve 4, pH 7.1; curve 5, pH 12.7. The experimental details are given in Table I (the curves are arbitrarily spaced along the potential axis for greater clarity).

it is found that the half-wave potential shifts -115 mv. per unit change in pH over the pH range from 0.2 to 6. An extrapolation of the data in Fig. 3 gives a value of 0.060 v. (vs. the S. C. E.) for the half-wave potential of iodate at a pH of zero. From a pH of 6 to a pH of 8 the half-wave potential shifts approximately -400 mv. per unit change in pH . The slope of the linear relation between $\log (i_d - i)/i$ and the potential also changes with the pH as shown in Table I. These facts are

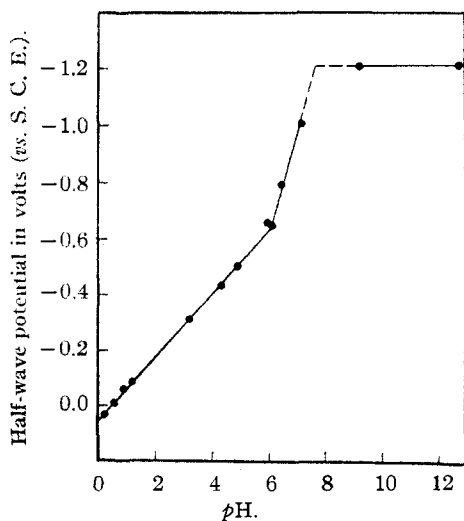


Fig. 3.—The relation between the half-wave potential of iodate and the pH in buffered solutions at 25° .

summarized in the following equations for the c. v. curves of iodate

$$\text{pH } 1 \text{ to } 5.5 \quad \pi = 0.06 - 0.12 \text{ pH} + 0.12 \log (i_d - i)/i \quad (5)$$

pH 6 to 8 Equation varies with pH ; see Table I and Fig. 3

$$\text{pH } 8 \text{ to } 14 \quad \pi = \text{const.} + 0.09 \log (i_d - i)/i \quad (6)$$

Current-Voltage Curves of Bromate in Buffered Solutions.—A few of the c. v. curves of bromate in buffered solutions are shown in Fig. 4. At pH values of 1 and 3 the c. v. curves of bromate yield a single continuous wave but at a pH of 5 only a small fraction of the bromate is reduced before a reduction of hydrogen ions occurs. No distinct bromate wave was obtained in a 0.05 M borax solution (pH 9). The c. v. curves of bromate in buffered solutions can therefore be studied only over a limited pH range.

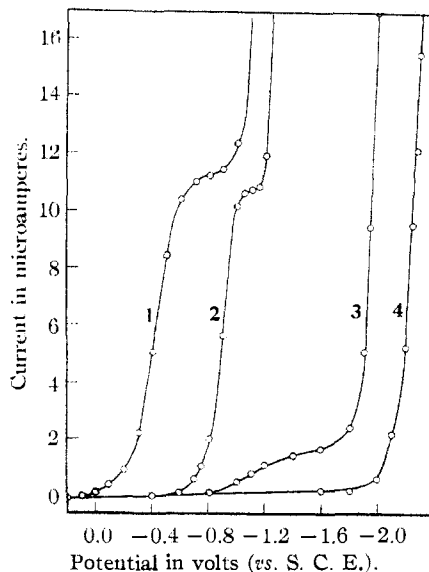


Fig. 4.—Current-voltage curves of 0.0004 M potassium bromate in buffered solutions: curve 1, 0.2 M sulfuric acid, 0.2 M potassium nitrate solution of pH 1.1; curve 2, 0.05 M biphthalate buffer of pH 2.85 in 0.1 M potassium nitrate; curve 3, 0.1 M acetate buffer of pH 5.0; curve 4, 0.05 M borax solution of pH 9.2.

From the equivalent conductance of bromate ions at infinite dilution the diffusion coefficient of this ion was calculated to be 1.44×10^{-5} $\text{cm}^2 \text{sec}^{-1}$ at 25° .⁷ Using this value of the diffusion coefficient of bromate and a value of n equal to six the constant K of the Ilkovic equation (see Eq. 3) was calculated to be 26.4 microamperes millimoles⁻¹ liters at a potential of -0.70 v. and 25.9 at a potential of -1.10 v., using the known values of m and t for capillary 2. From the diffusion currents of 4×10^{-4} M bromate obtained

with capillary 2 the observed values of K were found to be 26.8 at a potential of -0.70 v. in a solution of pH 1.1 and 26.3 at a potential of -1.10 v. in a solution of pH 2.85. Therefore the observed and calculated values of K agree within 1.5% at a pH of 1.1 and 2.85, thus confirming Eq. (2) for the net reduction of bromate. At these values of the pH the equation of the waves is given by Eq. (4) with a value of a equal to 155 mv. In agreement with this result it was found that the half-wave potential was independent of the concentration of bromate between 10^{-4} M and 10^{-3} M at a pH of 2.85. At a pH of 1.1 the half-wave potential was -0.412 v. and at 2.85, -0.888 v. The half-wave potential therefore appears to shift -270 mv. per unit change in pH in the pH range from 1 to 3. By extrapolation a value of -0.113 v. (*vs.* the S. C. E.) is found for the half-wave potential of bromate at a pH of zero. While this value, obtained from the very limited amount of data available, is questionable, it is interesting to compare it with the half-wave potential of iodate at a pH of zero, which was $+0.060$ v. (*vs.* S. C. E.). This comparison shows that bromate is reduced at a potential which is 0.173 volt more negative than that required for the reduction of iodate even though the standard electrode potential of bromate is 0.35 volt more positive than that of iodate for a reduction to bromide and iodide ions, respectively.

Current-Voltage Curves of Iodate and Bromate in Unbuffered Acid Solutions.—According to Eqs. (1) and (2), six hydrogen ions are removed from the electrode surface per molecule of iodate or bromate reduced. Therefore in dilute solutions of strong acids containing an indifferent electrolyte, one or two waves may be obtained depending on the ratio of hydrogen ions in the solution to the iodate or bromate present. If the hydrogen ions are in excess only one (an "acid") wave is obtained, as shown by some of the curves in Figs. 1 and 4. On the other hand, if the iodate or bromate ions are in excess, only part of the iodate or bromate will be reduced before the hydrogen ions are removed from the electrode as fast as they can diffuse to the surface and a second wave, due to the reduction of the remaining iodate or bromate in "neutral" medium will be found. In this case the magnitude of the diffusion current of the first wave (hereafter called the "hydrogen" wave) should correspond to the ordinary diffusion current of hydrogen ions whereas the total dif-

fusion current observed (sum of the two diffusion currents of both waves) is the diffusion current of iodate or bromate ions. Rylich⁸ found two waves of the type described above in his study of the reduction of iodate and bromate in unbuffered acid solutions. However, no attempt was made to compare the diffusion current of the "hydrogen" wave with the ordinary diffusion current of hydrogen ions.

It is of interest to consider under which conditions one or two waves are obtained. When two waves appear the diffusion current of the first wave is given by the relation

$$i_d(\text{"hydrogen" wave}) = K_{H^+} [H^+] \quad (7)$$

K_{H^+} in Eq. (7) is defined by Eq. (3) and is proportional to the square root of the diffusion coefficient of hydrogen ions. The diffusion current of the iodate ions is equal to $K_{IO_3^-} [IO_3^-]$. Obviously only the "hydrogen" wave is obtained when

$$K_{H^+} [H^+] \geq K_{IO_3^-} [IO_3^-] \quad (8)$$

The condition required by Eq. (8) is fulfilled when

$$[H^+] / [IO_3^-] \geq 6(D_{IO_3^-} / D_{H^+})^{1/2} \quad (9)$$

Using the equivalent conductances of hydrogen and iodate ions at infinite dilution the calculated value of D_{H^+} is 9.34×10^{-5} cm.² sec.⁻¹ and that of $D_{IO_3^-}$ is 1.09×10^{-5} cm.² sec.⁻¹ at 25°. Therefore, only one wave is obtained when the hydrogen ion concentration in the bulk of the solution is equal to or greater than 2.0 times the concentration of iodate. When the ratio of hydrogen ions to iodate is less than 2.0, two waves are obtained. Rylich's⁸ results are in agreement with the above conclusions.

The validity of Eq. (7) has been checked by comparing the diffusion currents found in dilute hydrochloric acid solutions containing an excess of iodate or bromate, with the ordinary diffusion currents found in the direct reduction of hydrochloric acid solutions. The results are shown in Fig. 5 and Table II. Curves 1, 2, and 3 in Fig. 5A are the c. v. curves corresponding to the reduction of hydrogen ions in hydrochloric acid solutions of varying concentration in the presence of 0.1 M potassium chloride. Curves 4, 5, and 6 were obtained in solutions of 0.05 M potassium chloride, 0.01 M potassium iodate and various concentrations of hydrochloric acid. Figure 5B shows similar curves obtained in a medium which was 0.1 M in potassium chloride and 0.05 M in potassium bromate. The exact conditions and the experimental values of K_{H^+} (referred to the

TABLE II

VALUES OF K_{H^+} OBTAINED FROM DIFFUSION CURRENTS OF HYDROGEN DISCHARGE AND OF ACID IODATE OR BROMATE WAVES

Curve, Fig. 5	Composition of medium	Type of wave ^a	HCl concn. $\times 10^4 M$	$i_d \times 10^4$ amp.	At π	K_{H^+} at $\pi - 0.6$	Dev. of K_{H^+} from av. in %
1A	0.1 M KCl	a	0.356	3.50	-1.8	10.7	1
2A	.1 M KCl	a	.960	9.50	-1.8	10.8	2
3A	.1 M KCl	a	2.07	20.60	-1.8	10.8	2
4A	.05 M KCl + 0.01 M KIO ₃	b	.575	6.03	-.8	10.5	-1
5A	.05 M KCl + .01 M KIO ₃	b	1.10	11.8	-.8	10.7	1
6A	.05 M KCl + .01 M KIO ₃	b	1.69	17.9	-.8	10.6	0
1B	.1 M KCl + .05 M KBrO ₃	c	0.520	5.40	-1.0	10.4	-1
2B	.1 M KCl + .05 M KBrO ₃	c	.900	9.30	-1.0	10.4	-2
3B	.1 M KCl + .05 M KBrO ₃	c	2.07	21.8	-1.0	10.6	0

Average value of K_{H^+} = 10.6^a a, hydrogen discharge; b, "hydrogen" wave (iodate); c, "hydrogen" wave (bromate).

same $m^{2/3} t^{1/6}$ values) are reported in Table II. All the experiments were carried out with capillary 2. It is evident from Table II that the diffusion currents of the "hydrogen" waves (when the iodate or bromate are in excess) are identical

fusion current of the acid iodate wave is found at a potential of the order of -0.8 v. and is well defined. At sufficiently high acid concentrations the ordinary diffusion current of hydrogen ions may be affected by the evolution of hydrogen at the

electrode. On the acid iodate or bromate waves there is no evolution of hydrogen and therefore no possibility of an interference of this sort.

The value of K_{H^+} calculated from the Ilkovic equation for capillary 2 is 11.2. The average experimental value found was 10.6. This result indicates that the diffusion coefficient of hydrogen ions calculated from the equivalent conductance of hydrogen ions at infinite dilution gives a value which is about 12% too large at an ionic strength of the order of 0.1.

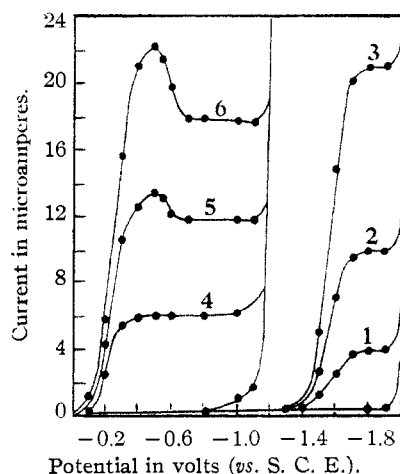


Fig. 5A.—Current-voltage curves of hydrochloric acid solutions of varying concentration in the presence of 0.1 M potassium chloride (curves 1, 2, 3) and in the presence of 0.05 M potassium chloride and 0.01 M potassium iodate (curves 4, 5, 6) curves 1, 2 and 3 correspond to 3.56×10^{-4} , 9.60×10^{-4} and 20.7×10^{-4} M hydrochloric acid, respectively. Curves 4, 5 and 6 correspond to 5.75×10^{-4} , 11.0×10^{-4} and 16.9×10^{-4} M hydrochloric acid, respectively.

with the ordinary diffusion currents of hydrogen ions. For several reasons this result is of practical interest. The ordinary diffusion current of hydrogen ions is not found until a potential of the order of -1.8 v. is reached where the residual current correction is quite large; whereas the dif-

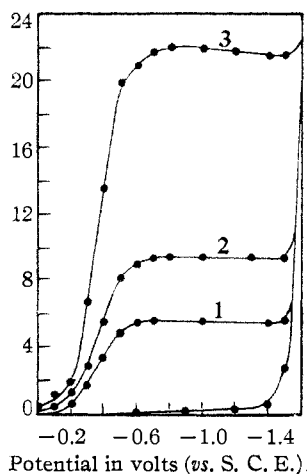


Fig. 5B.—Current-voltage curves of 0.1 M potassium chloride and 0.05 M potassium bromate solutions containing various amounts of hydrochloric acid: curves 1, 2 and 3 correspond to 5.20×10^{-4} , 9.00×10^{-4} and 20.7×10^{-4} M hydrochloric acid, respectively.

limited to allow a fundamental approach to the interpretation of a particular irreversible system. In a given case electrolysis studies only provide a limited amount of information about the initial and final products and the factors involved in the rate determining step in the reduction or oxida-

Discussion

It is evident from the observed equations for the c. v. curves of iodate and bromate that these reductions occur irreversibly at the dropping mercury electrode and require a considerable over-voltage before electrolysis begins. Our present knowledge of the general mechanism of electrode reactions is too

tion. As a survey of the many theories advanced for the irreversible reduction of hydrogen ions⁸ will show, there are generally many steps which might be assumed to be rate determining. More than one of these steps may lead to the same formal relation between current and potential and it is not always possible to differentiate between these steps on the basis of electrolysis studies alone. An interesting possibility for the interpretation of the reduction of iodate and bromate ions is suggested by Gurney's⁹ theory that the slow step in the reduction of hydrogen ions is the transfer of an electron from the electrode to a hydrogen ion in solution. It will be shown that this idea can be extended to the reduction of iodate and bromate ions, with modifications, and leads to an interpretation of the c. v. curves which is in agreement with most of the experimental facts. In the thesis of the junior author various other interpretations, such as a reduction of hydrogen ions to hydrogen atoms which then combine with the iodate or bromate, are considered and shown to be inconsistent with the facts. However, for the reasons given above, the interpretation proposed cannot be considered unique.

For convenience only the reduction of iodate will be treated in any detail and the equations developed will be extended to the reduction of bromate. It was shown in the experimental part of this paper that an "acid" and a "neutral" mechanism exist for the reduction of iodate and bromate ions. In a subsequent communication the "neutral" mechanism will be considered in detail; the present discussion is limited to the "acid" mechanism. In Fig. 6 the energy relations at the electrode are shown schematically. ϕ is the work function of the metal used as an electrode and ϕ' is the corresponding quantity when the electron is removed from the metal to the solution instead of to a vacuum. If the electrode has a potential π with respect to the solution, an additional amount of work equal to $F\pi$ per mole will be necessary to remove electrons from the electrode into the solution. The highest occupied level of an electron in the metal at absolute zero is therefore at a depth of $\phi' - F\pi$ (ϕ' is taken per mole of electrons instead of per electron for convenience). The vacant electron level in the iodate will be at a certain depth E ; that is, an amount of work E will be required to remove a

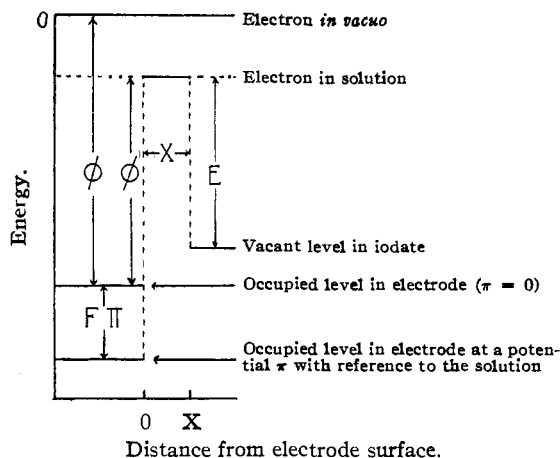


Fig. 6.—Schematic diagram of the energy relations involved in the electroreduction of iodate.

mole of electrons from a mole of IO_3^- ions and leave a mole of iodate ions and electrons at rest in the solution. When the potential of the electrode is such that there are occupied levels in the electrode equal to or greater than E (in a positive sense) there will be a certain finite probability of these electrons entering the iodate ions which are within a few Ångströms of the electrode surface. At temperatures above absolute zero some of the electrons in the metal will be in levels higher than $\phi' - F\pi$ and the number of electrons in levels equal to or greater than E is approximately given by the equation

$$n(E) = AE^{1/2} \exp. \frac{(\phi' - F\pi - E)}{RT} \quad (10)$$

The probability of an electron transfer across the energy barrier E will be given by the expression

$$P(E) = \exp. (-1.03 \sqrt{E(\text{in c. v.})} x) \quad (11)$$

In Eq. (11) x is the distance between the electrode and the iodate ion in Ångström units. The number of vacant levels of depth E at the distance x from the electrode will be taken as proportional to the concentration of iodate ions at this distance from the electrode. The potential difference π between the electrode and the solution will also be a function of the distance x from the electrode. Therefore, if the transfer of an electron from the electrode to an iodate ion is the slow step in the reduction of iodate the current at a time t will be given by the relation

$$i_t = k \int_{x=0}^{x=\infty} \exp(-1.03E^{1/2}x) \exp\left(\frac{-F\pi_x}{RT}\right) [\text{IO}_3^-]_x dx \quad (12)$$

Unfortunately the explicit relation between π_x and x is not known and depends upon the composition

(8) Cf. J. A. V. Butler, "Electrocapillarity," Chemical Publishing Co., Inc., New York, N. Y., 1940.

(9) R. W. Gurney, *Proc. Roy. Soc. (London)*, **A134**, 137 (1930).

of the solution, the temperature, and the charge on the electrode. We may define an average distance \bar{x} where the potential difference between the electrode and the solution is $\pi_{\bar{x}}$ by the equation

$$i_t = k' \exp(-1.03E^{1/2}\bar{x}) \exp(-F\pi_{\bar{x}}/RT) [\text{IO}_3^-]_0 \quad (13)$$

where $(\text{IO}_3)_0$ is the average concentration of iodate in the region where reduction occurs.

The quantity $\pi_{\bar{x}}$ may be replaced by $\alpha\pi$, where π is the total potential difference between the electrode and the bulk of the solution and the value of α must lie between zero and one. With this substitution we obtain the relation

$$i_t = k' \exp(-1.03E^{1/2}\bar{x}) \exp(-\alpha F\pi/RT) [\text{IO}_3^-]_0 \quad (14)$$

In Eq. (14) \bar{x} may be interpreted as the average distance from the electrode at which reduction occurs and $\alpha\pi$ as the fraction of the total potential difference between the electrode and the solution at the distance \bar{x} . It is not possible to predict values of \bar{x} and α but qualitative predictions may be made. Suppose, for simplicity, that the potential varies linearly with the distance from the electrode. If the electrode is more positive than the solution the quantities $\exp(-1.03E^{1/2}\bar{x})$ and $\exp(-F\pi_{\bar{x}}/RT)$ in Eq. (12) decrease rapidly with an increase in x and consequently the maximum rate of reduction is found as close to the electrode as the size of the iodate will permit. In this case we might expect α to be less than one. If the electrode is more negative than the solution the quantity $\exp(-F\pi_{\bar{x}}/RT)$, which is $\exp(-40\pi_{\bar{x}})$ at 25°, increases more rapidly as x increases than $\exp(-1.03E^{1/2}\bar{x})$ decreases. Consequently the maximum rate of reduction in this case occurs at the point where the value of α is one and α would be expected to have a value close to one.

In Eq. (14) i_t is an instantaneous value of the current, the average current found during the life of a mercury drop will be given by the expression

$$i = knF\bar{A} \exp(-1.03E^{1/2}\bar{x}) \exp(-F\pi\alpha/RT) [\overline{\text{IO}_3^-}]_0 \quad (15)$$

In Eq. (15) $[\overline{\text{IO}_3^-}]_0$ is the average concentration of iodate at the surface of the drop and \bar{A} is the average area of the drop. If m is the mass of mercury flowing per second and t is the drop time, $\bar{A} = \text{const. } m^{2/3}t^{1/3}$. By application of the Ilkovic equation we obtain the relation

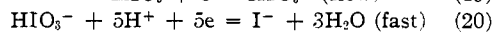
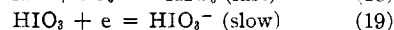
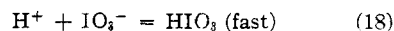
$$[\text{IO}_3^-]_0 = (i_d - i)/605nFD^{1/2}m^{2/3}t^{1/6} \quad (16)$$

where D is the diffusion coefficient of iodate ions.

Using these relations the equation for the c. v. curve may be written in the form

$$\pi = \text{const.} + \frac{RT}{2\alpha F} \ln \frac{i}{D} - \frac{1.03E^{1/2} RT}{\alpha F} \bar{x} + \frac{RT}{\alpha F} \ln \frac{(i_d - i)}{i} \quad (17)$$

Mechanism for Iodate Reduction at pH 1 to 5.5.—Iodic acid has an ionization constant of the order of 0.2 at 25° and in acid solutions there are an appreciable number of undissociated iodic acid molecules present. From Fig. 6 and Eq. (10) it can be seen that if the vacant level for an electron in an iodic acid molecule is lower than the vacant level in an iodate ion the iodic acid will be reduced at more positive potentials than the iodate ion. It is reasonable to suppose that the vacant level in the iodic acid is lower than that in an iodate ion and the mechanism proposed for the reduction of iodate in acid solution may be represented by the scheme



(this process must involve several steps)

Using this mechanism and substituting $[\text{HIO}_3]_0$ for $[\text{IO}_3^-]_0$ in the preceding derivation we find the following equation for the c. v. curves of iodate in acid solution (neglecting activity coefficients)

$$\pi = \text{const.} + \frac{RT}{2\alpha F} \ln \frac{i}{D} - \frac{1.03E^{1/2} RT}{\alpha F} \bar{x} + \frac{RT}{\alpha F} \ln [\text{H}^+]_0 + \frac{RT}{\alpha F} \ln \frac{i_d - i}{i} \quad (21)$$

From the previous discussion it is evident that if α is constant \bar{x} is constant and Eq. (21) may be written in the following form if α is constant

$$\pi = \text{const.} + \frac{RT}{2\alpha F} \ln \frac{i}{D} + \frac{RT}{\alpha F} \ln [\text{H}^+]_0 + \frac{RT}{\alpha F} \ln \frac{i_d - i}{i} \quad (22)$$

In well-buffered solutions $[\text{H}^+]_0$ may be taken equal to the concentration of hydrogen ions in the bulk of the solution. Equations (5) and (6) were obtained under conditions where t and D were essentially constant and the temperature was 25°. For this particular set of conditions Eq. (22) becomes

$$\pi = \text{const.} - \frac{0.06}{\alpha} \text{pH} + \frac{0.06}{\alpha} \log \frac{i_d - i}{i} \quad (23)$$

It is obvious that Eqs. (5) and (23) are in agreement when α has a value of one-half. Equation (5) was found to be valid from a pH of 1 to a pH of 5.5, and the half-wave potentials of iodate in this pH range varied from -0.05 to -0.55 v.

(*vs.* the S. C. E.). The mercury surface can be considered to be positive with respect to the solution when its potential is more positive than -0.6 v. (*vs.* the S. C. E.). It was shown previously that the value of α would be expected to be less than one at positively charged surfaces. In this connection it should be mentioned that the term $RT/\alpha F$ is found in electrolysis studies of the irreversible reductions of hydrogen and oxygen at many electrodes where α has a value of one-half. This fact suggests that a value of one-half for α may be of some fundamental significance in irreversible electrode phenomena and throws some doubt on the physical interpretation attached to α in the mechanism we have proposed for the reduction of iodate. At the same time the various theories proposed for the reduction of hydrogen ions also lead to rather accidental values of one-half for α .

Equation (22) predicts that the half-wave potential of iodate should be independent of the concentration of iodate and the mass of mercury flowing per second, but should shift with a change in drop time. The data in Table I show that, other factors being constant, the half-wave potential is independent of the concentration of iodate. To check the effect of the characteristics of the capillary on the half-wave potential, the half-wave potentials of $0.0005 M$ potassium iodate in a $0.1 M$ acetate buffer of pH 5 were determined at three different pressures of mercury on the capillary used. The results obtained are given in Table III. The column " $\pi_{1/2}$ calcd." in Table III has been obtained using Eq. (22) to calculate the shift in half-wave potential due to a change in drop time.

TABLE III

EFFECT OF m AND t ON $\pi_{1/2}$ OF IODATE AT pH 5 AT 25°

m , mg./sec.	t , sec.	$\pi_{1/2}$, v.	$\pi_{1/2}$ calcd., v.
1.16	4.40	-0.525	-0.528
1.70	3.10	- .537	...
2.32	2.20	- .550	- .546

It is evident from Table III that the predictions of Eq. (22) as to the effect of m and t on the half-wave potential of iodate are borne out.

No exact interpretation of the c. v. curves of iodate found in the pH range from 6 to 8 can be made using Eq. (22). It should be noted that the half-wave potential of iodate becomes more negative than -0.6 v. when the pH becomes 6 or greater. This means that in this pH region the

mercury surface is negatively charged during the iodate reduction, whereas it was positively charged when the pH was 5.5 or less. This fact may be partially responsible for the abrupt shift in the half-wave potential found when the pH becomes greater than 6 (see Fig. 2). There is also the possibility that at pH values greater than 6 the rate of formation of iodic acid may become too small to maintain an equilibrium concentration of iodic acid at the electrode. This would result in a larger value for the slope of the relation between $\log (i_d - i)/i$ and the potential than that predicted by Eq. (22). Finally there is the possibility that both the acid and neutral mechanisms involved in the reduction of iodate can occur at pH values of the order of 7 or greater since there is an overlapping of the iodate curves at pH 7 and pH 9 in Fig. 1.

Mechanism of the Bromate Reduction in Acid Media.—By analogy to the iodate mechanism previously discussed we may assume that the rate determining step in the reduction of bromate is the introduction of one electron into a bromic acid molecule. This mechanism leads to the following equation for the c. v. curves of bromate in acid media

$$\pi = \text{const.} + \frac{RT}{\alpha F} \ln [H^+] + \frac{RT}{\alpha F} \ln \frac{i_d - i}{i} \quad (24)$$

The experimentally observed relation between $\log (i_d - i)/i$ and the potential leads to a value of 0.38 for α in the above equation. However, the experimentally determined shift in half-wave potential with a change in pH is much greater than that predicted by Eq. (24) when α is given a value of 0.38. This large shift in half-wave potential may be partially due to the fact that the bromate reduction occurs at a positively charged surface at pH 1.1 and at a negatively charged surface at pH 2.85. Since the acid reduction of bromate can be studied only over a limited pH range (pH 1 to 3) no adequate check of Eq. (24) can be made. A partial confirmation of the mechanism proposed is found in the c. v. curves shown in Fig. 5B. Using the method of derivation shown in connection with a consideration of the iodate waves it can be shown that the equation for the c. v. curves of bromate in unbuffered acid solutions containing an excess of bromate is

$$\pi(\text{xs bromate}) = \text{const.} + \frac{RT}{2\alpha F} \ln \frac{36t}{D_{H^+}} + \frac{RT}{\alpha F} \ln [BrO_3^-] + \frac{RT}{\alpha F} \ln \frac{i_d - i}{i} \quad (25)$$

The equation for the c. v. curves of bromate in buffered solutions is

$$\pi(\text{Buffered}) = \text{const.} + \frac{RT}{2\alpha F} \ln \frac{i}{D_{\text{BrO}_3^-}} + \frac{RT}{\alpha F} \ln [\text{H}^+] + \frac{RT}{\alpha F} \ln \frac{i_d - i}{i} \quad (26)$$

The relation between $\log (i_d - i)/i$ and the potential in unbuffered solutions containing an excess of bromate is shown in Fig. 7. It is obvious

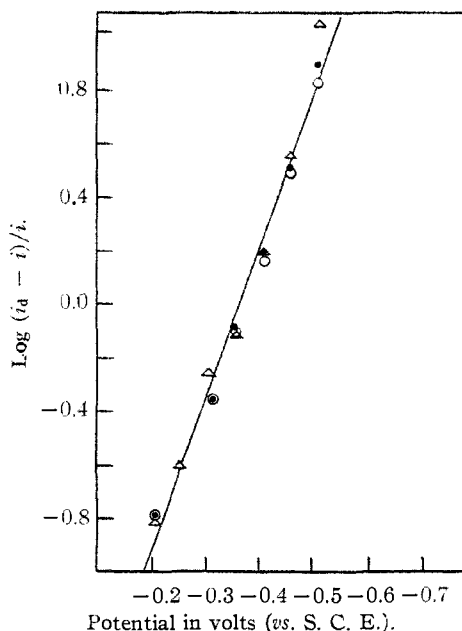


Fig. 7.—Analysis of the current-voltage curves obtained in 0.1 *M* potassium chloride, 0.05 *M* potassium bromate solutions containing the following concentrations of hydrochloric acid: solid circles, 6×10^{-4} *M*; open circles, 1×10^{-3} *M*; triangles, 2.2×10^{-3} *M* (see Fig. 5B).

from Fig. 7 that there is a linear relation between $\log (i_d - i)/i$ and the potential and that the half-wave potential is independent of the concentration of hydrogen ions. The slope of this linear relation was found to be 150 mv. which is the same

as the result previously found in buffered solutions. These facts are in agreement with the predictions of Eqs. (25) and (26). The value of the half-wave potential in a buffered solution of pH 1.15 was -0.415 v. and the half-wave potential in an unbuffered solution with $p_{\text{BrO}_3^-}$ of 1.3 was -0.360 v. According to Eqs. (25) and (26), since $2.30RT/\alpha F$ was found to be 150 mv., we should find that $\pi_{1/2}(p_{\text{BrO}_3^-} 1.3) - \pi_{1/2}(\text{pH } 1.15) = 0.075 \log (36.144/9.34) - 0.15(1.3 - 1.15) = 0.035$ v. The observed value for $\pi_{1/2}(p_{\text{BrO}_3^-} 1.3) - \pi_{1/2}(\text{pH } 1.15)$ was 0.050 v. This approximate agreement may be considered as a partial confirmation of the mechanism proposed for the reduction of bromate ions in acid solution.

Summary

1. In buffer solutions with a pH between 1 and 5.5 the equation of the wave obtained in the reduction of iodate is given by the expression: $\pi = 0.06 - 0.12 \text{ pH} + 0.12 \log (i_d - i)/i$. A similar expression between pH of 1 and 3 was found for the bromate wave: $\pi = -0.113 - 0.27 \text{ pH} + 0.158 \log (i_d - i)/i$.

2. In dilute solutions of strong acids two waves are obtained with iodate and bromate when the hydrogen ion concentration is smaller than 2.0 times the concentration of iodate or 2.3 times the concentration of bromate. The diffusion current of the first wave is equal to that of the hydrogen wave at the same hydrogen ion concentration.

3. The half-wave potentials of iodate and bromate vary with a change in drop time, but are independent of the iodate and bromate concentrations.

4. A mechanism is presented to account for the irreversible reduction of iodate and bromate in buffered solutions.

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