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

Voltammetry of Iodine and Iodide at Rotated Platinum Wire Electrodes

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The reduction of iodine and the oxidation of iodide were studied voltammetrically at a rotated platinum electrode in various media of *p*H 0 to 8. In acid solution the reaction $I_2 + 2e \rightleftarrows 2I^-$ proceeds reversibly. The corresponding cathodic and anodic diffusion currents are proportional to the concentration of iodide and iodine, respectively, in a concentration range between 5×10^{-6} and 10^{-3} *N*. Iodine yields an anodic wave and iodide yields—in most supporting electrolytes—a second anodic wave, both corresponding to the oxidation of iodine (or iodide) to I^+. In the presence of pyridine or hydrocyanic acid iodide yields only one wave which is well-defined and corresponds to a two-electron oxidation. The I^+ waves have a half-wave potential of +1.1 volt *vs.* S.C.E. in perchloric acid, 0.75 v. in dilute hydrochloric acid, 0.5 v. in 0.05 *M* hydrocyanic acid plus 0.1 *M* perchloric acid and 0.56 v. in 0.1 *M* pyridine in a buffer of *p*H 6.

Current–voltage curves of mixtures of iodine, iodide and iodate have been studied by Brunner[1] at platinum foil electrodes. For many years the diffusion current of iodine (and triiodide ion) at the rotated platinum electrode has been made use of in this Laboratory in micro-iodometric titrations.[2,3] while Harris and Lindsey[4] recommend the vibrating electrode for this purpose. No studies are reported in the literature on the anodic behavior of iodine and iodide at the rotated platinum electrode. In the present paper it is shown that under specified conditions iodide gives two anodic waves, the first corresponding to formation of elementary iodine and the second to unipositive iodine. In the presence of pyridine or hydrocyanic acid iodide yields only one wave corresponding to a two-electron transfer. Iodine in the absence of iodide yields a cathodic and an anodic wave of equal height. The cathodic behavior of iodine monochloride and iodine cyanide is briefly reported.

Experimental

Materials.—C.P. chemicals and conductivity water were used throughout.

Apparatus.—The electrical setup has been described in a previous paper.[5] Most of the results reported in this paper were obtained with a platinum wire electrode, A, approximately $^1/_2$ mm. in diameter and 4 mm. in length. When rotated at 600 r.p.m. this electrode yielded a diffusion current of 251 μa./millimole/liter for the thallous–thallic oxidation in 0.1 *M* sodium hydroxide. Some experiments were carried out with two other electrodes of somewhat different size: electrode B, approximately 1 mm. in diameter and 10 mm. in length and electrode C, about $^1/_4$ mm. in diameter and 5.5 mm. in length. The ratio of diffusion currents, $i_A : i_B : i_C$, obtained at these electrodes at equal rates of rotation was found to be equal to 1:2.5:0.64 for the thallous-thallic oxidation, the reduction of silver ion (in ammonia) and the reduction of oxygen. Results obtained in our present work with electrodes B and C have been referred to electrode A making use of the above ratio.

The platinum wire electrodes were sealed into glass and electrical contact was made with the aid of mercury. The platinum-glass joints were carefully annealed, because irregularities at the metal–glass interface give rise to abnormally large residual currents. The electrodes were pretreated as previously described[5] and yielded very small residual currents in the working range of potentials (see figures). Residual currents were subtracted from total limiting currents to compute diffusion currents.

In practically all of the work the electrodes were rotated at 600 r.p.m. by means of a synchronous motor and precision-machined gears. In some experiments the rate was changed to 300 and 900 r.p.m.

Procedure.—Aqueous solutions of iodine were prepared by shaking iodine with water and centrifuging. The concentration of iodine was determined in the supernatant liquid by amperometric titration[2] and the solution diluted to a concentration of 0.00100 *M* in iodine. The iodine solutions used were prepared from this stock solution which was stored in the dark in a well-stoppered bottle. Since a solution of iodine in water (no iodide) is extremely volatile, no effort was made to remove oxygen in the determination of cathodic current–voltage curves. Qualitatively it was ascertained that oxygen does not affect the current–voltage curve of iodine until the potential where oxygen is being reduced. Because of the volatility of iodine, the Sargent XXI automatic polarograph, which takes about 15 minutes to record a complete current–voltage curve, was only used for qualitative purposes with iodine as the electro-active compound. For quantitative purposes diffusion currents of iodine were measured with the manual apparatus[5] at predetermined potentials, within 30 seconds after the addition of the stock solution of iodine to the supporting electrolyte.

With iodide automatic and manual determinations of diffusion currents checked within 1%. If desired, solutions of iodide were deaerated using a gas train described previously[5] and a Corning fritted-glass cylinder bubbler.

All experiments were carried out at 25 ± 0.02°.

Results

The Anodic and Cathodic Behavior of Iodine.—Current–voltage (c.v.) curves of iodine in supporting electrolytes of *p*H 1 to 13 were recorded with the automatic polarograph from negative to positive potentials and *vice versa*. Some of the results are plotted in Figs. 1 and 2. It is seen from these figures that 10^{-4} *M* iodine yields a well defined diffusion current at potentials between 0 to +0.3 v. (*vs.* S.C.E.) in solutions of *p*H 1–8. The reduction corresponds to

$$I_2(aq) + 2e \rightleftarrows 2I^- \qquad (1)$$

The characteristics of the cathodic wave portions of the current–voltage curves were independent of the direction of potential change. The slopes of the waves varied with the *p*H.

When precautions were taken against the volatilization of iodine the diffusion current was found proportional to iodine concentration in the range between 5×10^{-6} and 5×10^{-4} *M*, i_d/c being equal to (190 ± 3) μa./millimole/liter using electrode A at zero applied potential.

In 0.1 *M* sodium perchlorate the i_d/c value was the same as in perchloric acid. This value was not measurably affected by the presence of 0.1 *M* potassium iodide. From conductance data[6] a value for the diffusion coefficient at infinite dilution of

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[1] E. Brunner, *Z. physik. Chem.*, **56**, 321 (1906).

[2] I. M. Kolthoff and J. J. Lingane, "Polarography," Second Edition, Vol. II, Interscience Publishers, Inc., New York, N. Y., 1952, p. 946.

[3] I. M. Kolthoff and W. E. Harris, *Anal. Chem.*, **21**, 963 (1949).

[4] E. D. Harris and A. J. Lindsey, *Analyst*, **76**, 647 (1951).

[5] I. M. Kolthoff and J. Jordan, THIS JOURNAL, **74**, 382 (1952).

[6] Gmelin's "Handbüch der anorganischen Chemie," 8th Edition, Verlag Chemie, Berlin, 1931, System No. 8, p. 170.

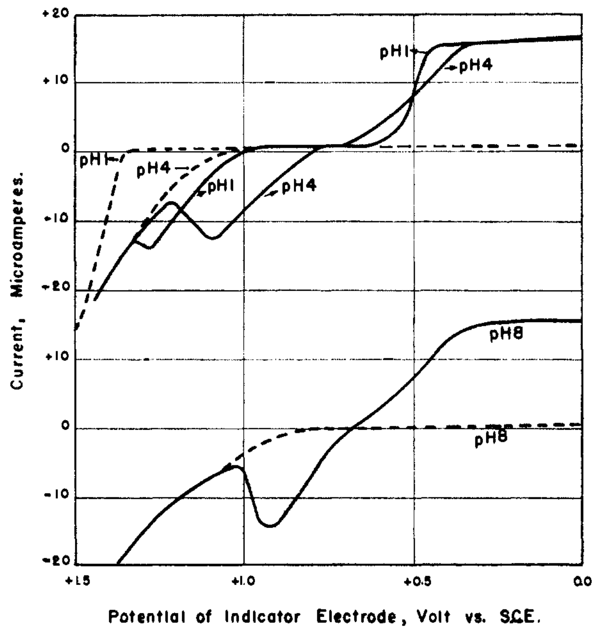

Fig. 1.—Current-voltage curves of 10^{-4} *M* iodine, run from negative to positive potentials. Supporting electrolytes: *p*H 1–0.1 *M*, perchloric acid; *p*H 4, acetate buffer; *p*H 8, phosphate buffer. Dotted lines indicate residual currents. Curves are shifted arbitrarily along vertical axis.

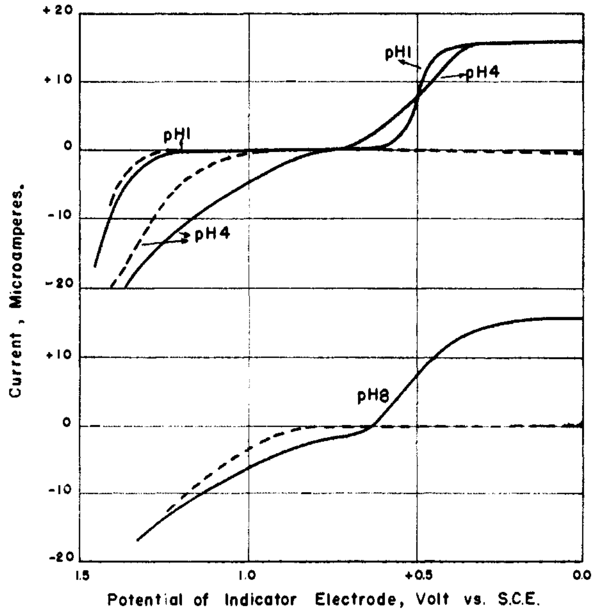

Fig. 2.—Current-voltage curves of 10^{-4} *M* iodine, run from positive to negative potentials. Supporting electrolytes are the same as in Fig. 1.

the triiodide ion of 1.11 × 10^{-5} cm.^{2}/sec. at 25° is calculated. No data are available in the literature on the diffusion coefficient of iodine in the absence of potassium iodide. From the equality of the cathodic diffusion currents of iodine and triiodide we conclude that $D_{I_2} = D_{I_3^-}$.

The characteristics of the *anodic* current-voltage curves of iodine depend on whether they are run from the negative or from the positive potential side (compare Figs. 1 and 2). Running from negative to positive potentials (Fig. 1) poorly developed and defined anodic waves are observed with a maximum followed by a minimum and no diffusion current region. In 0.1 *M* perchloric acid the c.v. curve has only a slight maximum where the current is equal to the cathodic diffusion current. This is also observed in a phosphate buffer of *p*H 8. The electrode reaction corresponding to the anodic wave can be formulated by

$$I_2 + 2xH_2O \longrightarrow 2[I(H_2O)_x]^+ + 2e^- \qquad (2)$$

For the sake of convenience we designate the $[I(H_2O)_x]^+$ ion as I^+. Neither maxima nor anodic limiting currents occur on c.v. curves run from positive to negative potentials (see Fig. 2), ill-defined waves being recorded. In the absence of stabilizers of I^+ (v.i.) reaction (2) appears to be highly irreversible at the rotated platinum electrode.

No cathodic or anodic waves were observed within the working potential range in 0.1 *M* sodium hydroxide.

Current-Voltage Curves of Iodide.—Iodide in acid medium yields two anodic waves. Characteristic c.v. curves of a 2 × 10^{-4} *M* potassium iodide solution, recorded with the automatic polarograph, are shown in Fig. 3. The first wave has a half-wave potential of +0.5 v. (*vs.* S.C.E.) at both *p*H 1 and 4 and is well defined at *p*H 1. The first diffusion current corresponds to the oxidation of iodide to iodine. For quantitative purposes it is recommended to determine iodide at a *p*H of 1, since the diffusion current at *p*H 4 is not clearly developed.

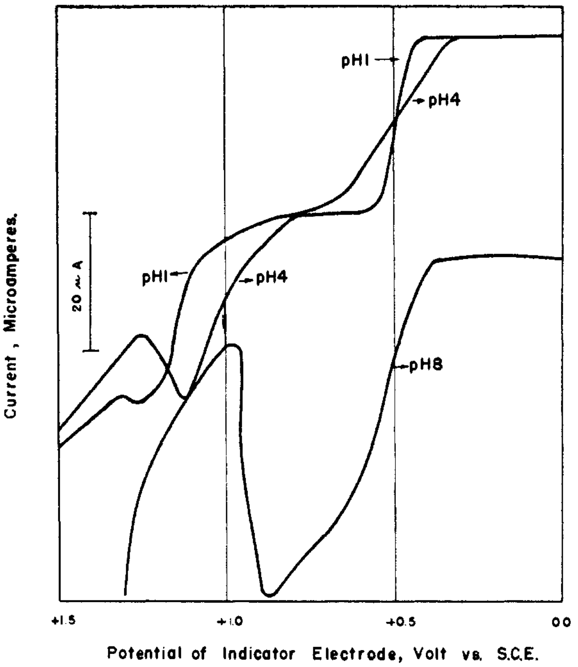

Fig. 3.—Current-voltage curves of 2 × 10^{-4} *M* potassium iodide, run from negative to positive potentials. Curves start at zero current and zero potential and are shifted arbitrarily along vertical axis. Supporting electrolytes and residual currents are the same as in Fig. 1.

A second wave with similar characteristics as the anodic iodine wave ($E_{1/2}$ in 0.1 *M* perchloric acid

≈ + 1.1 v.) is observed after the first one. The current at the maximum of the second wave is equal to twice the diffusion current of the first wave. The second wave corresponds to oxidation to I^+.

At *p*H 8 the two waves coalesce but the current at the sharp maximum again corresponds to the quantitative oxidation of I^- to I^+.

No anodic iodide currents are found in 0.1 *M* sodium hydroxide.

The anodic diffusion current of potassium iodide in 0.1 *M* perchloric acid, measured at +0.7 v. *vs.* S.C.E., was proportional to concentration in the 10^{-5} to 10^{-3} *M* range. Using electrode A, i_d/c was equal to (126 ± 2) μa./millimole/liter. The ratio of diffusion currents of equinormal concentrations of iodine (cathodic wave) and iodide (first anodic wave) was found to be 190 to 252 or 0.75. The diffusion coefficient at 25° of iodine is 1.11×10^{-5} cm.^{2}/sec. and of iodide ion is 2.05×10^{-5} cm.^{2}/sec. or a ratio of 0.54. If the diffusion currents were proportional to the square root of diffusion coefficients the calculated ratio of iodine and iodide diffusion currents would be 0.74 as compared to the experimental value of 0.75.

The I^-–I_2–I^+ System in the Presence of Other Halides.—Chloride and bromide are known to stabilize unipositive iodine.[7] We have found that anodic and cathodic c.v. curves of iodine in solutions of *p*H 4 or higher are not affected by 0.1 *M* potassium chloride. Well defined anodic iodine waves are observed in stronger acid chloride solutions. Some current–voltage curves of 10^{-4} *M* iodine in hydrochloric acid, obtained with the automatic polarograph are shown in Fig. 4. Manually it was found that in 0.1 *M* hydrochloric acid the anodic and cathodic waves of iodine are of equal height no maximum being exhibited by the anodic wave. The cathodic wave differs but slightly from the iodine wave in 0.1 *M* perchloric acid (*cf.* Fig. 1). Considering also that iodine is very volatile in 0.1 *M* hydrochloric acid it may be concluded that in this medium iodine is mainly present as I_2.[8]

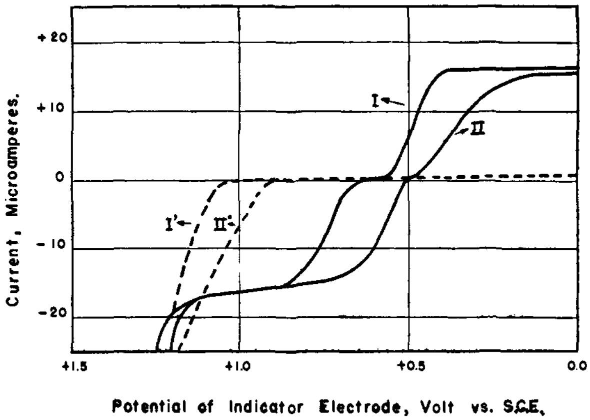

Fig. 4.—Current-voltage curves of iodine in hydrochloric acid: I, 10^{-4} *M* iodine in 0.1 *M* HCl; II, 10^{-4} *M* iodine in 4 *M* HCl; I', II', residual currents.

The anodic wave of iodine in 0.1 *M* hydrochloric acid ($E_{1/2}$ = 0.75 v., see Fig. 4, curve I) occurs at considerably less positive potentials than in 0.1 *M* perchloric acid (*cf.* Fig. 1). Chloride stabilizes I^+ by either of the reactions[9]

$$2Cl^- + I_2(aq) \longrightarrow 2ICl(aq) + 2e \quad (3)$$

$$4Cl^- + I_2(aq) \longrightarrow 2ICl_2^- + 2e \quad (4)$$

In 4 *M* hydrochloric acid (Fig. 4, curve II), 10^{-4} *M* iodine yields drawn out cathodic ($E_{1/2}$ = +0.36 v. *vs.* S.C.E.) and anodic waves ($E_{1/2}$ = +0.57 v.), which almost merge at the zero current potential. In this concentrated acid solution the anodic and cathodic waves yield equal limiting currents with the manual and automatic polarographs (15 μa. for 10^{-4} *M* iodine). These limiting currents are about 20% smaller than those of iodine in the other supporting electrolytes and do not vary with time of standing. In 4 *M* hydrochloric acid iodine is mainly present[8] as I_2Cl^- and the electrode reactions may be formulated as

$$\text{cathodic wave: } I_2Cl^- + 2e \longrightarrow 2I^- + Cl^- \quad (5)$$

$$\text{anodic wave: } I_2Cl^- + 3Cl^- \longrightarrow 2ICl_2^- + 2e \quad (6)$$

Current–voltage curves of potassium iodide were investigated in the presence of various other halides. Some characteristic polarograms, obtained with the automatic recording instrument, are presented in Fig. 5. It is seen that 2×10^{-4} *M* potassium iodide in 0.1 *M* hydrochloric acid (curve I) yields a double anodic wave. The wave heights measured manually and with automatic recording were equal. The first wave ($E_{1/2}$ = +0.48 v. *vs.* S.C.E.) is similar to the anodic iodide wave in 0.1 *M* perchloric acid (*cf.* Fig. 3) and corresponds to the oxidation of iodide to iodine. The second wave,

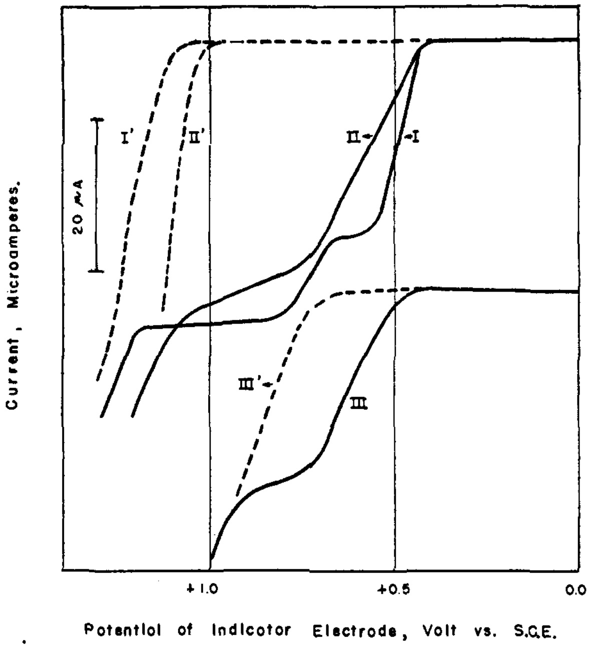

Fig. 5.—Current-voltage curves of iodide in the presence of other halides: I, 2×10^{-4} *M* KI in 0.1 *M* HCl; II, 2×10^{-4} *M* KI in 0.1 *M* KCl plus 1 *M* KCl; III, 2×10^{-4} *M* KI in 0.1 *M* HBr; I', II', III', residual currents. Curves are shifted arbitrarily along vertical axis.

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[7] See, *e.g.*, T. Kikindai, *Bull. soc. chim.*, 799 (1951).

[8] *Cf.* P. Ray and P. H. Sarkar, *J. Chem. Soc.*, **121**, 1449 (1922).

[9] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, p. 58.

with a half-wave potential of +0.75 v. *vs.* S.C.E., corresponds to the oxidation of I_2 to ICl. The second wave is considerably smaller in height than the first one. It was found that the difference in height increases with the rate of rotation of the electrode. The relevant data, obtained at an electrode rotated at various speeds between zero (stationary, steady state condition) and 900 r.p.m., are summarized in Table I.

TABLE I

ANODIC DIFFUSION CURRENTS OF 2 × 10^{-4} *M* POTASSIUM IODIDE IN 0.1 *M* HYDROCHLORIC ACID, AT VARIOUS SPEEDS OF ROTATION OF ELECTRODE A AT 25°

Rate of rotation, r.p.m.	i_{d_1}, μa. corrected for residual current; measured at +0.65 v. *vs* S.C.E.; corresponds to reaction: $2I^- \rightarrow I_2 + 2e$	i_{d_2}, μa. corrected for residual current; measured at +1.0 v. *vs.* S.C.E.; corresponds to reaction: $I_2 + 2Cl^- \rightarrow 2ICl + 2e$	$i_{d_2} - i_{d_1}$	$\frac{i_{d_2} - i_{d_1}}{i_{d_1}}$
Stationary (steady state)	1.20	2.40	1.20	1.00
300	20.0	30.5	10.5	0.53
600	26.0	36.5	10.5	.40
900	30.5	42.0	11.5	.38

A c.v. curve of 2 × 10^{-4} *M* potassium iodide in 1 *M* potassium chloride plus 0.1 *M* hydrochloric acid (Fig. 5, curve II) yields a single drawn-out wave corresponding to an over-all two-electron oxidation. This is somewhat analogous to the behavior of iodine in 4 *M* hydrochloric acid (*cf.* Fig. 4, curve II).

Iodide yields a well defined anodic wave in 0.1 *M* hydrobromic acid (curve III, Fig. 5). The wave corresponds to a one electron oxidation. Its half-wave potential is more positive than in other supporting electrolytes, *i.e.*, +0.62 v. *vs.* S.C.E., as compared to 0.50 in 0.1 *M* perchloric acid. The wave height, however, is the same. An $I_2 \rightarrow I^+$ wave is not obtained in hydrobromic acid, because the bromide ion is oxidized before the I^+ wave appears.

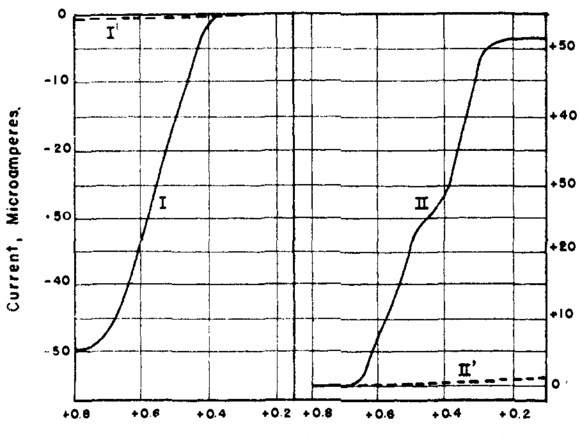

Fig. 6.—Current-voltage curves of iodide and iodine monochloride: I, 2 × 10^{-4} *M* KI, 0.125 *M* pyridine in acetate buffer of *p*H 6; II, 2 × 10^{-4} *M* ICl in 4 *M* HCl; I', II', residual currents. Curves are shifted arbitrarily along horizontal axis.

Effect of Pyridine.—Pyridine is known to stabilize I^+ compounds.[10] At *p*H 6 a well defined anodic wave is observed in the presence of pyridine (Fig. 6, curve I) corresponding to two-electron oxidation of I^- to $[I\ Py_2]^+$. At this *p*H pyridine does not affect the residual current.

Voltammetry of Iodine Monochloride and Iodine Cyanide.—Iodine monochloride solutions were prepared by mixing potassium iodate and iodine in stoichiometric ratios. From curve II in Fig. 6 it is seen that iodine monochloride yields two slightly separated reduction waves. The half-wave potentials are +0.56 and +0.36 v., corresponding to the over-all electrode processes

$$2ICl_2^- + 2e \longrightarrow I_2Cl^- + 3Cl^- \quad (7)$$

$$I_2Cl^- + 2e \longrightarrow 2I^- + Cl^- \quad (8)$$

In a medium containing 0.05 *M* potassium cyanide and 0.1 *M* perchloric acid both iodine and iodide yield well developed anodic waves (Fig. 7) with a half-wave potential of 0.5 v. (*vs.* S.C.E.). The wave height with iodide is twice that of an equinormal iodine solution. These results are accounted for by the equations

$$HCN + I_2 \rightleftarrows H^+ + I^- + ICN \quad (9)$$

$$I^- + HCN \longrightarrow ICN + H^+ + 2e \quad (10)$$

Under our experimental conditions the equilibrium of reaction (9) was quantitatively at the right. No cathodic waves were obtained in 0.1 *M* perchloric acid containing cyanide, indicating that iodine cyanide is not reduced at the platinum electrode and that no free iodine was present. In a buffer of *p*H 8, 0.05 *M* in potassium cyanide and 10^{-4} *M* in iodine, neither a cathodic nor an anodic wave was obtained.

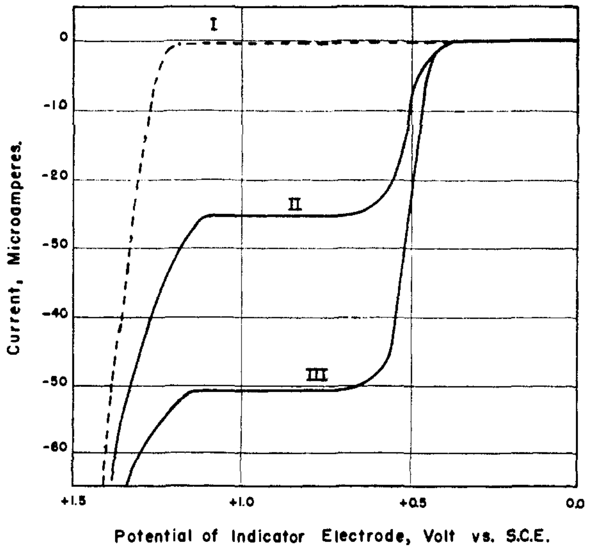

Fig. 7.—Current-voltage curves of iodine and iodide in the presence of hydrocyanic acid: I, 0.05 *M* KCN, 0.1 *M* $HClO_4$; II, 10^{-4} *M* I_2, 0.05 *M* KCN, 0.1 *M* $HClO_4$; III, 2 × 10^{-4} *M* KI, 0.05 *M* KCN, 0.1 *M* $HClO_4$.

Discussion

The c.v. curves described in this paper involve two types of primary electrode processes: (a) the

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[10] J. Kleinberg, "Unfamiliar Oxidation States and their Stabilization," University of Kansas Press, Lawrence, Kansas, 1950, p. 57.

reduction of I_2 to I^- (or the oxidation of iodide to elementary iodine) and (b) the oxidation of iodide and iodine to I^+.

The equation of a reversible wave corresponding to the I_2–I^- reduction (reaction 1) at 25° is

$$E_{\text{i.e.}} = E^0 - \frac{RT}{nF} \ln (f_{I^-} \times [I^-]_0^2/f_{I_2} \times [I_2]_0) = \text{const.} - 0.030 \log (i^2/i_d - i) \quad (11)$$

where $E_{\text{i.e.}}$ denotes the potential of the indicator electrode, f activity coefficients and the subscript zero concentration at the electrode surface. The plot of $E_{\text{i.e.}}$ *vs.* log $(i^2/i_d - i)$ of the c.v. curve of iodine in 0.1 *M* perchloric acid (Fig. 1) yielded a straight line with a slope of 0.027 which compares favorably with a value of 0.030 for a reversible reduction. According to equation (11) the half-wave potential $E_{1/2}$ = const. − 0.030 log i_d. Actually we found in 0.1 *M* perchloric acid half-wave potentials of +0.50 and +0.46 v. in 10^{-4} and 10^{-3} *M* iodine solutions while the calculated shift is 0.03 v. in the same direction. Thus the reduction of iodine in 0.1 *M* perchloric acid appears to be reversible. In supporting electrolytes of *p*H 4 to 8 the $E_{\text{i.e.}}$ *vs.* log $(i^2/i_d - i)$ plot yielded straight lines with slopes of 0.091 and 0.086 v., respectively. This indicates that in these solutions the current is controlled not only by the rate of diffusion but also by the rate of electroreduction.

An analysis of the first anodic wave of iodide in 0.1 *M* perchloric acid (Fig. 3) and in 0.1 *M* hydrochloric acid (Fig. 5, curve I) also corresponds to the reversible reaction 1. Theoretically the following relation should hold

$$E_{\text{i.e.}} = \text{const.} + 0.030 \log [i/(i_d - i)^2] \quad (12)$$

Plots of $E_{\text{i.e.}}$ *vs.* log $[i/(i_d - i)^2]$ yielded straight lines with slopes of 0.035 and 0.028 v., respectively.

Reversible oxidation of iodine to I^+ should yield a c.v. curve equation similar to 11. An analysis of the iodine wave in 0.1 *M* hydrochloric acid (Fig. 4, curve I) gave a straight line with a slope of 0.050 v. instead of the theoretical value of 0.030 indicating that the reaction is not completely reversible under our experimental conditions. All other $I_2 \rightarrow I^+$ waves were much drawn out and corresponded to an irreversible reaction. Similarly the second iodine wave in 1 *M* potassium chloride and 0.1 *M* hydrochloric acid (Fig. 5, curve II) does not correspond to a reversible electrode reaction.

If the two-electron single iodide waves in the presence of pyridine (Fig. 6, curve I) and hydrocyanic acid (Fig. 7) were reversible the following relation should hold

$$E_{\text{i.e.}} = \text{const.} + 0.030 \log (i/i_d - i) \quad (13)$$

The plot of $E_{\text{i.e.}}$ *vs.* log $(i/i_d - i)$ yielded straight lines with a slope of 0.065 in pyridine and of 0.060 in hydrocyanic acid instead of 0.030 expected if equilibrium were attained.

The variation of the ratio of the first and second anodic diffusion currents of iodide in 0.1 *M* hydrochloric acid (Table I) can be accounted for qualitatively. It has been shown that the rate of electroöxidation of iodide to iodine is so rapid that the currents on the first wave are diffusion controlled. On the other hand the oxidation of iodine to I^+ is partly rate controlled. Assuming that, at potentials corresponding to the I^+ wave, iodine is formed intermediately at the electrode, some of it may diffuse to the bulk of the solution and escape oxidation. Thus, the second anodic wave although sometimes well defined—like in 0.1 *M* hydrochloric acid (Fig. 5, curve I)—is smaller than the first one. The difference between the two wave heights increases with increasing rates of stirring, the theoretical 1:1 ratio being observed at the stationary wire electrode under steady state conditions.

Analytical applications of the work described in this paper will be reported in a subsequent communication.

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