[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

Electroreduction of Periodate at the Dropping Mercury Electrode. I. Behavior in Acidic Solutions of pH Less than 3¹

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Information concerning the polarography of periodate is limited to a meager reference by Heyrovsky⁴ who found that the reduction of periodate yielded two waves, the first of which was caused by its reduction to iodate and the second by reduction of iodate to iodide. He listed the tangent potential of the first wave as +0.15 volt vs. the normal calomel electrode in "acid" solutions. Because periodate is a very strong oxidizing agent, the first wave occurs at a "mixed potential"⁵ thereby limiting the conclusions that can be reached from a study of this wave. If the second wave is due to iodate, its characteristics should be similar to those reported for iodate by Orlemann and Kolthoff.^{6,7}

The present paper describes the polarographic behavior of periodate in strongly acid solutions. The behavior in solutions of higher pH will be presented in subsequent papers.

Experimental

Apparatus.—Three different types of polarographs were used. The first was a manually operated instrument similar to the one described by Lingane and Kolthoff.⁸ Later, a Leeds and Northrup "Electrochemograph" was used and still later a Sargent Model XX Polarograph. Polarograms recorded automatically by the Electrochemograph were used primarily for measurements of diffusion currents because the time-lag of the recorder introduced a large variable error into the value of the half-wave otential. Correct half-wave potentials were obtained only by manual operation of the instrument. Polaro-grams obtained with the Sargent instrument had halfwave potentials which agreed with those obtained manu-ally, but accurate readings of diffusion currents could only be obtained by using a potentiometer to measure the IRdrop across a standard resistance.

All potentials were measured through a salt bridge of potassium chloride against a saturated calomel electrode (S.C.E.) having a large surface area in order to minimize polarization errors. All half-wave potentials $(E_{1/2})$ were corrected for IR drop in the polarographic cell, and all diffusion currents were corrected for residual currents.

Prior to an analysis each polarographic solution was deoxygenated by a stream of nitrogen which had been passed successively through two or more gas-washing bot-tles containing a solution of ammoniacal copper(I) sulfate plus strips of copper, and finally through two solu-tions of sulfuric acid. During an analysis, the temperature of the solution was controlled at $25 \pm 0.1^{\circ}$ by means of a thermostated water-bath.

Two capillaries were used to obtain the data reported here: Capillary I, 1.670 mg.^{*/s} sec.^{-1/s} at -0.8 volt vs. the S.C.E. and Capillary II, 1.565 mg.^{*/s} sec.^{-1/s} at -0.6 volt vs. the S.C.E. The rate at which mercury issued from the capillary was determined in air for capillary I and in water for capillary II.

The pH of each buffer solution was checked, when possible, with a calibrated Beckman Model G pH Meter. Reagents and Solutions.—Distilled water was used throughout this study and all common chemicals were reagent grade. Orthoperiodic acid and potassium meta-periodate were obtained from the G. Frederick Smith Company and were used without further purification.

Solutions of potassium metaperiodate were prepared by direct weighing, but solutions of periodic acid were always standardized. The usual standardization procedure⁹ was modified so that both periodate and iodate could be determined in the same aliquot of solution. The new procedure, which was checked against the regular method, is as follows: The periodate content of the solution was determined by reduction of periodate to iodate by iodide in weakly alkaline solutions followed by titration of the resulting iodine with standard sodium arsenite. Subsequent addition of glacial acetic acid produced an amount of iodine equivalent to the total iodate content of the solution. By restoring the solution to an alkaline pH with sodium bicarbonate before titrating the iodine, it was possible to continue the analysis with sodium arsenite. Thus, the need for a standard thiosulfate solution and for a second aliquot of solution was eliminated.

The solutions of orthoperiodic acid were found to contain less than 2% by weight of iodic acid, an amount which could be disregarded in the present study. It was also found that a stock solution of approximately 0.02~Mperiodic acid changed its concentration less than 2% in six months. Consequently no special precautions were taken to prevent decomposition of stock solutions.

The supporting electrolyte for all of the determinations was a buffer consisting of 0.16 M potassium sulfate and sulfuric acid. Most of the solutions also contained 0.01%gelatin which was used as a maximum suppressor.

Results

General.—A typical current-voltage curve for periodic acid is shown in Fig. 1, and it confirms Heyrovsky's general conclusions. Using the curve in Fig. 1, calculations based upon the Nernst expression and the Ilkovic equation¹⁰ together with a diffusion coefficient derived from the data of Jones¹¹ revealed that the reductions required 1.7 and 5.5 faradays/mole of periodate. The deviations of these values from the expected values of 2.0 and 6.0 are not too serious, so, in the discussion that follows, the first wave will be referred to as the periodate wave and the second as the iodate wave.

Except in the presence of gelatin, maxima usually accompanied both waves. The maximum of the periodate wave was most serious because it

(9) W. W. Scott, "Standard Methods of Chemical Analysis," edited by N. H. Furman, D. Van Nostrand Co., Inc., New York, N. Y., 5th edition, Vol. I, 1939, p. 458.

⁽¹⁾ Taken in part from a thesis presented by R. H. Coe to the Department of Chemistry and to the Committee on Graduate Study of Stanford University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, April, 1947.

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 ⁽⁴⁾ J. Heyrovsky, "Polarographie," Springer, Vienna, 1941, p. 75.
 (5) Kolthoff and Miller, THIS JOURNAL, 62, 2171 (1940).

⁽⁶⁾ Orlemann and Kolthoff, *ibid.*, 64, 1044 (1942).
(7) Orlemann and Kolthoff, *ibid.*, 64, 1970 (1942).

⁽⁸⁾ Lingane and Kolthoff, ibid., 61, 825 (1939).

⁽¹⁰⁾ I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 79.

⁽¹¹⁾ Jones, THIS JOURNAL, 68, 240 (1946).

often prohibited a sharp definition of the two waves by extending into the iodate wave. The periodate maxima was greatest at a pH of 3 and practically non-existent at a pH of 1. On the other hand, the iodate maximum introduced no particular difficulty. It was absent at pH 3 but increased in size with decreasing pH.

In addition to the normal maximum of the periodate wave, a hump sometimes occurred on the diffusion current plateau. This hump appeared to be largest for fresh solutions of periodic acid, and its height was roughly proportional to the periodate concentration.

It was anticipated that careful buffering would be necessary because hydronium ions participate in the electrode reaction for each wave. Several experiments using unbuffered solutions indicated that the production and accumulation of hydroxyl ions at the cathode was sufficient to shift the iodate wave to more negative potentials. The periodate wave was not affected.

Although peculiarities were found in the electrocapillary curves of periodic acid, it was found that the difference in drop time for the two waves was insignificant because the waves were so close together.

Stability of Periodate in Polarographic Solutions.—The fact that a pure solution of periodic acid was stable was no guarantee that it would be stable under polarographic conditions where mercury, chloride, and excess acid might be in contact with it. For this reason, the experiments described below were carried out.

In sulfuric acid solutions of pH less than 2, periodic acid occasionally decomposed noticeably on This was evidenced after several hours standing. by a poorly defined iodate wave, a shift of the wave to more negative potentials, and a slight increase in its height. Ozone, produced by decomposition of periodate, was probably the source of these changes because deaeration immediately prior to an analysis (in contrast to deaeration followed by prolonged standing under a nitrogen atmosphere) often produced more clearly defined waves. On several occasions, however, no changes whatever were noted in the appearance of the polarograms of solutions which had stood for twenty hours. The solutions were always deaerated and analyzed soon after preparation to avoid any uncertainty arising from possible errors of this kind.

The importance of the effect of reaction between periodate in the solution and mercury lying on the bottom of the polarographic cell was briefly investigated. In an unstirred solution a light yellow precipitate, presumably of mercury iodate, covered the mercury pool in a short time. Despite this evidence of reaction, a solution containing 0.7 millimolar periodic acid and 0.1 N sulfuric acid showed no detectable change in the diffusion current after ninety minutes. In the absence of chloride, a similar solution stood twenty hours in



Fig. 1.—Typical polarogram of periodic acid: 8.10×10^{-4} M orthoperiodic acid, 0.16 M potassium sulfate, 0.01% gelatin and sulfuric acid; pH 1.80.

contact with mercury without producing an appreciable change in the polarogram. However, upon addition of chloride to this solution, mercury (I) chloride precipitated. This showed that a reaction between mercury and periodate had occurred and that its lack of effect upon the waves in the absence of chloride was due to the production of an equivalent amount of ions of mercury whose reduction compensated for the lost periodate. The fact that small amounts of chloride in the solution did not produce changes, under normal conditions, by precipitation of mercury was probably a result of the large volume of solution (40 ml.), the distance between the dropping electrode and the pool of mercury, and the short time required for an analysis.

In the absence of a mercury pool, the diffusion of small amounts of chloride from the salt bridge into the polarographic solution did not appear to have an undesirable effect even in strongly acidic solutions where periodate is known to oxidize chloride. On several occasions, when the shift in the reduction potential of the periodate wave indicated that chloride had diffused from the salt bridge, the solutions were set aside and allowed to stand for periods up to three hours before repeating their analyses. No differences were ever observed in either of the wave heights or in the $E_{1/2}$ of the iodate wave. After prolonged standing of about twenty hours, a decrease in the wave heights was noticed. During the short time required to make a normal analysis, even a relatively concentrated solution of potassium chloride (1.6M) at a pH of 1.7 exerted no effect on the wave heights. The only ill effect of chloride was the decrease in the separation of the two waves as a result of the shift of the periodate wave to a more negative potential.

Effect of Gelatin.—Ordinarily the amount of maximum suppressor added to a solution must be controlled because too little will not eliminate



Potential.

Fig. 2.—Effect of concentration of gelatin on increase in current with growth of mercury drop, concentration of gelatin: I, 0.000%; II, 0.004%; III, 0.008%; IV, 0.010%; V, 0.020%; VI, 0.040%.

the maximum, and too much will decrease the diffusion current. In the present study, the concentration of gelatin was found to be critical because it affected the $E_{1/2}$ of the iodate curve. Orlemann and Kolthoff⁶ reported a shift of -0.2 volt or more in the $E_{1/2}$ when gelatin was added to a solution of iodate or bromate which contained lanthanum chloride. They attributed the shift to the fact that gelatin prevented the formation of a film of lanthanum hydroxide on the surface of the dropping electrode. It appears, however, that the shift in potential is independent of the lanthanum.

The effect of gelatin described here is for acidic solutions, but the same effect, differing somewhat in magnitude, has also been observed in solutions buffered by ammonia and ammonium chloride at approximately pH 10. Considering first the effect of gelatin on the diffusion current, it was found that at concentrations larger than 0.04% the diffusion current of the periodate wave was decreased. At concentrations of gelatin larger than 0.01% the height of the iodate wave was decreased.

It was interesting to observe that the Sargent Model XX Polarograph, which follows the true current closely, was able to detect changes in the current associated with a growing drop of mercury whenever different concentrations of gelatin were used. This is illustrated by the series of diagrams shown in Fig. 2. These differences were most marked in the region where the average current was changing most rapidly with potential, and the differences disappeared when the diffusion current was reached.

The actual effect of gelatin upon the $E_{1/1}$ of the iodate wave is described by Fig. 3. This effect is



Fig. 3.—Effect of concentration of gelatin upon $E_{I/2}$ of the iodate wave: I, pH 2.10; II, pH 1.58.

independent of pH at the indicated acidities for the lines are separated by a value equivalent to 0.13 volt/pH unit. A plot of log % gelatin vs. $E_{1/2}$ gives two intersecting straight lines (Fig. 4),



Fig. 4.—Indication of complex formation with gelatin: I, pH 2.10; II, pH 1.58.

which indicate that complex formation of gelatin with iodate must occur and that it must take place at the electrode surface because the diffusion current is not affected by small concentrations of gelatin in the solution. The possibility of complex formation with periodate and iodide is not excluded. Further interpretation of the data was untrustworthy because the system was irreversible and the actual concentration of gelatin at the electrode surface was unknown.

Effect of pH on the Iodate Half-wave Potential.—Despite the fact that the reduction potential of periodate is undoubtedly influenced by pH, no change could be observed directly in the periodate wave because it occurs at a mixed potential of the dropping mercury electrode. Therefore changes in pH were reflected primarily in the iodate wave. The studies reported below were carried out in gelatin-free solutions buffered by bisulfate and, although maxima appeared, they did not interfere with the measurements of $E_{1/4}$'s.



Fig. 5.—Effect of pH on $E_{1/2}$ of the iodate wave. Iodate values from Orlemann and Kolthoff: solutions of 1.04 \times 10⁻³ *M* orthoperiodic acid, 0.16 *M* potassium sulfate and sulfuric acid: ----, similar solutions with 0.01% gelatin.

In Fig. 5, data obtained for solutions of iodate by Orlemann and Kolthoff are compared with data for solutions of periodate from the present study. Differences between the two sets of results were largest below pH 1.6. The presence of 0.01% gelatin not only shifted the $E_{1/2}$ as expected, but also eliminated one of the inflection points. Gelatin also influenced the symmetry of the iodate wave as shown in Fig. 6. In the absence of gelatin, the iodate wave appeared to be symmetrical although maxima obscured the results somewhat.

Effect of pH on Diffusion Current Constants.— This effect is described quite simply by Fig. 7. It was found that at pH 0.8, where the $E_{1/4}$ of the iodate wave reached a minimum, the height of the periodate wave also reached a minimum.

Effect of Concentration of Periodate.— Changes in the concentration of reducible ion may affect both the diffusion current constant



Fig. 6.—Symmetry of iodate waves in the presence of 0.01% gelatin, solutions of 5.58×10^{-4} M orthoperiodic acid, 0.16 M potassium sulfate and sulfuric acid: I, pH 0.1; II, pH 1.2; III, pH 2.0; IV, pH 3.0. (Not corrected for residual current.)

and the $E_{1/2}$. For this reason a series of solutions of orthoperiodic acid were analyzed at concentrations from 0.277 to 1.67 millimolar. The solutions contained 0.01% gelatin and, in addition, were **buffered** with 0.16 *M* potassium sulfate and sulfuric acid at approximately pH 2.



Fig. 7.—Effect of pH upon diffusion current constants, solutions of 5×10^{-4} M orthoperiodic acid, 0.16 M potassium sulfate, sulfuric acid and 0.01% gelatin: I, constant for the sum of the iodate and periodate waves; II, iodate wave; III, periodate wave.

Using capillary I, the diffusion current constant of the periodate wave was found to be 3.9 = 0.1



Fig. 8.—Effect of concentration of periodic acid upon diffusion current constants, solutions of orthoperiodic acid, 0.16 M potassium sulfate, sulfuric acid and 0.01% gelatin, at pH 2.0: I, sum of periodate and iodate waves; II, iodate wave.

microamp./mg.²/ $sec.^{-1/2}$ millimole. The average value of the iodate wave was 13.2 ± 0.3 . The data are graphed in Fig. 8, and they show that a minimum is reached at a concentration close to 1.0 millimolar.

A similar series of analyses for solutions of potassium metaperiodate at a pH of 1.6 was carried out, using capillary II. In the range of 0.238 to 1.78 millimolar, the diffusion current constants were 3.9 ± 0.1 and 12.1 ± 0.1 for the periodate and iodate waves, respectively. The discrepancy between the two values for the iodate wave was caused by the iodate impurity in the orthoperiodic acid and the fact that the metaperiodate analyses were made at a lower pH. The metaperiodate solutions differed from periodic acid solutions by exhibiting no minimum in the value of the diffusion current constant.

Both series of analyses revealed that the $E_{1/4}$ of the iodate wave was essentially independent of the concentration of periodate. At the highest concentrations, however, an abrupt shift in the $E_{1/4}$ to more negative values was observed. This was caused by insufficient buffering. For solutions at pH 2.0 the $E_{1/4}$'s, when corrected to 0.0% gelatin, were found to be -0.20 ± 0.01 volt vs. the S.C.E. At pH 1.6, the average value was $-0.150 \pm$ 0.005 volt vs. the S.C.E. The values were independent of drop time.

Discussion

Calculations based on the Ilkovic equation and the Nernst expression give diffusion current constants of 4.6 and 13.8 for the periodate and iodate waves, respectively. It can be seen in Fig. 7 that these values are approached under some conditions, namely, at pH 2 or higher. At pH less than 2, the decrease in the total current may be caused by a decrease in the diffusion coefficient. The sharper decrease in the iodate constant and the increase in the periodate constant in solutions of pH less than 0.8 may indicate that the periodate was reduced to some state intermediate to iodate and iodide, presumably iodine (III). The abrupt change in the value of the iodate $E_{1/1}$ at pH 0.8 (Fig. 5) further indicates that a reaction of this type occurs.

The effect of gelatin on the iodate $E_{1/2}$ was measured but an exact explanation for it cannot as yet be given. The effect, which is independent of pH, may be caused by complex formation at the electrode surface. For the suppression of maxima a concentration of 0.01% was found to be optimum. For concentrations of gelatin below 0.016% and a constant pH greater than 0.8, the iodate $E_{1/2}$ was found to be a linear function of log % gelatin.

 $E_{1/2} = -0.295 - 0.135 \log \%$ gelatin + 0.130 log [H₂O⁺]

The iodate $E_{1/2}$ is a linear function of pH both in the absence and presence of gelatin, although the relationships are dependent upon the pHrange and concentration of gelatin. Several equations were obtained in the absence of gelatin

pH 1.6 to 3.0; $E_{1/2} = +0.065 + 0.130 \log [H_2O^+]$ pH 0.6 to 1.6; $E_{1/2} = -0.5 + 0.16 \log [H_3O^+]$ pH 0.6 ; $E_{1/2} = -0.12 - 0.11 \log [H_3O^+]$

In the presence of 0.01% gelatin the following were found

$$pH 0.8 \text{ to } 3.0; E_{1/2} = -0.020 + 0.130 \log [H_3O^+]$$

$$pH 0.8 ; E_{1/2} = -0.15 - 0.09 \log [H_3O^+]$$

The equation of the iodate wave for solutions of about pH 2 containing 0.01% gelatin is

 $E_{\text{D.E.}} = -0.20 + 0.130 \log [\text{H}_{3}\text{O}^{+}] + 0.125 \log (I_{\text{d}} - I)/I$

The analytical application of polarographic waves from periodate appears to be useful, although somewhat limited. In the range of concentrations examined, acidic solutions of potassium metaperiodate could be determined within an accuracy of $\pm 2.5\%$ by measuring the periodate wave. This is approximately the accuracy with which measurements of its wave height could be made. By using the iodate wave, the error could be reduced to 1% or less. Solutions of orthoperiodic acid, on the other hand, could be not analyzed with an average error less than 2.5% regardless of which wave was used. The decrease in accuracy results from previously discussed changes in the diffusion current constant of solutions of orthoperiodic acid.

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Summary

Conditions effecting the stability of polarographic solutions of periodate have been described.

The electroreduction of periodate in acidic solutions at the dropping mercury electrode has been described. In the pH range from 0.8 to 3.0, the reduction occurred in two steps. The first wave, corresponding to reduction to iodate, occurred at a mixed potential. The half-wave potential of the second wave, which corresponded to reduction of iodate to iodide, varied with the pH, but it was independent of the drop time and the concentration of periodate.

Gelatin was effective in shifting the half-wave

potential of the iodate wave in a manner similar to that exhibited when complexes are formed.

Equations have been derived to express the changes in the iodate half-wave potential due to pH and gelatin.

The accuracy of the analytical application of the polarographic reduction of periodate has been mentioned.

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[CONTRIBUTION FROM EDWARD DAVIES CHEMICAL LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH]

The Conductance of Potassium Iodate at 25°, and Comments on the Conductances of Some Salts of Oxyacids

By C. B. Monk

Conductance measurements on potassium iodate at 25° have been made by several workers; a review and discussion of these has been given by Krieger and Kilpatrick,¹ who report fresh data. A closer examination of their results for the more dilute solutions suggested that a further study of these concentrations might be worth while. Accordingly fresh measurements have been made and the extrapolation method of Owen² applied. This method is found to give satisfactory results in certain cases where the method of Shedlovsky⁸ fails. Some other reported measurements⁴ have been similarly analysed and, using these fresh results, dissociation constants have been calculated by the method of Davies.⁵

Experimental

"AnalaR" grade potassium iodate was purified and dried as described before.1 A fused quartz conductivity cell was used, the apparatus and technique being similar to that described else-where.⁶ The cell constant was obtained by measurements on potassium chloride solutions in the concentration range 0.0001 to 0.002 gram equivalent per liter and employing equation (2) in the paper just quoted. This, in effect, is a method of finding cell constants on the Jones and Bradshaw standard⁷ for cells used in measurements on very dilute solutions. The thermometer was checked against one recently calibrated at the National Physical Laboratory. Table I contains the data. In this table C is the concentration in gram equivalents per liter, Λ is the conductance of the solution corrected for that of the water,⁸ and K is the dissociation constant of the potassium iodate calculated in the manner described below. The con-

(1) Krieger and Kilpatrick, THIS JOURNAL, 64, 7 (1942).

(2) Owen, ibid., 61, 1393 (1939).

(3) Shedlovsky, ibid., 55, 1405 (1932).

(4) (a) J. H. Jones, *ibid.*, **66**, 1115 (1944); (b) **67**, 855 (1945); (c) **68**, 240 (1946); (d) **69**, 2065 (1947).

(5) Davies, Trans. Faraday Soc., 23, 351 (1927).

(6) Davies, J. Chem. Soc., 432 (1937).

(7) Jones and Bradshaw, THIS JOURNAL, 55, 1780 (1933).

(8) Davies, "Conductivity of Solutions," Chapman and Hall Ltd., London, p. 72.

		Table I		
Run	С	\sqrt{c}	Δ	K
a	0.00018265	0.01352	113.07	1.1
a	.00035295	.01879	112.61	2.0
a	.00070430	.02624	111.91	1.9
a	.00099845	.03160	111.45	1.8
ь	.0017117	.04137	110.55	1.7
Ъ	.0025362	.05037	109.78	
b	.0032859	.05732	109.19	
b	.0039118	.06255	108.78	

Specific conductance of water, $ohm^{-1} \times 10^{-7}$ (a) 2.39, (b) 2.38.

ductances, together with those of Krieger and Kilpatrick¹ which cover the same range, are plotted in Fig. 1, against the square root of C.



Fig. 1.—Conductivity of potassium iodate: O, present data; Θ , ref. 1.

Discussion

Examination of the experimental curve in Fig. 1 shows that while excellent agreement is obtained