until a satisfactory agreement between the theoretical and experimental curves was obtained. The procedure was essentially one of trial and error combined with semi-quantitative predictions of the effects of changes in the values of the constants.

In Fig. 7 are shown typical theoretical curves for $(A_0) + (B_0)$, (A_1), (A_2), (X) and (P). These curves are for the reaction of hexyne-1 with $a = 0.40$ mole liter^{-1}, $b = 0.20$ mole liter^{-1}, and with the following values of the rate constants: $k_1 = 1.1 \times 10^{-2}$ sec.$^{-1}$, $(k_{-1} + k_1)/k_2 = 3.6 \times 10^2$ moles liter^{-1}, $k_3 = 8 \times 10^{-3}$ sec.$^{-1}$.

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PITTSBURGH, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. V. The Electroreduction of Diphenyliodonium Salts[1,2]

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The electroreduction of diphenyliodonium salts has been investigated both by polarography at the dropping mercury electrode and by coulometry at controlled potential. The three polarographic waves are shown to correspond to the processes: (I) $R\overset{+}{I}R + e \rightleftarrows R\dot{I}R$; (II) $R\overset{+}{I}R + 2e + H^+ \rightarrow RH + RI$; (III) $R\overset{+}{I}R + 4e + H^+ \rightarrow RH + R^- + I^-$ (slow); $R^- + H^+ \rightarrow RH$ (fast). Diphenyliodine produced by controlled-potential electrolysis is unstable and decomposes rapidly to iodobenzene and other products. Those variables whose effects on the polarographic reduction have been investigated include the nature of the anion, the composition of the solvent, the concentration of the diphenyliodonium ion, the ionic strength and the *p*H and nature of the buffer system. A paper on the effects of substituents follows directly.

Introduction

The preceding papers in this series of publications on iodonium salts include discussions of the synthesis[3] and reactions[2,4,5] of these compounds; the present paper will discuss their electrochemical reduction at both small and large mercury electrodes.

The only previously reported work[6] on the polarography of iodonium salts was restricted to unsubstituted diphenyliodonium salts and to phenyl-β-chlorovinyliodonium salts. For both groups of salts the authors reported polarograms with four waves and postulated a stepwise reduction involving a total of four electrons. Reduction *via* the phenylmercury free radical was postulated in analogy with the reduction of a phenylmercuric salt.[7] Wawzonek, however, in his recent review article[8a] has reinterpreted Colichman's data and has proposed another mechanism, also involving phenylmercury intermediates. The question of organomercury compounds as possible intermediates in the electroreduction of iodonium salts will be considered later.

A large-scale electrolysis of diaryliodonium hydroxide at 4.5 volts led to products which indicated to the investigators that aryl radicals were reduction products.[9]

Included among the various other 'onium salts for which the polarographic or electrolytic reduction has been investigated are quaternary ammonium,[10a] N-alkylpyridinium,[10b] tetrazolium,[10c] benzenediazonium,[10d] triphenylsulfonium,[10e] tetraarylphosphonium[10f] and aryltrialkylphosphonium[10f] salts.

The polarography of aliphatic and aromatic halides is discussed by Kolthoff and Lingane[11] and has been brought up to date in the review articles by Wawzonek.[8] In the majority of cases the halide is reduced to the hydrocarbon. This mechanism has been confirmed coulometrically.[12]

$$RX + 2e^- + H^+ \longrightarrow RH + X^-$$

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[1] This paper is based on a dissertation submitted by Miss Hilde Elizabeth Bachofner in partial fulfillment of the requirements of the degree of Doctor of Philosophy in 1957 and was presented in part at the 130th National Meeting of the American Chemical Society at Atlantic City in September, 1956 (Abstracts of Papers, p. 85-O).

[2] Previous paper: F. M. Beringer, E. J. Geering, M. Mausner and I. Kuntz, *J. Phys. Chem.*, **60**, 141 (1956).

[3] F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

[4] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *ibid.*, **75**, 2708 (1953).

[5] F. M. Beringer and E. M. Gindler, *ibid.*, **77**, 3200, 3203 (1955).

[6] (a) E. L. Colichman and H. P. Maffei, *ibid.*, **74**, 2744 (1952); (b) E. L. Colichman and J. T. Matschiner, *J. Org. Chem.*, **18**, 1124; (1953).

[7] R. Benesch and R. E. Benesch, THIS JOURNAL, **73**, 3391 (1951). These workers reported the separate addition of two electrons, the first to form the phenylmercury free radical, the second, with addition of a proton, to form benzene and metallic mercury. Colichman and Maffei (ref. 6a) found the half-wave potential for their wave III of diphenyliodonium iodide to be −0.87 to −1.22 *vs.* S.C.E., depending on *p*H while Benesch and Benesch had found that the phenylmercuric salt took up the second electron at −0.8 to −1.2 v., depending on *p*H and concentration.

[8] (a) S. Wawzonek, *Anal. Chem.*, **26**, 65 (1954); (b) **24**, 32 (1952); (c) **28**, 638 (1956).

[9] E. V. Zappi and R. F. Mastropaolo, *Anales asoc. quim. arg.*, **29**, 88 (1941); *C. A.*, **35**, 6516 (1942).

[10] (a) W. Kemula and D. Sybilska, *Roczniki Chem.*, **26**, 480 (1952); *C. A.*, **48**, 8674 (1955); M. Shinagawa and H. Matsuo, *Japan Analyst*, **4**, 213 (1955); (b) P. C. Tompkins and C. L. A. Schmidt, *Univ. California Pub. Physiol.*, **8**, 237, 247 (1944); F. Sorm and Z. Sormova, *Chem. Listy*, **42**, 82 (1948); *C. A.*, **45**, 618 (1953); W. Ciusa, P. M. Strocchi and G. Adamo, *Gazz. chim. ital.*, **80**, 604 (1950); *C. A.*, **45**, 9059 (1953); (c) H. Ried and M. Wilk, *Ann.*, **581**, 49 (1953); B. Jambor, *Nature*, **173**, 774 (1954); H. Campbell and P. O. Kant, *J. Chem. Soc.*, 3130 (1956); (d) E. T. Atkinson, H. H. Warren, P. I. Abell and R. E. Wing, THIS JOURNAL, **72**, 915 (1950); R. M. Elofson, R. L. Edsberg and P. A. Mecherly, *J. Electrochem. Soc.*, **97**, 166 (1950); P. Reutschi and G. Trumpler, *Helv. Chim. Acta*, **36**, 1649 (1953); J. K. Kochi, THIS JOURNAL, **77**, 3208 (1955); (e) W. A. Bonner, *ibid.*, **74**, 5080 (1952); E. L. Colichman and D. L. Love, *J. Org. Chem.*, **18**, 40 (1953); (f) E. L. Colichman, *Anal. Chem.*, **26**, 1204 (1954).

[11] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, New York, N. Y., p. 647.

[12] (a) E. Gergely and T. Iredale, *J. Chem. Soc.*, 13 (1951); (b

The polarographic reduction of iodobenzene[12d] and of non-ionizable organic iodo compounds[12a] is reported to be independent of *p*H, while half-wave potentials of ionizable compounds are dependent on *p*H.[12b]

In a recent paper[12c] half-wave potentials of substituted iodobenzenes were correlated successfully with electron densities and with polarization energies defining the orienting properties of the substituents. Colichman and Liu[13] reported a linear relationship between the half-wave potentials and Hammett's sigma functions for a group of 29 substituted iodobenzenes.

The three purposes of the present work were to clarify the electrochemical processes corresponding to the reduction steps, to check on organomercury compounds as possible intermediates and to investigate diphenyliodine, a reasonable first reduction product.

An article on the effect of substituents on the electroreduction of diphenyliodonium salts directly follows the present article.

Experimental

Starting Materials.—Iodonium salts were prepared by Beringer and co-workers by methods previously reported.[2,3,4,5,14]

Tetraethylammonium hydroxide was of Eastman Kodak white label grade. Inorganic chemicals were C.P., reagent or N.F. grade. Ethanol was of 95% U.S.P. grade. Water was triply distilled in all-glass equipment and boiled before use to expel carbon dioxide. Gelatin was highest purity grade supplied by Fisher Scientific Co.; solutions were not stored but were used only on the day on which they had been prepared. Mercury was double-distilled. Prepurified nitrogen gas was used without further treatment.

Supporting Electrolytes.—Buffer systems of constant ionic strength in the range *p*H 2.2 to 8.0 were prepared double strength (2.0 *M*) from aqueous stock solutions of disodium phosphate, citric acid and potassium chloride as described in a recent paper by Elving and co-workers.[15] For polarographic determinations buffer solutions were mixed with equal volumes of aqueous solutions of iodonium salts, so that the final concentration of salts corresponded to unit ionic strength.

Clark and Lubs buffer mixtures in the range *p*H 1.0 to 9.5 were prepared[16] double strength from stock solutions of hydrochloric acid, potassium chloride, potassium acid phthalate, sodium hydroxide, potassium dihydrogen phosphate and boric acid. Dilution with an equal volume of aqueous diphenyliodonium salt solution did not change the *p*H. Dilution with an equal volume of 95% ethanolic solution of diphenyliodonium salt resulted in an apparent *p*H approximately one unit higher than that of the corresponding aqueous solution. In the region *p*H 1.0 to 2.2, buffer mixtures also were prepared from sulfuric acid and potassium sulfate, in proportions similar to those required for the Clark and Lubs buffer mixtures.

Tetraethylammonium sulfate (0.2 *M*) was prepared by neutralizing tetraethylammonium hydroxide to *p*H 8.5 with sulfuric acid. Tetraethylammonium phosphate (0.2 *M*) was prepared by neutralizing the base to *p*H 7.45 with phosphoric acid (ratio of monohydrogen phosphate to dihydrogen phosphate about 4:1). Dilution with an equal volume of water did not change the *p*H; dilution with an equal volume of 95% ethanol gave an apparent *p*H about one unit higher than that of the corresponding aqueous solution.

Tetraethylammonium bromide and hydroxide were not suitable for use as supporting electrolytes, since bromide ion gives an interfering anodic wave, while the iodonium salts were unstable in strongly alkaline media.

Gelatin (0.02%) was added as a maximum suppressor.

Equipment.—Polarograms were recorded with a Leeds and Northrup Type E Electrochemograph, using a conventional H-cell of 10-ml. capacity provided with a saturated calomel electrode and an agar-saturated potassium chloride bridge. Samples were deaerated for ten minutes with nitrogen gas which previously had been bubbled through some of the buffer solution. During the recording of the polarogram, the solution was blanketed with nitrogen. No corrections were made for *iR* drop. All polarographic measurements were made at 25 ± 0.5°.

Controlled potential electrolyses were carried out in a double diaphragm cell[17] with the aid of an Analytical Instruments, Inc. (Bristol, Connecticut) potentiostat and current integrator, using the procedure previously described.[17] Reduction normally was complete in about 15 minutes.

Measurements of pH were made with a Beckman glass electrode *p*H meter.

Results and Discussion

Polarograms of iodonium salts were composed of three waves. The first appeared at about −0.2 volt[18]; the second wave was of nearly equal height and appeared between −0.7 and −1.3 volts depending on concentration and *p*H; and the third wave, which appeared at about −1.7 volts, was equal in height to the sum of the heights of the first two waves. A typical polarogram is shown in Fig. 1.

The reduction is believed to proceed as

$$\text{Wave I: } R\overset{+}{I}R + e^- \rightleftarrows RIR$$

$$\text{Wave II: } R\overset{+}{I}R + 2e^- + H^+ \longrightarrow RH + RI$$

$$\text{Wave III: } R\overset{+}{I}R + 4e^- + H^+ \xrightarrow{\text{slow}} RH + R^- + I^-$$

$$R^- + H^+ \xrightarrow{\text{fast}} RH$$

Evidence supporting this sequence and details concerning it will now be presented.

Supporting Electrolyte. Effect of Anion.—The polarogram was characteristic of the iodonium cation; the anion was irrelevant and did not interfere except when it was reduced or oxidized at the dropping mercury electrode at a potential close to that of one of the waves of the iodonium cation.[19] The interference of bromide ion (when its concentration was equal to or less than that of the diphenyliodonium cation) could be corrected for by measuring the residual current separately with a portion of the supporting electrolyte containing an equal concentration of bromide ion. Compensation for the anodic wave of the iodide ion could not conveniently be made.

The anodic wave of the iodide ion is responsible for some aspects of the data reported by Colichman and co-workers.[6] Their first and second ("surface limiting" or "extraneous") waves are in reality the result of the addition of the anodic wave of iodide ion to the first wave of the iodonium cation.

3502 (1951); (c) 3226 (1953); (d) M. von Stackelberg and W. Stracke, *Z. Electrochem.*, **53**, 118 (1949).

[13] E. L. Colichman and S. K. Liu, THIS JOURNAL, **76**, 913 (1954).

[14] A second paper on the synthesis of iodonium salts, including some used in the present work, has been submitted to THIS JOURNAL.

[15] P. J. Elving, J. M. Markowits and I. Rosenthal, *Anal. Chem.*, **28**, 1179 (1956).

[16] N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 1127.

[17] L. Meites, *Anal. Chem.*, **27**, 1116 (1955).

[18] All potentials are referred to the saturated calomel electrode.

[19] Polarograms of diphenyliodonium chloride, tosylate and bisulfate were identical in all respects. Addition of 0.05 *M* nitrate ion 0.07 *M* sulfate ion or 0.9 *M* chloride ion did not change the appearance of the curve. Both diphenyliodonium bromide and iodide gave the anodic wave of the halide ions.

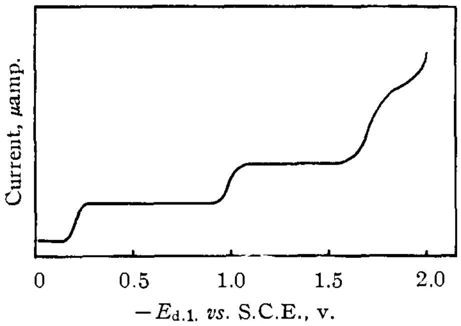

Fig. 1.—Typical polarogram of diphenyliodonium cation.

The polarogram always had the same appearance, whether the supporting electrolyte was unbuffered or buffered, whether the solution was aqueous or 50% ethanolic, and over a wide range of *p*H values. The half-wave potentials of waves I and III were similar in all media, and those of wave II were similar when *p*H values were comparable. Values of i_d/C in aqueous solution were identical from one supporting electrolyte to another; however, values in 50% ethanolic solution were lower.[20]

Ionic Strength.—The half-wave potentials of waves I and III were sensitive at constant *p*H to changes in ionic strength.[21] As shown in Fig. 2, increasing ionic strength shifts the half-wave potential of wave I to more negative values and shifts that of wave III to less negative values. The half-wave potential for wave II remains unchanged over the range of 0.5 to 1.0 ionic strength.

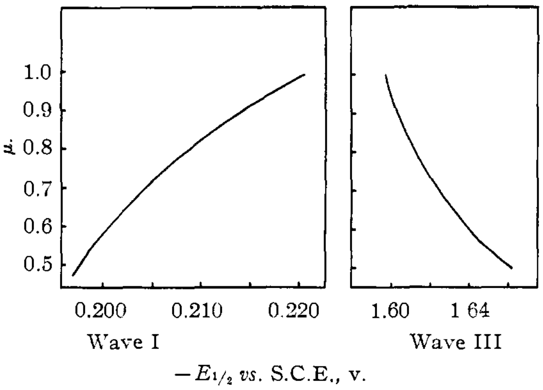

Fig. 2.—Variation of half-wave potential of the diphenyliodonium cation with ionic strength (supporting electrolyte disodium phosphate plus citric acid, *p*H 7, with potassium chloride added to adjust ionic strength).

It is doubtless this influence of ionic strength which is responsible for the breaks observed in the plot of half-wave potential *versus* *p*H for the data secured with the Clark and Lubs buffer solutions (Fig. 3); these occur where the components of the buffer mixtures are changed. The effect is particularly pronounced for wave II when the phthalate buffer replaces the hydrochloric acid–potassium chloride buffer. In buffers of constant ionic strength,[15] half-wave potential varies smoothly and continuously with changing *p*H (Fig. 4) over the range *p*H 2.2 to 8.0.

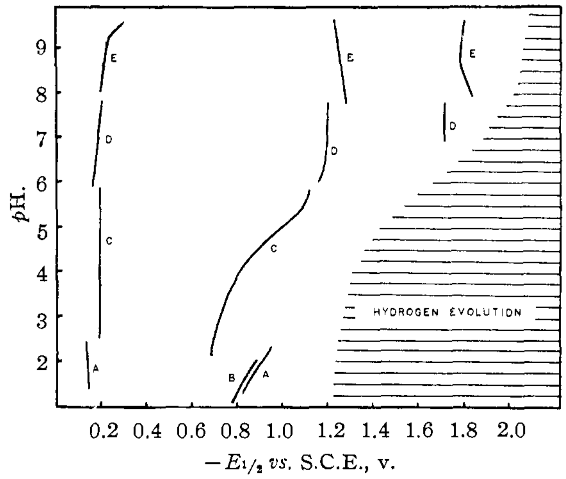

Fig. 3.—Variation of half-wave potential with *p*H: Clark and Lubs buffers· diphenyliodonium cation 0.2 m*M*. A, H_2SO_4–K_2SO_4; B, HCl–KCl; C, phthalate; D, phosphate; E, borate.

Wave I.—Provided that the concentration of diphenyliodonium ion is less than about 1 m*M*, wave I satisfies the customary criteria of polarographic reversibility. The half-wave potential at an apparent *p*H of 8.6 was found to be independent of diphenyliodonium ion concentration from 0.05 to 1 m*M*. Controlled-potential coulometric analyses carried out in an aqueous potassium phosphate buffer of *p*H 8 gave an *n*-value of 1.03 ± 0.03. For a reversible one-electron reduction the slope of a plot of $-E_{d.e.}$ vs. log $i/(i_d - i)$ should be 59.1 mv. at 25°, while experimental measurements at *p*H 3.2 and 8.0 gave slopes between 53 and 55 mv. Since at unit ionic strength $E_{1/2}$ remained constant at -0.204 ± 0.005 v. as the *p*H was varied from 2.2 to 8.0 with 0.4 m*M* diphenyliodonium ion, the electrode reaction may be written

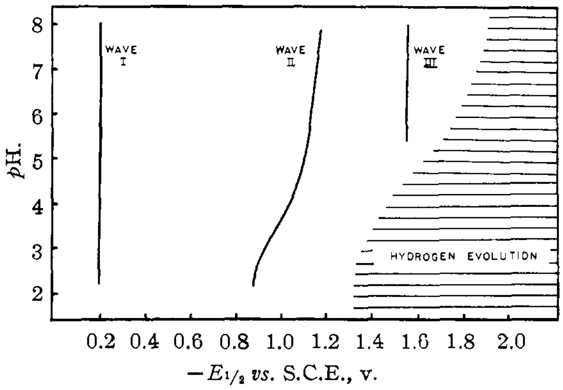

Fig. 4.—Variation of half-wave potential of diphenyliodonium cation with *p*H at unit ionic strength.

$$R\overset{+}{I}R + e \rightleftarrows R\overset{\cdot}{I}R$$

Attempts were made to prepare diphenyliodine by exhaustive controlled-potential electrolysis of solutions of diphenyliodonium tosylate at potentials on the plateau of wave I. However, a solution thus reduced contains no material which was

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[20] O. D. Shreve and E. C. Markham, This Journal, **71**, 2993 (1949).

[21] P. J. Elving, J. C. Komyathy, R. E. VanAtta, C. S. Tang and I. Rosenthal, *Anal. Chem.*, **23**, 1218 (1951).

reducible on the plateau of wave II, indicating that the diphenyliodine formed during the first reduction decomposed before the second electrolysis could be begun. A possible mode of decomposition would be

$$\mathrm{R\dot{I}R} \longrightarrow \mathrm{RI} + \mathrm{R\cdot} \xrightarrow[\mathrm{H_2O}]{\mathrm{C_2H_5OH}} \mathrm{R{-}R} + \mathrm{R{-}H}$$

Ultraviolet absorption assays of hexane extracts of solutions prepared by electrolysis in this manner showed iodobenzene to be present in about the expected amounts, while up to 60% of the possible benzene and 7–10% of the possible biphenyl were also identified. These values are approximate because of the interference of the strong biphenyl absorption with that of benzene. The presence of iodobenzene in the electrolyzed solutions was further confirmed by the appearance of the familiar iodobenzene wave.[12d]

The fact that wave I is reversible at low concentrations of diphenyliodonium ion indicates that the rate of decomposition of diphenyliodine is small at low concentrations. If this decomposition were a first-order reaction, it is evident that reversible behavior would persist even at high concentrations of diphenyliodonium ion (*i.e.*, diphenyliodine), but there is no *a priori* reason to suppose that this is the case. Experimentally, it is found that the half-wave potential of wave I is no longer independent of diphenyliodonium concentration above 1 m*M* (Fig. 5), which shows that the rate of decomposition of diphenyliodine is dependent on its concentration, and therefore cannot be first order.

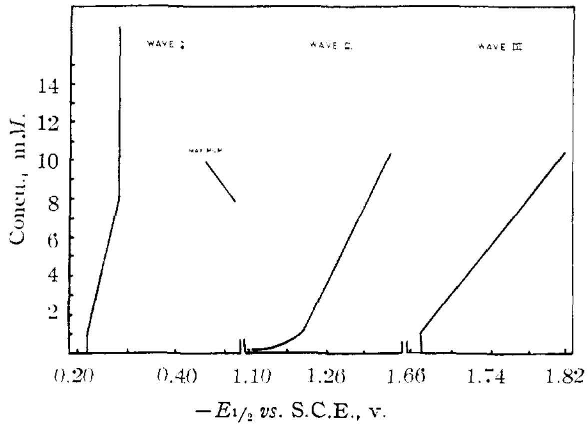

Fig. 5.—Variation of half-wave potential of diphenyliodonium cation with concentration.

The total height of wave I is proportional to diphenyliodonium concentration up to 10 m*M*. At a diphenyliodonium ion concentration of 8 m*M*, however, the wave divides into two parts, Ia and Ib: the height of wave Ia is unaffected by increasing the diphenyliodonium ion concentration above 8 m*M*. This shows that wave I at low concentrations and wave Ia at higher concentrations are due to reduction of diphenyliodonium ion to adsorbed diphenyliodine; wave Ib appears when the electrode surface is "saturated" with diphenyliodine, and represents reduction to dissolved diphenyliodine.

The behavior of diphenyliodonium ion cannot be investigated at concentrations above 10 m*M* because of the appearance of a large maximum which obscures much of the polarogram.

Wave II.—The diffusion current of this wave was proportional to concentration between 0.05 and 10 m*M*; at higher concentrations this wave was obscured by the maximum accompanying wave I. However, the half-wave potential for wave II did not remain constant but was shifted to more negative values with increasing concentration (Fig. 5). Above a concentration of 1 m*M* the relationship was linear, but below 1 m*M* it was not. This continuous shift of half-wave potential with changing concentration is conclusive proof of the existence of a slow step in the half-reaction responsible for wave II. This conclusion is further supported by the fact that the slope of a plot of $-E_{\mathrm{d.e.}}$ *vs.* log $i/(i_{\mathrm{d}} - i)$ was 110 mv., which is appreciably larger than the value corresponding to any reversible reduction.

When *p*H was varied between the values of 2.2 and 8.0, using buffer mixtures of unit ionic strength, the half-wave potential of wave II became more negative with increasing *p*H (see Fig. 4). This argues for a simultaneous take-up of electrons and protons, but both the irreversibility of the wave and the non-linear variation of $E_{1/2}$ with *p*H render impossible any decision as to the number of protons involved.

Controlled potential electrolysis was carried out at −1.35 to −1.40 volts (on the plateau between waves II and III) in aqueous potassium phosphate buffer at *p*H 8. A total of 2.08 electrons was taken up. Since one electron was taken up in the half-reaction corresponding to wave I, a single additional electron is required for the half-reaction taking place on wave II. The fact that the height of wave I is essentially equal to the height of wave II is additional evidence that the numbers of electrons required for the separate reactions are equal.

On the basis of these considerations, the over-all half-reaction occurring at wave II must be

$$\mathrm{R\overset{+}{I}R} + 2e^- + \mathrm{H^+} \longrightarrow \mathrm{RH} + \mathrm{RI}$$

Organomercury Compounds as Possible Intermediates.—The reduction scheme postulated by Colichman and Maffei[6] to account for the addition of the first two electrons to diphenyliodonium ion was

I: $\mathrm{R\overset{+}{I}R} + \mathrm{Hg} + e^- \longrightarrow \mathrm{RHg\cdot} + \mathrm{RI}$
II: "surface-limiting" or "extraneous"
III: $\mathrm{RHg\cdot} + \mathrm{H^+} + e^- \longrightarrow \mathrm{RH} + \mathrm{Hg}$

This mechanism was suggested because the half-wave potential of the wave representing the addition of the second electron to the iodonium cation was similar to that for the corresponding process with phenylmercuric salts. Polarograms of phenylmercuric acetate, secured under the same conditions as were used in studying the diphenyliodonium ion, showed, however, that there are pronounced differences between these waves. For example, the half-wave potential of the second wave of phenylmercuric acetate varied linearly with the phenylmercuric acetate concentration between 0.2 and 1 m*M*; this was not true of the diphenyliodonium wave. Maxima were observed on the wave representing reduction of the phenylmercury radical even when the phenylmercuric ion concentration was as low as 0.4 mM, whereas the corresponding wave on a polarogram of diphenyliodonium ion showed no maximum up to 10 mM. It therefore seems very unlikely that wave II of the diphenyliodonium ion represents the reduction of the phenylmercury radical.

Wawzonek[8a] suggested that Colichman's observations could be explained by the mechanism

$$\begin{aligned} \text{I:}\quad & \mathrm{R\overset{+}{I}R} + e \longrightarrow \mathrm{RI} + \mathrm{R}\cdot \\ & \mathrm{R}\cdot + \mathrm{Hg} \longrightarrow \mathrm{RHg}\cdot \\ & \mathrm{RHg}\cdot \longrightarrow {}^1/_2\mathrm{R_2Hg} + {}^1/_2\mathrm{Hg} \\ \text{II:}\quad & \text{"kinetic process unknown"} \\ \text{III:}\quad & \mathrm{R_2Hg} + 2\mathrm{H}^+ + 2e \longrightarrow 2\mathrm{RH} + \mathrm{Hg} \end{aligned}$$

However, Benesch and Benesch[7] reported that diphenylmercury was not reducible at the dropping electrode in 50% ethanol, and we have confirmed this result. Consequently diphenylmercury is excluded as an intermediate in the polarographic reduction of the diphenyliodonium cation.

It is evident that, if wave I led to the formation of either diphenylmercury or the phenylmercury radical, the solution resulting from a controlled-potential electrolysis of diphenyliodonium ion at a potential on the plateau of wave I would necessarily contain organomercury compounds. The fact that no such compounds could be detected in solutions thus prepared appears to be conclusive refutation of the suggestion that the reduction of diphenyliodonium ion proceeds *via* arylmercury intermediates.

Wave III.—Just as for the two preceding waves, the value of i_d/C was a constant when concentration was varied between 0.05 and 10 mM. The half-wave potential remained constant at -1.67 v.[22] up to concentrations of 1 mM, but at higher concentrations it became more negative, linearly, as concentration was increased (Fig. 5).

The number of electrons taken up at wave III could not be determined coulometrically, since no well-defined plateau exists between this wave and the wave for hydrogen discharge, so that hydrogen is evolved at potentials sufficiently negative to bring about the desired reduction. However, since n already had been shown to be 1 for each of the preceding waves, and since the ratio of wave heights was 1:1:2, a two-electron reduction was assigned to wave III.

The half-wave potential remained constant at -1.560 ± 0.002 volt when pH was varied between the values of 5.6 and 8.0 using the buffer mixtures of unit ionic strength[16] (Fig. 4). At lower pH values wave III was concealed by the final current rise due to hydrogen evolution. The lack of change of half-wave potential with pH indicates that the proton does not take part in the rate-determining step and that the over-all half-reaction is not reversible. This is confirmed by the slope of a plot of $-E_{\mathrm{d.e.}}$ *vs.* log $i/(i_d - i)$ which has a value of 104 mv. There is no published report of any reversible reduction of a carbon–halogen bond at the dropping mercury electrode. The over-all reaction taking place at wave III can therefore be written

$$\mathrm{R\overset{+}{I}R} + 4e^- + \mathrm{H}^+ \xrightarrow{\text{slow}} \mathrm{RH} + \mathrm{R}^- + \mathrm{I}^-$$

$$\mathrm{R}^- + \mathrm{H}^+ \xrightarrow{\text{fast}} \mathrm{RH}$$

The postulation that wave III corresponds to the reduction of iodobenzene is confirmed by the fact that the half-wave potential for iodobenzene is identical with that for wave III in the same buffer system, within the limits of error of the measurement. Further, the reported half-wave potentials for iodobenzene in 66% ethanolic tetraethylammonium bromide[12a] and in 90% ethanolic lithium chloride–potassium acetate[13] are very close to the value obtained for wave III in the present work. The similarity of half-wave potentials and of values of $E_{3/4} - E_{1/4}$ make it extremely likely that wave III corresponds to the reduction of iodobenzene. It has been reported by other investigators[12a,d] that iodobenzene undergoes a two-electron reduction at the dropping electrode.

Influence of Mercury Pressure on Wave Height.—The data in Table I were obtained in an effort to determine whether the heights of the waves in the polarogram of diphenyliodonium chloride are diffusion controlled. The values for $i_d/h_{\mathrm{corr}}{}^{1/2}$ for the first wave show only a slight increase with increasing mercury pressure, indicating that the height of this wave is certainly predominantly diffusion controlled, but that it may have a small kinetic factor.[23] The values determined at -1.4 volts show a decided increase with increase of mercury pressure; the height of wave II is therefore in part kinetically controlled.

TABLE I

INFLUENCE OF MERCURY PRESSURE ON WAVE HEIGHT[a]

	$h_{\mathrm{corr.}}$, cm.	t, sec.	i_d, microamp.	$i_d/h_{\mathrm{cor.}}{}^{1/2}$
Wave I	19.0	7.24	1.49	0.342
-0.5 v.	29.0	4.84	1.85	.344
	39.0	3.63	2.18	.350
	49.0	2.88	2.48	.354
Wave II	19.0	6.28	1.21	.277
-1.4 v.	29.0	4.18	1.62	.301
	39.0	3.15	1.95	.312
	49.0	2.45	2.32	.330

[a] Diphenyliodonium chloride (1 mM) in 1:1 ethanol: water containing 0.1 M tetraethylammonium phosphate; apparent pH 8.6.

Effects of Substituents.—A study of the effects of substituents on the electroreduction of diphenyliodonium salts is reported in the following article.

Diphenyliodine as an Intermediate in Copper-catalyzed Reactions.—Once it has been demonstrated that diphenyliodine may be formed in the electroreduction of the diphenyliodonium cation, it is reasonable to ask if diphenyliodine is an intermediate in reactions involving chemical reducing agents. It now seems a rational hypothesis that diphenyliodine is formed in the decomposition of diphenyliodonium chloride when catalyzed by cuprous chloride.

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[22] In the tetraethylammonium phosphate buffer whose composition is given in the legend of Fig. 5, as noted below, a different value was obtained in buffers of unit ionic strength.

[23] This is probably a reflection of the partial decomposition of diphenyliodine in the diffusion layer surrounding the drop. Naturally this process would have no effect on the height of the first wave, but it would lead to a decrease in the height of the second wave, in agreement with what is observed.

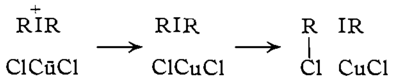
In the article by Beringer and co-workers[2] on this reaction a sequence was proposed

$$\mathrm{CuCl} + \mathrm{Cl}^- \rightleftharpoons \mathrm{CuCl_2}^-$$

$$\text{(free ions)}\quad R_2\overset{+}{I} + \mathrm{CuCl_2}^- \rightleftharpoons R_2\overset{+}{I}\,\mathrm{CuCl_2}^- \quad \text{(ion pair)}$$

$$R_2\overset{+}{I}\,\mathrm{CuCl_2}^- \longrightarrow \mathrm{RCl} + \mathrm{RI} + \mathrm{CuCl}$$

It is now proposed that this last step proceeds as



$$\begin{array}{c} R\overset{+}{I}R \\ \mathrm{ClCuCl} \end{array} \longrightarrow \begin{array}{c} \mathrm{RIR} \\ \mathrm{ClCuCl} \end{array} \longrightarrow \begin{array}{cc} R & \mathrm{IR} \\ | & \\ \mathrm{Cl} & \mathrm{CuCl} \end{array}$$

As electron-transfer reactions not involving bond-breaking generally have only a low energy of activation, the formation of diphenyliodine would be expected to proceed rapidly. The diphenyliodine and the cupric chloride may react in their solvent cage or on collision after separation. Alternatively, if phenyl free radicals are formed from diphenyliodine, they might be converted to chlorobenzene by cupric chloride.

For the ideas expressed above we are in part indebted to investigators of the closely related Sandmeyer and Meerwein reaction of diazonium salts. Cowdrey and Davies[24] have reviewed the Sandmeyer reaction and have concluded that the effective catalytic species is the dichlorocuprate (I) anion. Kochi[25] and Dickerman and co-workers[26] have proposed that the initial step is electron transfer from anion to cation.

$$\mathrm{RN_2}^+\,\mathrm{CuCl_2}^- \longrightarrow \mathrm{RN_2}\cdot\,\mathrm{CuCl_2}$$

Further, both Kochi[10d] and Reutschi and Trumpler[10d] have shown coulometrically that the diazonium ion can accept one electron.

It is not clear whether the subsequent decomposition

$$\mathrm{RN_2}\cdot\,\mathrm{CuCl_2} \longrightarrow \mathrm{RCl} + \mathrm{N_2} + \mathrm{CuCl}$$

occurs in one or two steps. However, some phenyl radicals add to double bonds or abstract hydrogen from solvent and have thus apparently escaped from the solvent cage.

From the above it may be predicted that an addition reaction or a displacement reaction will be catalyzed by cuprous ion when the nucleophilic reagent complexes with the cuprous ion and when the electrophilic reagent easily can accept one electron.

Acknowledgments.—The authors wish to acknowledge the helpful discussions with Dr. Joseph Steigman and Dr. Milton Allen during the early stages of this work and with Dr. Jay K. Kochi and Dr. S. Carleton Dickerman on details of the mechanism of copper catalysis.

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BROOKLYN 1, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. VI. Polarography of Substituted Diphenyliodonium Salts[1,2]

BY H. ELIZABETH BACHOFNER, F. MARSHALL BERINGER AND LOUIS MEITES

RECEIVED AUGUST 9, 1957

Polarograms of substituted iodonium salts showed the effects of the size, electronegativity, charge and reducibility of the substituents on the three reduction waves.

The preceding paper[2] of this series on the chemistry of diaryliodonium salts surveyed the literature on the electroreduction of 'onium salts and showed that very probably the polarographic reduction of the diphenyliodonium cation proceeded as

$$\text{Wave I:}\quad R\overset{+}{I}R + e^- \rightleftharpoons \mathrm{RIR}$$

$$\text{Wave II:}\quad R\overset{+}{I}R + 2e^- + H^+ \longrightarrow \mathrm{RH} + \mathrm{RI}$$

$$\text{Wave III:}\quad R\overset{+}{I}R + 4e^- + H^+ \xrightarrow{\text{slow}} \mathrm{RH} + R^- + I^-$$

$$R^- + H^+ \xrightarrow{\text{fast}} \mathrm{RH}$$

In this paper the effects of substituents on these three waves are reported.

Experimental

Solvents, buffers, supporting electrolytes and unsubstituted diphenyliodonium salts were prepared as described.[2] Substituted diphenyliodonium salts were prepared by known methods,[3] though in some cases the individual salts have not been reported as yet.[4] Cyclic iodonium salts in which the 2- and 2'-positions of the diphenyliodonium cation are joined by a methylene bridge or $-(CH_2)_3-$ were kindly made available by Dr. Reuben Sandin of the University of Alberta, Edmonton, Canada.[5] Polarograms were recorded with a Leeds and Northrup Type E Electrochemograph, as described.[2] Unless otherwise specified polarograms were run with 0.4 mM iodonium salt and 0.1 M tetraethylammonium phosphate in 1:1 ethanol–water of apparent pH 8.6. Half-wave potentials are referred to the saturated calomel electrode (S.C.E.).

Results and Discussion

Table I lists the three half-wave potentials of a number of substituted diphenyliodonium salts. These values are plotted against the values of Hammett's sigma constant in Fig. 1.

For either the unsubstituted iodonium cation or substituted cations containing strongly electron

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(1) Taken from the doctoral dissertation of Miss Hilde Elizabeth Bachofner, submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June, 1957.

(2) Preceding paper (on the electroreduction of unsubstituted diphenyliodonium salts): H. Elizabeth Bachofner, F. Marshall Beringer and Louis Meites, THIS JOURNAL, **80**, 4269 (1958).

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