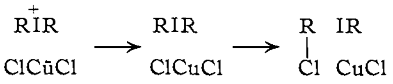
In the article by Beringer and co-workers[2] on this reaction a sequence was proposed

$$CuCl + Cl^- \rightleftharpoons CuCl_2^-$$

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

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

It is now proposed that this last step proceeds as



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

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.

$$RN_2^+\,CuCl_2^- \longrightarrow RN_2\cdot\,CuCl_2$$

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

$$RN_2\cdot\,CuCl_2 \longrightarrow RCl + N_2 + CuCl$$

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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[24] W. A. Cowdrey and D. S. Davies, *J. Chem. Soc.*, Supplements, 548 (1949); *Quart. Revs.*, **6**, 358 (1952).

[25] J. K. Kochi, This Journal, **77**, 5090 (1955); **78**, 1228 (1956); **79**, 2942 (1957).

[26] S. C. Dickerman, K. Weiss and A. K. Ingberman, *J. Org. Chem.*, **21**, 380 (1956); This Journal, **80**, 1904 (1958).

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

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

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

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

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

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).

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

[4] F. M. Beringer, *et al.*, an article on the synthesis of substituted diphenyliodonium salts has been submitted to This Journal.

[5] J. D. Collette, D. McGreer, R. Crawford, F. Chubb and R. B. Sandin, *ibid.*, **78**, 3819 (1956).

TABLE I

SUBSTITUTED DIPHENYLIODONIUM SALTS

Substituents	Half-wave potentials,[a] v. Wave I	Wave II	Wave III
4-NH_2	−0.200	−1.120	−1.695
4-OCH_3	− .186	−1.120	−1.660
4,4'-$(OCH_3)_2$	− .205	−1.122	−1.650
4,4'-$(C_6H_{11})_2$	− .093[b] − .292[c]	−1.200[d]	−1.676
4,4'-$[C(CH_3)_3]_2$	− .110[b] − .300[c]	−1.160[d]	−1.675
sym-$(CH_3)_6$[k]	− .243	−1.175	−1.672
2-CH_3	− .180[l]	−1.065[l]	−1.640[l]
4,4'-$(CH_3)_2$	− .192	−1.131	−1.672
None	− .193	−1.142	−1.645
4-F	[e]	−1.128	−1.615
4,4'-F_2	− .200	−1.135	−1.615
4,4'-Cl_2	− .200	−1.132	−1.550
4-Br	− .190	−1.148	−1.575
4,4'-Br_2	− .202	−1.150	−1.557
3-Br	− .185	−1.138	−1.410 −1.645
4,4'-I_2	− .190	−1.132	[f]
2-NO_2	[g]	[h]	−1.69[i]
3,3'-$(NO_2)_2$	− .20	[h]	−1.72[i]
4-NO_2	− .21	[h]	−1.70[i]
2-COOH	− .512[l]	−0.955[l]	−1.3[l] −1.645[l]
3,3'-$(COOH)_2$	− .45	−1.13	−1.588

[a] In 1:1 ethanol–water with 0.4 m*M* iodonium salt and 0.1 *M* tetraethylammonium phosphate supporting electrolyte of apparent *p*H 8.6. [b] Adsorption wave. [c] True wave. [d] The half-wave potential may be influenced by adsorption on wave I. [e] Obscured by the anodic wave of the iodide ion. [f] The wave was a composite of those for iodobenzene and *p*-diiodobenzene. [g] Varies with concentration. [h] Obscured by the reduction of the nitro group. [i] Because of the reduction of the nitro group to the amino group, these values correspond to the half-wave potentials for the 2-NH_2, 3-NH_2, and 4-NH_2 groups, respectively. [k] The 2,4,6,-2',4',6'-hexamethyldiphenyliodonium cation. [l] *o*-Substituents frequently give anomalous values for half-wave potentials; see ref. 8.

releasing or withdrawing substituents, the half-wave potentials for wave I fell within the narrow range of −0.185 to −0.205 v. It is apparent that the ease of the first step in the reduction of the diphenyliodonium cation is not strongly influenced by the nature of the substituent in the benzene ring. Iodonium cations with bulky hydrocarbon substituents are discussed separately below since adsorption of the substituted diphenyliodine produced by reduction of the iodonium cation caused wave I to consist of two portions, an adsorption pre-wave and a diffusion-controlled normal wave.

The half-wave potential of wave II is largely unaffected by the nature of the substituents. Since the nitro group is reducible at the dropping mercury electrode at potentials close to those for wave II, the nitro-substituted iodonium cations are discussed separately. Half-wave potentials for both waves I and II for the 2-carboxy- and the 3,3'-dicarboxydiphenyliodonium cations differ markedly from those for most of the substituted diphenyliodonium cations. Therefore these two cations also are discussed separately.

In agreeement with our suggestion that wave III corresponds to the reduction of iodobenzene and with previously reported work on the polarography of iodobenzenes,[6,7] a marked influence of substituent on the half-wave potential of wave III was demonstrated. Electron-releasing substituents hindered addition of electrons, as shown by a more negative half-wave potential; electron-attracting substituents facilitated reduction, as shown by the less negative half-wave potential.

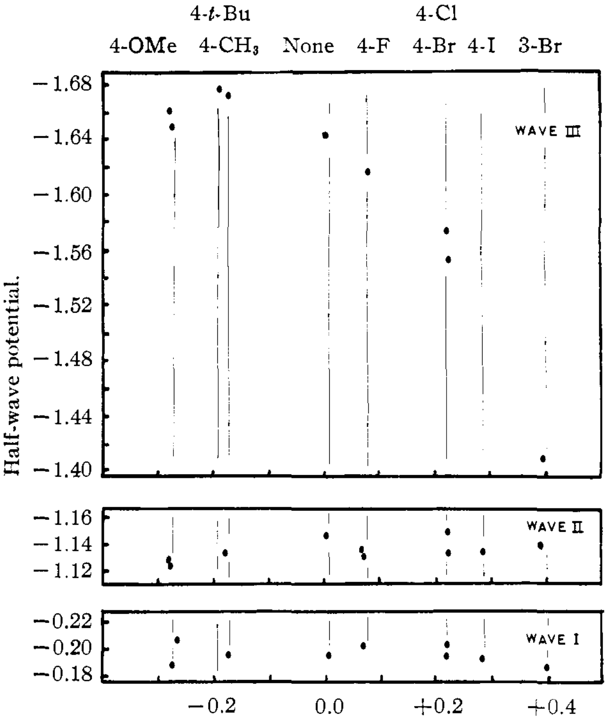

Fig. 1.—Variation of half-wave potential of substituted diphenyliodonium cations with Hammett's sigma constant.

Adsorption.—Adsorption was demonstrated for diphenyliodines with bulky aliphatic substituents, namely, 4,4'-dicyclohexyl- and for 4,4'-di-*t*-butyldiphenyliodine (Table II, Fig. 2).

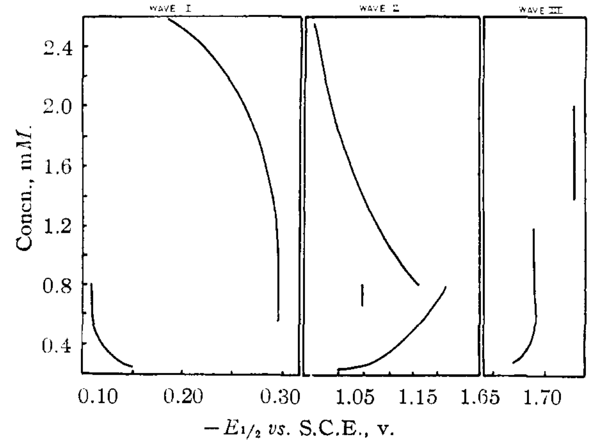

Fig. 2.—Variation of half-wave potential of 4,4'-di-*t*-butyldiphenyliodonium cation with concentration.

At concentrations up to 0.4 m*M*, normal ad· sorption phenomena were observed. When ad·

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[6] E. Gergely and T. Iredale, *J. Chem. Soc.*, 3226 (1953).

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

TABLE II

ADSORPTION IN REDUCTION OF SUBSTITUTED DIPHENYLIODONIUM CATIONS[a]

Concn.	Adsorption wave I i_d	Adsorption wave I $E_{1/2}$	Normal wave I i_d	Normal wave I $E_{1/2}$	$\Sigma(i_d)/C$
4,4'-Dicyclohexyldiphenyliodonium cation					
0.10	0.20	−0.112	..	.....	2.00
.20	.40	− .108	..	.....	2.00
.30	.38	− .104	0.20	−0.290	1.93
.40	.39	− .096	.37	− .295	1.90
.50	.39	− .100	.57	− .292	1.92
4,4'-Di-*t*-butyldiphenyliodonium cation					
0.096	0.20	−0.130	..	.....	2.08
.12	.24	− .130	..	.....	2.00
.24	.39	− .120	0.15	−0.305	2.25
.36	.40	− .110	.37	− .295	2.14
.48	.40	− .110	.58	− .300	2.04
.60	.40	− .110	.90	− .295	2.17

[a] Concentration is in millimoles/liter; current is in microamperes; potential is in volts *vs.* the saturated calomel electrode.

sorption occurred, wave I was split into two portions: an adsorption pre-wave whose height was independent of the concentration above a certain minimum value, and a normal reduction wave. The pre-wave was conclusively shown to be the result of an adsorption process by the fact that its height varied directly with the corrected pressure of mercury (Table III).

TABLE III

INFLUENCE OF MERCURY PRESSURE ON HEIGHT OF PRE-WAVE I[a]

$h_{cor.}$, cm.	i_a, microamp.	$i_a/h_{cor.}$
45.7	0.46	0.0101
40.7	.42	.0103
35.6	.37	.0104
30.5	.33	.0108
25.4	.26	.0102

[a] 0.2 m*M* 4,4'-di-*t*-butyldiphenyliodonium chloride in 0.1 *M* tetraethylammonium phosphate, apparent *p*H 8.6.

When both waves I were present, the sum of their diffusion currents was proportional to the square root of the corrected mercury pressure. The total diffusion current (sum of the pre-wave and the normal one) was proportional to the concentration of the iodonium salt. The value of i_d/C for the normal wave decreased with decreasing concentration of iodonium cation until at concentrations of 0.2 m*M* for the 4,4'-di-*t*-butyldiphenyliodonium cation and of 0.16 m*M* for the 4,4'-dicyclohexyldiphenyliodonium cation, the normal wave disappeared and only the adsorption wave was observed.

Wave II of the 4,4'-di-*t*-butyldiphenyliodonium cation also split into two parts as the concentration of this ion was raised above about 0.4 m*M*. The height of the new pre-wave which appeared was independent of the pressure of mercury above the capillary (Table IV); this is the characteristic behavior of a kinetic wave. The most likely rate-controlling process is the decomposition of the diaryliodine to give a *t*-butylphenyl radical which is reducible at a less negative potential than the undecomposed diaryliodine

$$R\dot{I}R \longrightarrow R\cdot + RI$$
$$R\cdot + H^+ + e^- \longrightarrow RH$$

Although similar behavior would be expected with the unsubstituted diphenyliodonium cation, this could not be demonstrated. However, the same splitting of wave II was noted with a diphenyliodonium cation in which the two *ortho* positions are linked with a methylene bridge (see below). As this compound also exhibits adsorption, it is possible that the behavior is related to adsorption.

TABLE IV

VARIATION OF DIFFUSION CURRENT OF PRE-WAVE ON WAVE II OF 4,4'-DI-*t*-BUTYLDIPHENYLIODONIUM CATION[a]

$h_{cor.}$, cm.	Diffusion current (μ amp.) Pre-wave	Normal wave	Total	(i_d) total $/h^{1/2}$
50.5	0.48	1.20	1.68	0.236
45.5	.47	1.09	1.56	.232
40.5	.48	0.94	1.42	.223
35.5	.50	.82	1.32	.221
30.5	.54	.65	1.19	.216
25.5	.55	.53	1.08	.212

[a] 0.6 m*M* 4,4'-di-*t*-butyldiphenyliodonium chloride in 0.1 *M* tetraethylammonium phosphate, apparent *p*H 8.6.

At concentrations higher than 0.6 m*M*, the pre-wave of wave II merged with a sloping shoulder which developed on the plateau between waves I and II, and a maximum appeared at a potential about 0.1 volt more negative than wave II. Concurrently with the appearance of the maximum, values for i_d/C of wave II decreased and the half-wave potential for wave III was shifted to more negative values. The variation of half-wave potential with concentration for 4,4'-di-*t*-butyldiphenyliodonium cation is shown in Fig. 2.

Surface phenomena also were noted for the unsubstituted diphenyliodonium cation and for dimesityliodonium cation. At concentrations of 10 and 4 m*M*, respectively, wave I was split into what appeared to be a pre-wave and a normal adsorption wave, and maxima were observed on wave II.

The effective areas of the adsorbed species were calculated by the method of Benesch and Benesch[8] and Meites,[9] and are given in Table V. The areas obtained for the two 4,4'-disubstituted diphenyliodines are of the expected order of magnitude, but those calculated for diphenyliodine and dimesityliodine are unexpectedly small. It is possible that the adsorbed films of the latter two radicals are not unimolecular in thickness, as is assumed in the calculations.

TABLE V

CALCULATED AREAS OF ADSORBED DIARYLIODINES

Species	Area, sq. Å.
Diphenyliodine	1.0
Dimesityliodine	2.5
4,4'-Di-*t*-butyldiphenyliodine	48
4,4'-Dicyclohexyldiphenyliodine	47

Electrocapillary Curves.—Additional evidence for adsorption was obtained from electrocapillary curves secured in aqueous tetraethylammonium phosphate buffer solution. Typical curves for

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[8] R. E. Benesch and R. Benesch, *J. Phys. Chem.*, **56**, 648 (1952).

[9] L. Meites, THIS JOURNAL, **76**, 5927 (1954).

TABLE VI

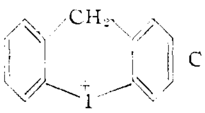
HALF-WAVE POTENTIALS OF SALTS I AND II[a]

		Wave I		Wave II		
	Concn., mM	Adsorption	Normal	First	Second	Wave III
Salt I	0.2	−0.13	.....	.....	−1.15	−1.57
	.4	− .12	− .30	.....	−1.22	−1.57
	.6	− .12	− .31	−0.98	−1.25	−1.57
	.8	− .11	.29	0.97	−1.27	−1.58
Salt II	Approx. 0.02	− .14	.....	.....	−1.25	−1.63
Diphenyliodonium cation	0.4	.....	− .193	−1.142		−1.645
4,4'-Di-*t*-butyldiphenyliodonium cation	.4	− .110	− .300	.....	−1.160	−1.675
	.6	− .110	− .295	−1.08	−1.215	−1.675

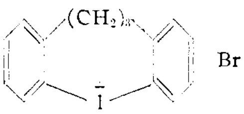
[a] In 1:1 ethanol–water containing 0.1 M tetraethylammonium phosphate supporting electrolyte of apparent *p*H 8.6.

solutions containing diphenyliodonium ion and 4,4′-di-*t*-butyldiphenyliodonium ion are shown in Fig. 3. On each of these curves there is a pronounced discontinuity at a potential which is a few hundredths of a volt less negative than the half-wave potential of wave I of the ion involved: *i.e.*, at a potential which corresponds to the first appearance of significant amounts of the diaryliodine at the electrode surface. In each case the adsorption of the diaryliodine results in a considerable decrease of the interfacial tension, and this persists until a potential is reached at which the diaryliodine is further reduced to the substituted iodobenzene, whereupon the electrocapillary curves merge. This behavior provides strong confirmation of the adsorption of these radicals on the electrode surface.

Cyclic Iodonium Salts.—It was of interest to investigate how the configuration of the ring system of the iodonium cation affect the polarograms.



Salt I



Salt II

Table VI compares half-wave potentials for salts I and II with these of the unsubstituted diphenyliodonium and the 4,4′-di-*t*-butyldiphenyliodonium cations. The behavior of salt I is similar in all respects to that of the diphenyliodinium cations with bulky aliphatic substituents. The solubility of compound II was so low (saturated solution in 95% ethanol at room temperature was about 0.04 mM) that adsorption could not be demonstrated. However, the value of −0.14 v. for the half-wave potential of wave I indicates that this is probably an adsorption pre-wave since its potential corresponds well with that of adsorption pre-waves of the 4,4′-di-*t*-butyldiphenyliodonium and the 4,4′-di-*p*-cyclohexyldiphenyliodonium cations.

Nitro-substituted Diphenyliodonium Cations.—As the nitro group is reducible at the dropping mercury electrode, the polarography of the nitro-substituted diphenyliodonium cations is somewhat more complex than that of the iodonium cations previously mentioned. It is reported[10] that the nitro group is reduced to the amine by the addition of six electrons (in waves of 4 and 2 electrons, respectively) at a *p*H less than 5, but that at higher *p*H value, reduction proceeds only to the hydroxylamine which is stable to further reduction. Wave II is a composite of the normal wave II of the iodonium cation with the two reduction waves for the nitro group. The relative wave heights confirm the reduction by seven electrons in this step. It appears that reduction to the amine takes place even at an apparent *p*H of 8.6. Table VII lists the half-wave potentials for the nitro-substituted diphenyliodonium cations studied.

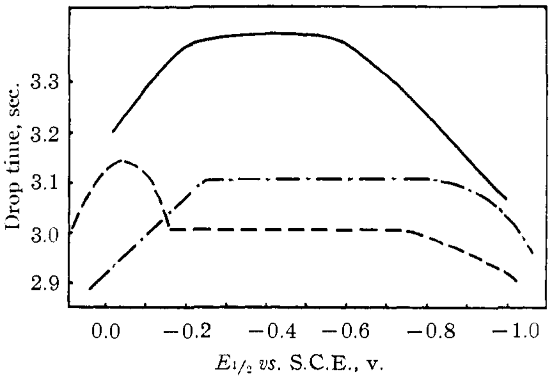


Fig. 3.—Electrocapillary curve determined in tetraethylammonium phosphate: ——, supporting electrolyte; — — —, supporting electrolyte containing 1 mM diphenyliodonium cation; — - —, supporting electrolyte containing 1 mM 4,4′-di-*t*-butyldiphenyliodonium cation.

TABLE VII

NITRO-SUBSTITUTED DIPHENYLIODONIUM CATIONS[a]

	Half-wave potentials, v.		
Substituents	Wave I	Wave II	Wave III
2-NO_2	[b]	[c]	−1.69
3,3′-$(NO_2)_2$	−0.20	[c]	−1.72
4-NO_2	− .21	[c]	−1.70
None	− .193	−1.142	−1.645

[a] In 1:1 ethanol–water with 0.1 M tetraethylammonium phosphate supporting electrolyte of apparent *p*H 8.6. [b] Varies with concentration. [c] Obscured by reduction of the nitro group.

Waves I for the 3,3'-dinitro and for the 4-nitro compound have the expected half-wave potential. The half-wave potential for the 2-nitro compound varies with concentration and is less negative at higher concentrations and more negative at lower concentrations. Wave II could not be studied as it was obscured by the waves for the reduction of the nitro groups. Wave III had a normal appearance for all three compounds. Although the nitro

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(10) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, Interscience Publishers, New York, N. Y., 1952, p. 748.

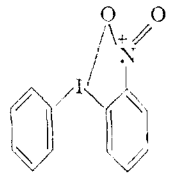
group is strongly electron-attracting, the shift in half-wave potential of wave III is typical of a strongly electron-donating substituent. At a potential sufficiently negative to reduce the substituted iodobenzene, all nitro groups have been reduced to the amino group which is strongly electron donating. As shown in Table VIII, the wave heights of the 3,3′-dinitro and the 4-nitro compound have the expected ratio, assuming a 6-electron reduction of the nitro group.

TABLE VIII

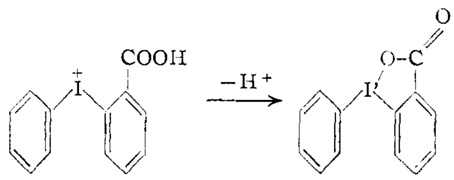
RATIO OF DIFFUSION CURRENTS OF NITRO-SUBSTITUTED DIPHENYLIODONIUM CATIONS

Substituents	Theoretical Wave I	Theoretical Wave II	Theoretical Wave III	Found Wave I	Found Wave II	Found Wave III
2-NO_2	1	7	2	0.13	7.81	2
3,3′-$(NO_2)_2$	1	13	2	0.95	12.2	2
4-NO_2	1	7	2	1.1	7.0	2

For the 2-nitro compound, the ratio of wave heights makes it appear that the concentration of iodonium cation has been reduced markedly. A possible explanation is the formation of a five-membered ring through the iodine atom and one oxygen atom of the nitro group. Apparently this substance takes up electrons less easily than the iodonium cation. The sum of the diffusion currents for waves I and II agrees with a total electron take-up of eight, as would be expected for reduction to the amino compound. Since wave I is diffusion controlled (wave height proportional to $h^{1/2}$) this behavior cannot be attributed to adsorption or kinetic effects.



The 2-Carboxy- and the 3,3′-Dicarboxydiphenyliodonium Cations.—By analogy with the behavior of the 2-nitrodiphenyliodonium cation it was felt that the conjugate base of the 2-carboxydiphenyliodonium cation (formed in the buffer of *p*H 8.6) should give a cyclic compound which would be less easily reduced.

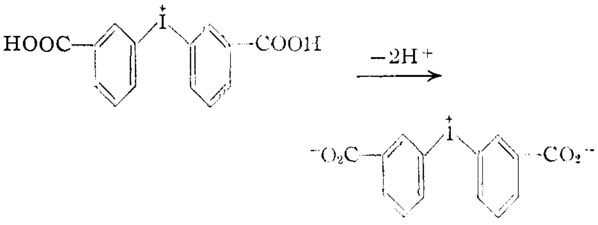


This prediction as to the decreased ease of reduction is borne out by the results in Table IX. The explanation of ring formation cannot be invoked to rationalize the decreased ease of reduction of the anion derived from the 3,3′-dicarboxydiphenyliodonium cation in the buffer solution.

TABLE IX

HALF-WAVE POTENTIALS OF THE CARBOXY-SUBSTITUTED DIPHENYLIODONIUM CATIONS

Substance	$E_{1/2}$, volts Wave I	Wave II	Wave III
Diphenyliodonium cation	−0.193	−1.142	−1.645
2-Carboxydiphenyliodonium cation	− .512	−0.955	−1.3 (20%) −1.645 (80%)
3,3′-Dicarboxydiphenyliodonium cation	− .45	−1.13	−1.588



It is not known whether electrostatic considerations are adequate to account for the lessened reducibility of this material.

The double wave III for the 2-carboxydiphenyliodonium salt indicates that the product of reduction of wave II split to form about 80% iodobenzene and about 20% 2-iodobenzoic acid.

Half-wave potentials are listed in Table IX.

Acknowledgments.—We wish to thank the many students[4,5] who supplied the iodonium salts used in this work.

BROOKLYN 1, N. Y.