Electroreduction of Diphenyliodonium, Dibenziodolium, and 4,5-Phenanthryleneiodonium Ions[1]

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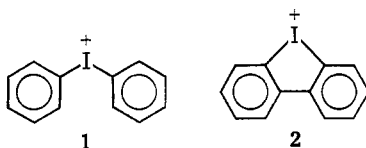
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The electroreduction of diphenyliodonium (1), dibenziodolium (2), and 4,5-phenanthryleneiodonium (3) ions has been investigated by both polarography at the dropping mercury electrode and by coulometry at controlled potential. Ions 1 and 2 appear to undergo three reduction processes corresponding to the total uptake of one, two, and four electrons, respectively. The polarographic behavior of ion 1 was affected by its concentration and by the nature and concentration of the supporting electrolyte and the maximum suppressor. For all three species controlled-potential electrolysis on wave I gave mercury-containing products. Ion 3 appears to undergo only two electroreduction processes, corresponding to the uptake of two and of three electrons. An attempt is made to explain this result in terms of the structure and behavior of free-radical intermediates.

The electrochemical reduction of iodonium salts has been investigated by three different groups over the past 20 years,[2,3] and at least four different schemes have been proposed to account for the processes occurring at the dropping mercury electrode in the course of the reduction.[2-4] Further, some question has recently arisen[3] concerning the products of the electrochemical reduction of the diphenyliodonium ion.

The aim of the present work was to clarify and compare the processes occurring during the electroreduction of the diphenyliodonium ion (species 1), the dibenziodolium ion (species 2), and the 4,5-phenan-

thryleneiodonium ion (species 3) at the mercury
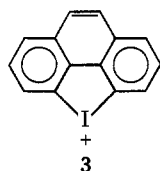
cathode. To accomplish this, we have employed reduction at the dropping mercury electrode as well as coulometry at controlled potential.

Results

Diphenyliodonium Ion (1). Polarography.—The polarogram of 1 was sensitive to its concentration and to the nature and concentration of the supporting electrolyte and of the maximum suppressor. A previous report[2b] stated that in a tetraethylammonium phosphate (TEAP) buffer of pH 7.45 (less than $1 \times 10^{-3} M$ in 1) the polarogram consisted of three waves whose heights were in the ratio 1:1:2. Up to concentrations of $8 \times 10^{-3} M$ in 1 the polarogram did not change significantly except for slight shifts in half-wave potentials. The polarogram was reported to be unaffected by

changes in the supporting electrolyte. That work was carried out by using 0.02% gelatin as a maximum suppressor. In the present work 0.002% Triton x-100 (a polyethylene glycol ether of monoisooctyphenol) was employed, but all other conditions were identical. These results are reported in Table I.

In the TEAP buffer at concentrations of 1 below $1 \times 10^{-3} M$ the polarogram consisted of only two waves (waves IA and II/III) whose half-wave potentials were -0.13 and -1.36 V (*vs.* Ag/AgCl), respectively. The wave heights were in the ratio 1:3. In the citrate buffer[5] at similar concentrations of 1 the polarogram showed three waves, IA, II, and III, whose heights were in the ratio 1:1:2 and whose half-wave potentials were -0.13, -1.17, and -1.53 V, respectively. As the concentration of 1 was increased beyond $1 \times 10^{-3} M$, another wave (IB) appeared at -0.53 V. Above this concentration the height of wave IA remained virtually constant while wave IB increased in height. The combined height of waves IA and IB increased proportionally with the concentration of 1. This effect was observed in both the TEAP and citrate buffers. In TEAP at a $4 \times 10^{-3} M$ concentration of 1 wave II/III divided into two waves of equal height (waves II and III) whose half-wave potentials were -1.03 and -1.53 V, respectively. The $E_{1/2}$ of wave 1A was shifted to less negative potentials with increasing concentration of 1. At a $5 \times 10^{-4} M$ concentration of 1 in TEAP the slope of wave IA was 91.02 mV.

Measurements correlating the heights of waves IA and IB with mercury column height are reported in Table II. These results indicate that when only wave 1A appears, its height varies as does $(h_{corr})^{1/2}$. When both IA and IB appear, the height of IA varies more closely as does h_{corr}. The height of waves IA and IB combined varies approximately as does $(h_{corr})^{1/2}$.

In order to compare our present results with those previously reported,[2b] we recorded the polarogram of 1 in both buffer systems employing 0.02% gelatin as a suppressor (Table I). Wave IB was completely suppressed by the gelatin even at concentrations of 1 as high as 0.010 M. At a concentration of 1 of $5 \times 10^{-4} M$ in TEAP only two waves (IA and II/III) were observed when no suppressor whatever was present.

Diphenyliodonium Ion (1). Electrolysis at Controlled Potential.—Electrolyses were carried out at a potential on the plateau between waves IA and IB

(1) Taken from the dissertation of S. Messing in partial fulfillment of the degree of Doctor of Philosophy (Chemistry), 1972.

(2) (a) E. L. Colichman and H. P. Maffei, *J. Amer. Chem. Soc.*, **73**, 2744 (1951); (b) H. E. Bachofner, F. M. Beringer, and L. Meites, *ibid.*, **80**, 4269 (1958).

(3) J. A. Azoo, F. G. Coll, and J. Grimshaw, *J. Chem. Soc. C*, 2521 (1969).

(4) S. Wawzonek, *Anal. Chem.*, **26**, 65 (1954).

(5) P. J. Elving, J. M. Markowitz, and I. Rosenthal, *ibid.*, **28**, 1179 (1956).

TABLE I
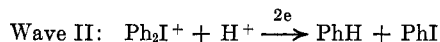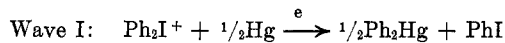#### HALF-WAVE POTENTIALS ($E_{1/2}$) OF IODONIUM SALTS

Ion	[Ion]^a	pH	Electrolyte	IA	IB	II	II/III^b	III	Ratio^c of I:II:III
1	4×10^{-4}	7.45	0.1 M TEAP	−0.13			−1.36		1:3
1	1×10^{-3}	7.45	0.1 M TEAP	−0.13			−1.35		1:3
1	2×10^{-3}	7.45	0.1 TEAP	−0.08	−0.53		−1.35		1:3
1	4×10^{-3}	7.45	0.1 M TEAP	−0.06	−0.53	−1.03		−1.44	1:1:2
1	1×10^{-3}	8.0	0.003 M Citrate	−0.13		−1.17		−1.53	1:1:2
1	2×10^{-3}	8.0	0.003 M Citrate	−0.10	−0.53	−1.22		−1.53	1:1:2
1	3×10^{-3}	8.0	0.003 M Citrate	−0.09	−0.53	−1.22		−1.53	1:1:2
1^d	5×10^{-4}	7.45	0.1 M TEAP	−0.20			−1.25		1:3
1^e	5×10^{-4}	7.45	0.1 M TEAP	−0.15		−1.03		−1.43	1:1:2
1^e	1×10^{-3}	7.45	0.009 M Citrate	−0.14		−1.00		−1.47	1:1:2
2	$4.0\text{–}8.0 \times 10^{-4}$	7.45	0.1 M TEAP		−0.60		−1.20		1:3
2	4×10^{-4}	7.45	0.009 M Citrate		−0.62	−1.17		−1.42	1:1:2
2	8×10^{-4}	8.0	0.003 M Citrate		−0.65	−1.17		−1.46	1:1:2
3^d	$\sim 1 \times 10^{-4}$	8.0	0.05 M Potassium phosphate		+0.016	−0.78			1:1

^{a} In mol/l. ^{b} Actually a composite of waves II and III. ^{c} When both waves IA and IB are present, the combined height is used. ^{d} Without suppressor. ^{e} With 0.02% gelatin as maximum suppressor.

TABLE II
INFLUENCE OF MERCURY PRESSURE ON WAVE HEIGHT POLAROGRAM OF DIPHENYLIODONIUM ION

| Wave	Potential, V	[Ph$_2$I$^+$], mM	h_{corr}, cm	Time, sec	Diffusion current, μA	100 (id/h)	100 ($id/h^{1/2}$)
IA	−0.13	2	62.8	5.07	1.005	1.60	1.27
			82.8	3.90	1.275	1.54	1.40
			92.8	3.48	1.420	1.53	1.48
			102.8	3.15	1.575	1.53	1.55
IA	−0.35	0.5	62.8	5.07	0.0776	0.1235	0.9810
			82.8	3.90	0.0864	0.1043	0.950
			92.8	3.48	0.0928	0.1000	0.965
			102.8	3.15	0.0992	0.0965	0.978
IA + IB	−0.75	2	62.8	5.13	5.10	8.12	64.5
			82.8	3.90	5.70	6.88	62.6
			92.8	3.48	6.21	6.69	64.6
			102.8	3.15	6.57	6.39	64.8

(−0.20 to −0.40 V). A value of 0.92 mfaraday/mmol was observed. A determination carried out at a potential between waves IB and II (−0.40 to −0.60 V) gave a value of 0.98 mfaraday/mmol. In both cases the only products found were iodobenzene (vpc) and diphenylmercury. The amounts of these products accounted for virtually all of **1**. Determinations carried out on the plateau between waves II and III (−1.20 to −1.30 V) gave a value of 1.92 mfaraday/ mmol. The only products obtained were iodobenzene and benzene.

$$\text{Wave I:} \quad \text{Ph}_2\text{I}^+ + {}^{1}/_{2}\text{Hg} \xrightarrow{\text{e}} {}^{1}/_{2}\text{Ph}_2\text{Hg} + \text{PhI}$$

$$\text{Wave II:} \quad \text{Ph}_2\text{I}^+ + \text{H}^+ \xrightarrow{2\text{e}} \text{PhH} + \text{PhI}$$

Dibenziodolium Ion (2).—The results of the polarographic measurements made on this species are reported in Table I. Low solubility of **2** prevented measurements at concentrations higher than 1.6×10^{-3} M. There was no wave IA observed for **2** (*i.e.*, no wave with $E_{1/2} \sim -0.13$ V). The first wave is therefore designated as IB. As with species **1** only one wave appears between −1.0 and −2.0 V in the TEAP buffer, while two waves are observed in this region in the citrate buffer.

Electrolyses at controlled potential on the plateau between waves IB and II (−0.6 to −0.8 V) gave a

value of 1.06 mfaraday/mmol and afforded biphenyl, 2-iodobiphenyl, and 2,2'-diiodobiphenyl as minor products.
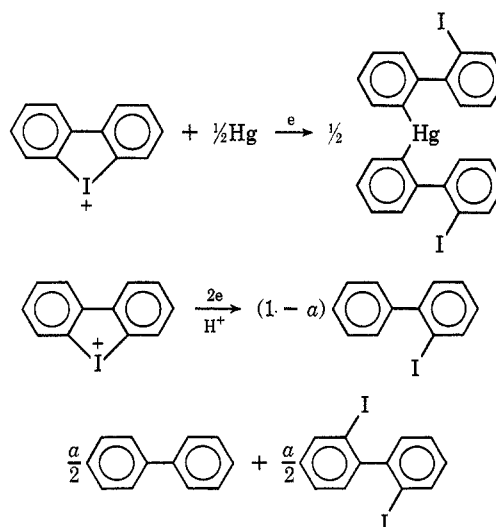
Evidence strongly suggests that the second electron needed for the formation of these products is acquired through reduction by mercury. A white solid containing both iodine and mercury obtained as the major product (*ca.* 70%) is tentatively identified as impure bis-2-

(2'-iodobiphenylyl)mercury (see Experimental Section). Electrolysis on the plateau between waves II and III (-1.20 to -1.30 V) gave a value of 1.98 mfaraday/mmol. The products obtained after such electrolyses were biphenyl, 2,2'-diiodobiphenyl (*ca.* 95% combined) and, as a minor component, biphenylene.

4,5-Phenanthryleneiodonium Ion (3).—Because of the low solubility of the iodonium bisulfate **3** in the phosphate buffer, polarograms were obtained only at concentrations of about 1×10^{-4} *M*. In a potassium phosphate buffer of pH 8.0 the polarogram consisted of two waves of equal height, whose half-wave potentials were at 0.16 and -0.78 V, respectively.

Electrolysis at controlled potential on the plateau of wave I (-0.6 to -0.8 V, 1.97 mfaraday/mmol) afforded phenanthrene (vpc analysis) as well as a brown solid with a decomposition temperature of about 300°. The properties and behavior of this mercury-containing material are presented and discussed in the Experimental Section. Electrolysis on the plateau of wave II (-1.20 to -1.30 V) gave a value of 3.13 mfaraday/mmol. The only organic products obtained were phenanthrene and a trace amount of the brown solid.
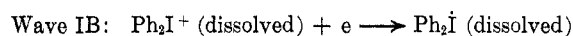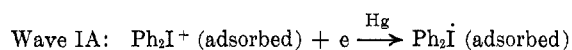
Discussion

Diphenyliodonium Cation.—There are two principal differences between the polarograms reported here and those previously reported:[2b] (1) the appearance of wave IB at -0.53 V at concentrations of **1** as low as 1×10^{-3} *M*, and (2) the appearance of only one wave between -1.0 and -2.0 V in TEAP at low concentrations of **1**. Both differences may be attributed to the different nature and concentration of the maximum suppressors. This is evidenced by the fact that we were able to duplicate the previous results when 0.02% gelatin was substituted for 0.002% Triton x-100. It appears that a concentration of 0.02% gelatin was sufficiently high to distort the polarogram of **1**. A concentration of 0.005% is presently recommended[6a] as being adequate. A concentration of 0.01% is considered by some[6b] to be maximal. It is well known that too high a concentration of suppressor may completely obscure the appearance of a wave or in some other way distort the polarogram.[6b] Polarograms of **1** obtained in the absence of any suppressor (Table I) were like those obtained using 0.002% Triton x-100, including wave IB and the region from -1.0 to -2.0 V. We are reasonably certain, then, that the 0.002% Triton is not distorting the polarogram or obscuring any waves.
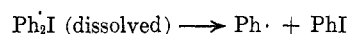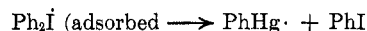
Of particular interest is the behavior of waves IA and IB. Both the concentration dependence and the data in Table II (see previous section) would indicate that wave IA is an adsorption wave whereas wave IB is the "true" or "normal" wave corresponding to the formation of products in solution.[6c]

The formation of diphenylmercury during the electrolysis at controlled potential indicates the presence of a mercury intermediate. The presence of such intermediates has been subjected to debate for some time.[2-4]

We propose the following processes to account for waves IA and IB.

Wave IA: $\text{Ph}_2\text{I}^+ \text{ (adsorbed)} + \text{e} \xrightarrow{\text{Hg}} \text{Ph}_2\dot{\text{I}} \text{ (adsorbed)}$

Wave IB: $\text{Ph}_2\text{I}^+ \text{ (dissolved)} + \text{e} \longrightarrow \text{Ph}_2\dot{\text{I}} \text{ (dissolved)}$

Wave IB is observed when the surface of the mercury has become "saturated" with the adsorbed product. The decomposition of the adsorbed diphenyliodine results mainly in the formation of phenylmercury radicals and iodobenzene. The formation of (dissolved) diphenyliodine results mainly in the formation of iodobenzene and phenyl radicals.

$\text{Ph}_2\dot{\text{I}} \text{ (adsorbed)} \longrightarrow \text{PhHg} \cdot + \text{PhI}$

$\text{Ph}_2\dot{\text{I}} \text{ (dissolved)} \longrightarrow \text{Ph} \cdot + \text{PhI}$

Formation of diphenylmercury can then result from either disproportionation of the phenylmercury radical or by its reaction with phenyl free radicals.

$2\text{PhHg} \cdot \longrightarrow \text{Ph}_2\text{Hg} + \text{Hg}$

$\text{PhHg} \cdot + \text{Ph} \cdot \longrightarrow \text{Ph}_2\text{Hg}$
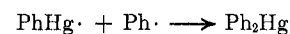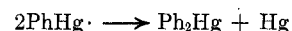
The occurrence of adsorption has already been indicated in cyclic voltammetric measurements on solutions of **1**.[7] The involvement of mercury in wave IA is further indicated by the absence of the latter when platinum[8] or graphite is substituted for mercury.

The slope of wave IA as well as its shift in position with increasing concentration would indicate that it is not reversible.

The overall reaction taking place at wave II may be written as

Wave II: $\text{Ph}_2\text{I}^+ + 2\text{e} + \text{H}^+ \longrightarrow \text{PhH} + \text{PhI}$
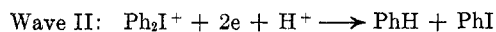
We may also consider wave II to be due to the reduction of the phenylmercury radical formed upon reduction of **1** at wave I.

$\text{PhHg} \cdot + \text{e} + \text{H}^+ \longrightarrow \text{PhH} + \text{Hg}$
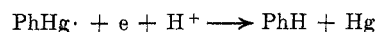
A previous study of the electroreduction of phenylmercuric compounds[9] has shown that these compounds do exhibit a second cathodic wave in the region of wave II. This wave supposedly corresponds to the reduction of PhHg$\cdot$. A polarogram of a solution containing equal concentrations (6×10^{-4} *M*) of phenylmercuric chloride and diphenyliodonium chloride showed only one wave in this region with an $E_{1/2}$ of -1.22 V. The presence of phenylmercuric radicals after electrolysis on wave I as well as the known reducibility of such radicals at the potential of wave II would indicate that the reduction of PhHg$\cdot$ is responsible for the second wave. The products obtained after electrolysis on the plateau of this wave as well as the results of coulometry confirm this.

The overall process at wave II may be written as

Wave III: $\text{Ph}_2\text{I}^+ + 4\text{e} + 2\text{H}^+ \longrightarrow 2\text{PhH} + \text{I}^-$
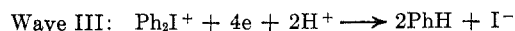
This is consistent with the previous report[2] and with our present wave height and coulometry measure-

(6) (a) L. Meites, "Polarographic Techniques," Wiley, New York, N. Y., 1965, p 322; (b) p 325; (c) p 187.
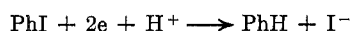
(7) W. C. Danen and D. G. Saunders, *J. Amer. Chem. Soc.*, **91**, 5924 (1969).

(8) O. A. Pitsyna, S. I. Orlov, and B. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1947 (1966); *Chem. Abstr.*, **66**, 74533 (1967).

(9) R. Benesch and R. E. Benesch, *J. Amer. Chem. Soc.*, **73**, 3391 (1951).

ments. The third wave (III) may also be considered to be due to the reduction of iodobenzene.

$$PhI + 2e + H^+ \longrightarrow PhH + I^-$$

It has been shown[2b,10] that iodobenzene is reduced at this potential and that two electrons per molecule are involved. Iodobenzene is stable at the potentials of both waves I and II, as indicated by its presence after electrolysis at wave II.

Dibenziodolium Ion (2).—The polarogram of this species did not show a IA wave. However, a wave appeared in the same general region as did the IB wave for **1**. It is likely, then, that similar processes are occurring in both cases, namely the formation and further reaction of a diaryliodine radical. The main product (*ca.* 70%) is a diarylmercury, **11**, arising from
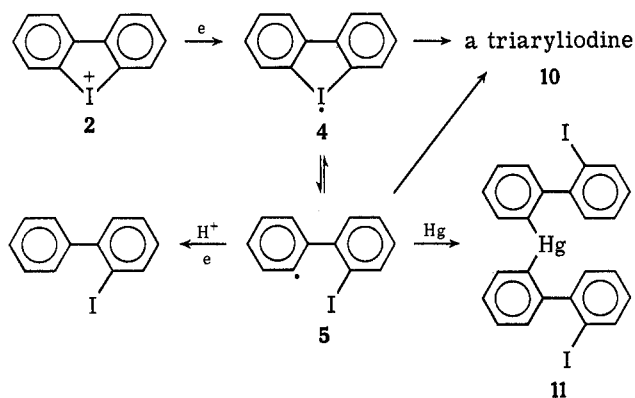
the reaction of radical **5** with mercury. This compound is accompanied by smaller amounts of related diarylmercury compounds with one or no iodines (*m/e* 634 and 508, respectively). A minor product, 2-iodobiphenyl, is apparently formed by the further reduction of radical **5**.

In addition there are products whose formation involves iodine transfer: biphenyl and 2,2'-diiodobiphenyl. It is suggested that these are formed by the coupling of **4** and **5** to give a triaryliodine, **10**, whose subsequent homolysis may result in overall iodine transfer.
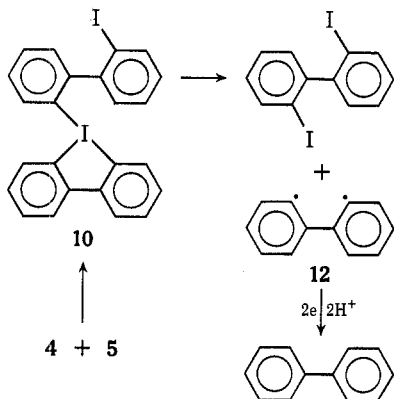
The formation of iodobiphenyl and biphenyl at this potential requires a source of electrons other than the electrode. The mass spectroscopic observation of mercuric iodide (*m/e* 456 and 329) in the solid product strongly supports the involvement of mercury as a reducing agent. Since species 2 does not itself react with

(10) A. Gergely and T. Iredale, *J. Chem. Soc.*, 13 (1951).

mercury, this reduction must occur after the initial electrode reduction.

Wave II may result from the reduction of the biphenylene diradical **12**. Here again, some reduction by mercury may occur.

The third wave of the polarogram of **2** may correspond to the reduction of 2-iodobiphenyl to biphenyl.

4,5-Phenanthryleneiodonium Ion (3).—The polarogram of this species was different from those of **1** and **2** in that under no circumstances did it show three waves. In the phosphate buffer two waves were observed whose wave heights were in the ratio 1:1. Coulometry showed these waves to correspond to the uptake of two and of three electrons, respectively, through the circuit. The products of the electrolysis were also different in that no aryl iodide was obtained.

The mass spectroscopic data obtained from the brown solid (see following section) as well as those obtained from its thermal and chemical degradation products suggest a mixture of phenanthrene derivatives containing mercury, specifically, 4-phenanthrylmercuric iodide and di-4-phenanthrylmercury. From the weights of material obtained and the elemental analysis it is calculated that this mixture accounts for *ca.* 75% of the starting quantity of **3**. The absence of any products in which both mercury and iodine were bound to the 4 and 5 positions of phenanthrene is understandable in view of the steric requirements of the two large atoms. For wave I we may then write
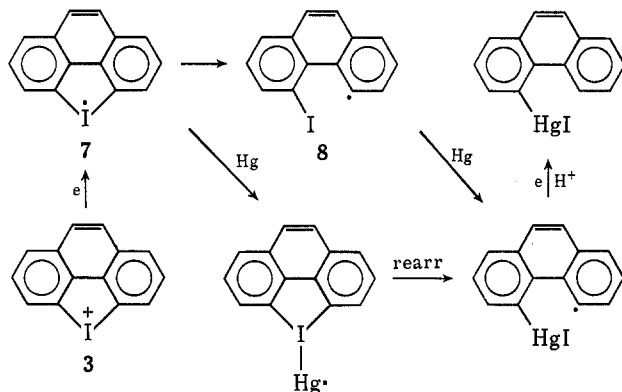

Homolysis of **7** would yield a 5-iodo-4-phenanthryl free radical, **8**, whose reaction with mercury (perhaps involving several steps) and subsequent reduction would give 4-phenanthrylmercuric iodide.

The cyclic iodine **7** may also react with mercury to give a trisubstituted iodine, whose rearrangement and further reduction may also give 4-phenanthrylmercuric iodide.

Still unexplained, however, is the formation of phenanthrene and the apparent intermediacy of the 4-phenanthryl free radical under the conditions of wave I (uptake of two electrons from the electrode). A partial answer may lie in the oxidation of mercury to mercuric iodide, followed by reduction of the 4,5-phenanthrylene diradical.

The formation of phenanthrene from the scheme below requires the uptake of three electrons. At the potential of wave I only two of these may come from the electrode. In analogy with the pathway suggested for species **2**, a reduction by mercury after the initial electrode reduction is proposed, although specific intermediates are not offered at this time.
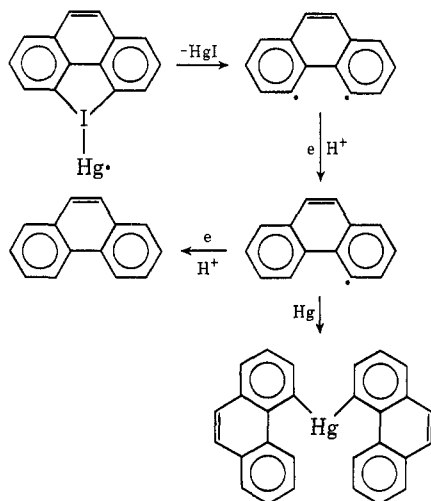
We may also note that, while the ratio of wave heights in the polarogram of **3** is 1:1, the coulometry measurements indicate that two electrons are consumed on the first wave while only one additional (a total of three) electron is consumed on wave II. This discrepancy arises from the different natures of the polarographic and large-scale reduction experiments. The reduction of **3** to phenanthrene and iodide ion requires four electrons.
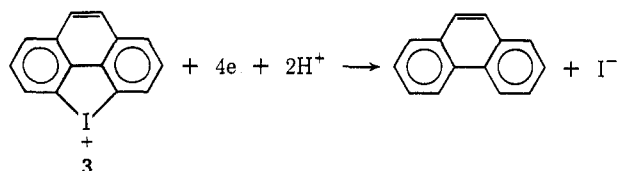
In the polarographic reduction this is apparently accomplished in two two-electron steps (waves I and II). In the large-scale electrolysis, however, where mercury is acting as a reducing agent as well, only about three quarters of the needed electrons are coming from the electrode, the rest being supplied by mercury. Since the coulometer only records the passage of electrons through the circuit, this latter reduction is unrecorded.

Experimental Section

Materials.—Iodonium salts were prepared by well-known routes and converted to the tosylate and fluoroborate by metathesis.[11-13] The 4,5-phenanthryleneiodonium salt was prepared by a recently published synthesis.[14]

Tetraethylammonium hydroxide was of Eastman White Label grade. Inorganic chemicals were CP, reagent, or NF grade. Water was distilled in all-glass equipment. Mercury was triple distilled. Triton x-100 (Rohm and Haas Co.) was diluted to make a 0.1% stock solution. Gelatin was highest purity grade supplied by Fisher Scientific Co. Prepurified nitrogen was bubbled through solutions of chromous chloride in order to remove any traces of oxygen.

Supporting Electrolytes.—Tetraethylammonium phosphate (TEAP) (0.1 M) was prepared by neutralizing the base to pH 7.45 with phosphoric acid. Dilution with an equal volume of water did not change the pH. Citrate buffers were prepared as outlined in ref 5. The potassium phosphate buffers used for electrolysis of species 1 and 2 were made as follows: 400 ml of 0.1 M KH$_2$PO$_4$, 370 ml of 0.1 M NaOH, total volume, 1 l., pH

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(11) J. Nachtigal, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1967.
(12) M. Yudis, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1970.
(13) L. Chang, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1971.
(14) F. M. Beringer, L. L. Chang, A. N. Fenster, and R. R. Rossi, *Tetrahedron*, **25**, 4339 (1969).

8.0; for species 1 the buffer was also 1 M in KCl; for species 2, the buffer was made 0.5 M in K$_2$SO$_4$. The polarograms in both cases were identical with those in the citrate medium. Electrolyes of **3** were carried out in a phosphate buffer, pH 8.0, containing no additional salt.

Equipment and Procedures.—Polarograms were recorded on a Sargeant Model XXI automatically recording polarograph. A conventional H cell with a Ag/AgCl anode was employed in all measurements. Samples were thoroughly deaerated and blanketed with nitrogen prior to measurement. No corrections were made for iR drop. Measurements were made at 25–28°.

Gas chromatography was carried out on 6-ft columns packed with 50% OV-1 on Chromosorb W with an Aerograph 1520 gas chromatograph: for iodobenzene, column temperature 90°, injector temperature 190°, detector temperature 300°; for phenanthrene and halophenanthrenes, column temperature 215°, injector temperature 250°, detector temperature 300°; for biphenyl and iodobiphenyls, column temperature 175°, injector temperature 250°, detector temperature 300°. Melting points were taken in capillary tubes on a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 521 grating infrared spectrophotometer. Mass spectra, taken on a Hitachi Perkin-Elmer RMU-6E instrument, were calibrated using perfluorokerosene as an internal standard. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., or Chemalytics Inc., Tempe, Ariz.

Measurements of pH were made with a Leeds and Northrup glass electrode pH meter.

Controlled-potential electrolyses were carried out in a doublediaphragm cell with the aid of an Analytical Instruments, Inc. (Bristol, Conn.) potentiostat and current integrator, using the previously described procedure.[2]

Electrolysis of Diphenyliodonium Tosylate (1). Wave I.—Solutions of diphenyliodonium tosylate (0.5–2.0 mM) were electrolyzed between −0.6 and −0.8 V. Electrolysis was complete in less than 30 min. A value of 0.98 mfaraday/mmol was obtained (six determinations). The two-phase system (aqueous solution–mercury) was separated into its components. Each phase was extracted several times with ether. The ether extracts were combined, dried (MgSO$_4$), and then concentrated. A white solid could be obtained from the cooled concentrate. The solid, when recrystallized from 95% ethanol, melted at 122–123°. Authentic diphenylmercury had mp 123–124°. Infrared and mass spectra were identical with those of authentic diphenylmercury. Vpc analysis of the concentrated ether extracts showed the presence of iodobenzene. In many cases it was possible to remove the solid before extraction.

Electrolysis of Diphenyliodonium Tosylate (1). Wave II.—Electrolyses were carried out on the plateau of wave II (−1.20 to −1.30 V). Electrolyzed solutions were worked up in the manner described above. No solid residues were found. A value of 1.92 mfaraday/mmol was obtained (six determinations). Vpc analysis of the ether extracts showed iodobenzene and benzene to be the only products.

Electrolysis of Dibenziodolium Tetrafluoroborate (2). Wave I.—Solutions (1.0 mM) of the dibenziodolium tetrafluoroborate in the phosphate buffer were electrolyzed in the same manner as for species 1 (−0.6 to −0.8 V). An average value of 1.06 mfaraday/mmol was obtained (12 determinations). The electrolyzed solutions were extracted with several equal volumes of ether. The combined ether extracts were dried (MgSO$_4$) and then concentrated. As in the case of compound 1, a white solid precipitated from the cooled, concentrated solution. This solid exhibited the following properties: mp 159–160°; ir (KBr) 3040, 1570, 1550, 1465, 1420, 1410, 1270, 1240, 1150, 1110, 1070, 1045, 1010, 995, 770, 755, 750, 735, 640, 615, 540, and 460 cm^{-1}; mass spectrum (50 eV) m/e 760,* 634,* 558,* 508,* 456,* 329,* and 279 (starred signals showed characteristic isotopic cluster of mercury; values reported are for ^{202}Hg).

Anal. Calcd for bis-2-(2′-iodobiphenylyl)mercury (C$_{24}$H$_{16}$-HgI$_2$): C, 37.99; H, 2.13; Hg, 26.44; I, 33.45. Found: C, 37.69; H, 2.16; Hg, 27.40; I, 31.60.

Recrystallization of this material from a variety of solvents did not significantly change the analytical results.

The ether extracts were shown by vpc to contain biphenyl, 2-iodobiphenyl, and 2,2′-diiodobiphenyl (confirmed by mixed injection with authentic samples).

Electrolysis of Dibenziodolium Tetrafluoroborate (2). Wave II.—Electrolyses were carried out at −1.20 to −1.30 V and were

worked up in the usual manner. A value of 1.98 mfaraday/mmol was obtained (six determinations). Vpc analysis of the ether extracts showed them to contain 2,2'-diiodobiphenyl, biphenyl (in substantially larger amounts than after electrolysis on wave I), and a trace amount of a third component that was trapped at the exit port of the gas chromatograph. The retention time of this material as well as a mass spectroscopic comparison with authentic material showed it to be biphenylene. Trace amounts of the white solid (mp 160–162°) were also sometimes present after electrolysis, especially in those runs where n was less than 2.0.

Electrolysis of 4,5-Phenanthryleneiodonium Bisulfate (3). Wave I.—Electrolyses were carried out on 0.150 mM solutions in the usual manner at −0.4 to −0.6 V. A value of 1.97 mfaraday/mmol was obtained (six determinations). Work-up in the usual manner afforded a brown solid from the ether extracts as well as phenanthrene (vpc). The brown solid was washed with ether and dried under vacuum. It exhibited the following properties: mp ~366° dec; ir (KBr) 3040 (w), 1440 (w), 1395 (w), 1290 (w), 1180 (vw), 1140 (vw), 990 (vw), 820 (s), 730 and 710 cm^{-1}; mass spectrum (50 ev) m/e 556,* 506,* 456,* and 329.*

Anal. Found: C, 42.98; H, 2.37; Hg, 45.02; I, 9.36.

The chemical (see below) as well as the spectroscopic evidence accumulated strongly suggest a mixture of di-4-phenanthrylmercury and 4-phenanthrylmercuric iodide as the chemical composition of this material.

When decomposition of this solid was effected in a capillary tube, the lower portion of which was immersed in an oil bath, a yellow solid was deposited on the upper (cooler) portion of the tube. A mass spectrum (80 eV) of this material (90°) was identical with that of phenanthrene except for a characteristic mercury cluster between m/e 198 and 204. At 160° the spectrum became more complicated with the highest m/e observed being at 456 (mercury containing). A comparison of this spectrum with that of authentic mercuric iodide (above m/e 202) showed them to be virtually identical.

Electrolysis of 4,5-Phenanthryleneiodonium Bisulfate (3). Wave II.—Electrolysis of the bisulfate was carried out in the usual manner between −1.20 and −1.30 V. Work-up afforded phenanthrene as the major product. Only trace amounts of the brown mercury-containing solid were obtained. A value of 3.13 mfaraday/mmol was obtained (five determinations) by coulometry.

Reactions of the Electrolysis Product of 3 at Wave I. Reaction with Hydrochloric Acid.—The brown solid was suspended in about 1 ml of THF. To this suspension was added approximately an equal volume of concentrated HCl. An immediate exothermic

reaction occurred along with a color change from clear to yellow. Extraction of the mixture with ether followed by drying (MgSO$_4$) afforded phenanthrene (vpc) as the organic product.

Reaction with Aqueous Halide/Halogen.—The brown solid was suspended in about 1 ml of an aqueous potassium bromide (or iodide) solution. Addition of several drops (milligrams) of bromine (or iodine) was followed by heating on a steam bath for about 1 hr. Extraction with ether, drying (MgSO$_4$), and vpc analysis subsequently revealed the 4-halophenanthrene as the product (determined by mixed injection with 4-iodo- and 4-bromophenanthrenes).

Reaction with Glacial Acetic Acid/THF.—The brown solid was suspended in about 3 ml of THF. To the suspension was added approximately 6 ml of glacial acetic acid. The suspension was heated for 3 hr on a steam bath. At the end of this period some of the solid remained undissolved while some appeared to have gone into solution. After the solution had cooled, the undissolved material was filtered and was washed with water and ether. After drying (under vacuum) the solid melted at ~240°. This material is apparently not a pure compound.

Anal. Calcd for 4-phenanthrylmercuric iodide (C$_{14}$H$_9$HgI); C, 33.38; H, 1.60; I, 25.19. Found: C, 28.62; H, 1.54; I, 27.58.

A second solid was obtained from the solution by addition of water to the solution. After similar treatment this material melted at 210°.

Anal. Calcd for 4-phenanthrylmercuric acetate (C$_{16}$H$_{12}$HgO$_2$): C, 43.99; H, 2.77. Found: C, 40.95; H, 2.36; I, 4.20.

This solid also showed a strong carbonyl stretching band at 1580 cm^{-1} identical with that shown by phenylmercuric acetate.

Neutralization of the acidic solution with sodium carbonate, followed by extraction with ether and drying, afforded phenanthrene (vpc).

Although treatment of the electrolysis product with acetic acid apparently did result in the formation of 4-phenanthrylmercuric acetate while leaving the 4-phenanthrylmercuric iodide unreacted, separation of these materials into analytically pure samples was not accomplished.

Registry No.—**1**, 10182-84-0; **1** tosylate, 6293-66-9; **2**, 244-54-2; **2** tetrafluoroborate, 18116-06-8; **3**, 25504-50-1; **3** bisulfate, 34737-75-2; bis-2-(2'-iodobiphenylyl)mercury, 34737-76-3; di-4-phenanthrylmercury, 34737-77-4; 4-phenanthrylmercuric iodide, 34737-78-5; 4-phenanthrylmercuric acetate, 34737-79-6.

Substituent Effects upon the Reductive Fission of Aryl Alcohols

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Reductive fission of substituted 1-phenyl-1-ethanols by potassium metal in *tert*-butyl alcohol occurs most readily when strongly electron-withdrawing substituents are present. In competitive reductions, the relative reactivity increases for electron-withdrawing substituents (−I), but decreases for several +I substituents as the amount of added potassium is increased. The former behavior is believed to be associated with the importance of a dianion pathway and the latter, a radical-anion pathway. Halide substituents (except *p*-F) are anomalous, with the initial reaction being the loss of halogen. Reactivity is diminished by increasing side chain substitution.

Reductive cleavages of allyl and benzyl alcohols to propene and toluene were first studied by Chablay over 60 years ago.[1] Similar cleavages of alkyl–aryl ethers with sodium and liquid ammonia were investigated by Freudenberg and coworkers,[2] and later also investigated by Birch, who determined the order of activating influence of aromatic substituent: *o*-OCH$_3$ > *m*-OCH$_3$ > H > *o*-CH$_3$ > *m*-CH$_3$ > *p*-CH$_3$ > *p*-OCH$_3$.[3] Sowa and coworkers found similar substituent effects upon the mode of cleavage of certain diaryl ethers.[4] Two mechanisms have been advanced for these active metal reductions, a radical-anion pathway and a dianion

(1) (a) E. Chablay, *C. R. Acad. Sci.*, **140**, 1343 (1905); (b) *ibid.*, **143**, 829 (1906); (c) *ibid.*, **143**, 173 (1906); (d) see also L. Bouveault and G. Blanc, *ibid.*, **136**, 1676 (1903).

(2) (a) K. Freudenberg, K. Engler, F. Klink, E. Flickinger, and A. Sobek, *Chem. Ber.*, **71**, 1810 (1938); (b) K. Freudenberg, F. Klink, E. Flickinger, and A. Sobek, *ibid.*, **72**, 217 (1939).

(3) (a) A. J. Birch, *J. Chem. Soc.*, 102 (1947); (b) A. J. Birch, A. Fogiel, and G. J. Harvey, *Aust. J. Chem.*, **7**, 261 (1954).

(4) F. C. Weber and F. J. Sowa, *J. Amer. Chem. Soc.*, **60**, 94 (1938).