ON THE ELECTROREDUCTION MECHANISM OF HALOBENZENES: DETECTION OF INTERMEDIATES IN REDUCTION OF MONOHALOBENZENES

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Experimental results from electrochemical behaviour of halobenzenes in DMF at a mercury cathode are used to discuss alternative mechanisms of reduction. Intermediates of these mechanisms, such as phenyl anion, phenylmercury radical and phenylmercury cation have been detected at the electrode by using cyclic voltammetry and a rotating ring-disk electrode.

In the first part of this work[1] we tried a quantum chemical approach to the first steps of electrochemical reduction of halobenzenes and dihalobenzenes. In this paper we deal with the experimental behaviour of monohalobenzenes in DMF, focusing on the detection of intermediates formed at mercury electrodes. For this purpose we have used cyclic voltammetry (CV) and voltammetry at a rotating ring-disk electrode (RRDE).

The existing literature on these compounds[1] agrees at present on the following mechanism:

$$XPh + e \rightleftarrows XPh^{\overset{\bullet}{-}} \tag{1}$$

$$XPh^{\overset{\bullet}{-}} \rightarrow X^- + Ph^{\bullet} \tag{2}$$

$$Ph^{\bullet} + e \rightleftarrows Ph^- , \tag{3}$$

where the radical anion is very unstable, i.e. step (2) is fast. A single irreversible two-electron wave is observed and it is commonly accepted that step (1) is rate determining, since the phenyl radical is easier to reduce than the halobenzene. Afterwards, benzene is formed as the main product[2] either by step (4) or (5):

$$Ph^- + H^+ \rightarrow PhH \tag{4}$$

$$Ph^{\bullet} + SH \rightarrow PhH + S^{\bullet} . \tag{5}$$

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Although phenyl anion trapping with CO_2 has been reported[3] and byproducts of electrolysis, such as diphenylmercury[2,4,5] suggest the existence of phenylmercury radical as intermediate, radical and anion intermediates of the above mechanism had not been detected at the electrode, to the best of our knowledge.

EXPERIMENTAL

Chemicals used, their purification and polarographic techniques have been described before[1]. An Ag/AgI electrode has been used as reference.

The RRDE assembly was controlled by a bipotentiostat Tacussel BI-PAD, equipped with an AMEL wave generator 566. The *i–E* curves were drawn with a Philips X–Y recorder PM 8120. The platinum Tacussel RRDE was coated with Hg before each experiment[6]. The disk radius was 0·20 cm. The ring radii were 0·22 cm (internal) and 0·24 cm (external). The electrode collection coefficient (*N*) was empirically determined to be 0·20 ± 0·01. The rotation speed was controlled by an apparatus Tacussel Asservitex 10,000. The cell (200 ml) was Tacussel XLRC 10. Electrode and cell were mounted on a heavy support Tacussel S/EAD.

CV experiments were carried out with the same equipment. In experiments at concentrations higher than $1 \cdot 10^{-3}$ mol l^{-1} we used a Hg coated platinum electrode made as follows. A hanging drop of melted Pt was slowly cooled and coated with silver from a solution of 0·08M-$AgNO_3$ at constant current (0·23 mA cm^{-2}) for 20 h. The resulting electrode can be coated with mercury by immersion in Hg and its surface (0·11 cm^2) was renewed in this way before each experiment. A polished glassy carbon electrode (area 0·07 cm^2) was also used.

All potential measurements were corrected for ohmic drop[11]. Working temperature was 25·0°C.

RESULTS AND DISCUSSION

Reduction mechanisms

Cyclic voltammograms of monohalobenzenes in DMF/0·1M tetraethylammonium perchlorate (TEAP) present a single, irreversible and diffusion controlled reduction peak. The CV results obtained in $1 \cdot 10^{-3}$M solutions of monohalobenzenes are summarized in Table I. These results are consistent with the mechanism cited above. The slow decrease of the current function with increasing sweep rate agrees with the expected behaviour for an ECE process where the standard potential for the second electron transfer is less cathodic than for the first electron transfer[7]. The small value of $dE_p/d\log v$ for chlorobenzene (ClPh) seems to indicate the participation of C—Cl bond breaking in kinetic control. That is consistent with the larger bond energy of this bond and the greater standard rate constant (k^0) for electron transfer to ClPh with respect to bromobenzene (BrPh) (ref.[8]). A similar case has been reported for 4,4'-dichlorobiphenyl[9]. Moreover, values as small as $5-10$ mV of potential displacement when passing from 1 to 10 V s^{-1} have been published for some chlorobenzenes[10] and were used to support an EC mechanism kinetically controlled by the chemical step.

Monohalobenzenes also present a single reduction wave at the rotating disk electrode and, concomitantly, a small anodic current, i_R, appears at the ring electrode,

TABLE I

Voltammetric results of 1·0 mM solutions of monohalobenzenes in DMF/0·1M TEAP. Cathode area 0·126 cm^2, reference electrode Ag/AgI, 25°C

Compound	$-E_p$, V[a]	$-E_{p/2}$, V[a]	$dE_p/d \log v$, mV[c]	i_p, μA[a]	$i_p v^{-1/2b}$	$i_p v^{-1/2a}$
IPh	1·21	1·12	40 (0·991)	90	7·3	6·4
BrPh	1·86	1·72	51 (0·996)	88	7·3	6·2
ClPh	2·26	2·16	31 (0·996)	92	8·2	6·5

[a] Sweep rate 200 mV s^{-1}; [b] sweep rate 10 mV s^{-1}; [c] from 10 to 200 mV s^{-1}, correlation coefficients are given in parenthesis.

TABLE II

Results of reduction of halobenzenes in DMF/TEAP 0·1M at the RRDE. Disk area 0·126 cm^2, E_R 0 V vs Ag/AgI, 25°C

Compound	ω, rpm	$-E_{1/2}$, V	i_D, μA	i_R, μA	$N_k \cdot 10^3$
IPh	70	1·11	45	0·4	8·9
	170	1·14	76	0·7	9·2
	500	1·16	125	1·1	8·7
	1 000	1·17	180	1·4	7·7
	2 000	1·19	260	1·6	6·2
	4 000	1·20	365	1·7	4·6
	6 000	1·21	450	1·8	4·0
BrPh	70	1·71	65	1·5	23
	170	1·74	95	2·2	23
	500	1·78	160	3·2	20
	1 000	1·80	220	3·6	16
	2 000	1·82	310	4·0	13
	5 000	1·85	465	4·2	9·0
	10 000	1·88	610	4·3	7·1
ClPh	70	2·12	62	—	—
	170	2·13	97	—	—
	500	2·16	170	—	—
	1 000	2·18	250	—	—

fixed at a potential of 0 V vs Ag/AgI. Limiting disc currents, i_D are controlled by mass transfer. Quantitative results obtained with the RRDE are summarized in Table II. ClPh does not show limiting currents at the ring electrode due to merging of the wave in the background discharge. In this case, tentative values of experimental collection coefficients (N_k) were calculated from i_R/i_D at -2.30 V. The resulting N_k (0.027 at 170 rpm and 0.023 at 2 000 rpm) are similar to those obtained for BrPh and other dihalobenzenes[11].

Table III shows the transfer coefficients measured with different techniques, including polarography, in several media. The close agreement of the different values for iodobenzene (IPh) is noteworthy. In contrast, the agreement is poor for ClPh due to interference of the background discharge. For IPh the values are larger than 0.50, indicating that $E_{1/2} > E^0$ (ref.[12]) and, taking into account the value of $dE_p/\log v$ (Table I), they suggest a mixed kinetic control of steps (1) and (2), as pointed out by Saveant et al.[8]. That would imply the real existence of the radical anion and a value of k^0 larger than that for the rest of the halobenzenes, provided that the C—I bond is easier to break than the C—Br and C—Cl ones. On the other hand, BrPh has transfer coefficients consistently lower than 0.50, thus indicating $E_{1/2} < E^0$ (ref.[12]). Agreeing with this, a difference of $E^0 - E_{1/2} = 0.10$ V has been reported[8].

As shown by our results of macroscale electrolysis of halobenzenes[2], protons of step (4) are preferentially provided by tetraethylammonium perchlorate (TEAP) via Hofmann degradation. However supporting electrolyte and residual water in DMF

TABLE III
Charge transfer coefficients (α) of monohalobenzenes as a function of techniques and solvents employed. Supporting electrolyte 0.1M TEAP, 25°C

Technique	Solvent	α		
		IPh	BrPh	ClPh
CV[b]	DMF	0.55	0.35	0.45
RDE[a]	DMF	0.57	0.37	0.61
RDE[c]	DMF	0.55 (0.998)	0.38 (0.999)	0.53 (0.991)
Polarogr.[a]	DMF	0.61	0.43	0.52
	AN	0.56[d]	0.35	—
	DMSO[d]	0.56	0.45	0.60

[a] Tomes criteria, averaged; [b] from $E_p - E_{p/2}$ (peak width), averaged for v between 0.01 and 0.2 V s^{-1}; [c] from $E_{1/2}$ vs ln ω, correlation coefficients in parenthesis; [d] with 0.1M tetraethylammonium bromide as supporting electrolyte.

(c. 0·1%) cannot account for the amount of benzene obtained. This last fact and the structure of some byproducts[2] suggest effective involvement of step (5) in DMF, leading to radical ·CONMe$_2$. Nevertheless the number of electrons/molecule transferred (almost 2) indicates that "ionic" mechanism (steps (1)−(4)) is the main pathway of this reduction.

Addition of phenol increases moderately (5−21%) the reduction currents and the number of electrons/molecule in coulometries[11,13] since, as a proton donor, it can favour the ionic (bielectronic) mechanism against the monoelectronic mechanism (steps (1), (2), (5) and other reactions of phenyl radical that do not consume electrons, such as dimerization, formation of mercury derivatives, ...). On the other hand, there are no significant changes in potentials or transfer coefficients upon adding phenol. That means protonation is not prior to the potential determining step. Since that potential is governed by steps (1) and (2), protonation must take place after breaking of the C—X bond.

The electron transfer in solution:

$$XPh^{\overset{-}{\cdot}} + Ph^{\cdot} \rightleftarrows XPh + Ph^{-} , \tag{6}$$
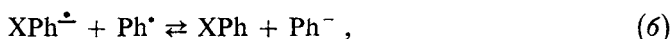
although favored by the easier reduction of phenyl radical relative to the parent compound, must be, if any, a minor pathway since radical anions have a very short life-time.

Role of Organomercury Compounds

Since we have obtained phenylmercury compounds from iodobenzene electrolysis[2], phenylmercury radical should be an intermediate. This intermediate has been previously proposed in IPh and BrPh reduction[5]. Therefore one should include reactions:

$$Ph^{\cdot} + Hg \rightleftarrows PhHg^{\cdot} \tag{3a}$$

$$PhHg^{\cdot} + e \rightarrow Ph^{-} + Hg \tag{3b}$$

as alternatives to step (3). A reaction similar to (3a) has been proposed for alkylmercury radicals[14]. Such equilibrium reactions are not surprising taking into account the low dissociation energy of the C—Hg bond[15,16].

Mairanovskii et al.[4] observed a severe change in diphenylmercury yield from IPh electrolysis in hydroalcoholic medium at different potentials. They found a maximum yield (9%) at −1·45 V vs SCE, at the beginning of the rise of the polarographic wave, but they did not provide any explanation. This phenomenon can be understood as a result of competition between step (3b) and reaction(7):

$$2 PhHg^{\cdot} \rightarrow PhHgPh + Hg . \tag{7}$$
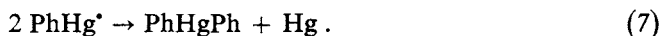
This reaction has been proposed by several authors[2] to explain diphenylmercury formation upon electrolysis of some benzene derivatives.

Detection of Intermediates

CV of monohalobenzenes at higher concentrations $(3-5 \cdot 10^{-3} \text{ mol } l^{-1})$ showed a set of secondary peaks, in the second and following sweeps, common to all of them (Figs 1, 2 and 3), although the potentials were slightly different $(\pm 0.1 \text{ V})$. In general only one anodic peak is observed on the reverse sweeps. However for IPh it has been possible to resolve peaks B and C (Fig. 1), which are more or less overlapped in other cases. The most important features of secondary peaks are the following: 1. They only appear if the substrate is previously reduced and if the sweep rates are not too slow. 2. They increase with the time of substrate reduction. 3. They increase in consecutive cycles, while the main peak A decreases. 4. They decrease if the solution is stirred, while peak A increases.

This behaviour indicates that secondary peaks are due to species formed at the electrode. Since these peaks are common to the three substances cited above, intermediates or products that generate them must be also common. In addition, the same experiment, but for a $1.5 \cdot 10^{-3}$M solution of diphenylmercury revealed the same behaviour (Fig. 4). Thus, halide ions are ruled out since the peaks also appear in diphenylmercury reduction, where no halogen is present. The following reaction has been proposed[16] for diphenylmercury reduction in aprotic medium:
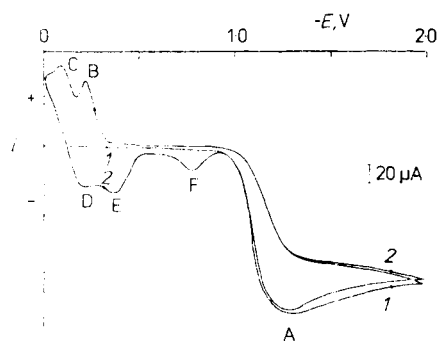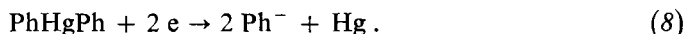
$$\text{PhHgPh} + 2\,\text{e} \rightarrow 2\,\text{Ph}^- + \text{Hg}. \tag{8}$$

FIG. 1

Cyclic voltammogram of $5 \cdot 10^{-3}$M IPh in DMF/0·1M TEAP at 0·1 V s^{-1}. In this and the following figures numbers refer to the ordinals of sweeps and anodic currents are labeled $^+$. Reference electrode Ag/AgI (in all figures)
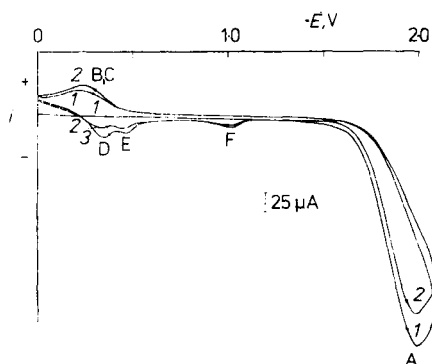

FIG. 2

Cyclic voltammogram of $3 \cdot 10^{-3}$M BrPh in DMF/0·1M TEAP at 0·2 V s^{-1}

Thus phenyl anion, benzene, phenyl radical and phenylmercury radical are species whose oxidation might lead to peak B (Figs 1—4). Two species (aside from the starting compound) can be present on the the first back scan at potentials more negative than peak B, i.e. phenyl anion formed in peak A (reactions $(1)-(3)$ or (8)) and benzene, mainly formed by protonation of Ph^- (reaction (4)). Phenyl and phenylmercury radicals are obviously not present after substrate reduction in peak A. The species oxidized in peak B is Ph^-, since: a) Benzene is not electroactive at this potential. b) Peak B disapperas upon phenol addition, thus indicating that it is produced by a basic species.

The oxidation of Ph^- in peak B must lead to the phenyl radical:

$$Ph^- - e \rightleftarrows Ph^{\bullet} . \tag{9}$$

Since Hg is a good radical trap, the phenyl radical could remain adsorbed at the mercury surface and form the phenylmercury radical (reaction $(3b)$) (ref.[16]). Phenylmercury radical could produce peak C:

$$PhHg^{\bullet} - e \rightleftarrows PhHg^+ . \tag{10}$$

In the following cycle, three cathodic peaks are observed (D, E, F) but in some cases D and E are overlapped. Peaks D and E correspond to the same reduction:

$$PhHg^+ + e \rightleftarrows PhHg^{\bullet} , \tag{11}$$

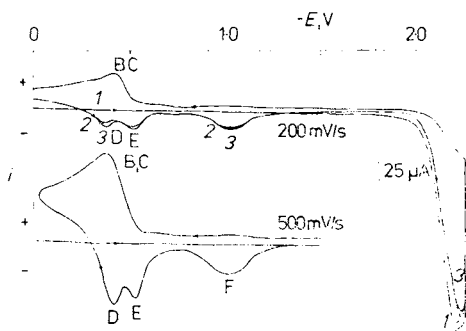where peak D is controlled by adsorption and peak E by diffusion[18]. Similar pre-

FIG. 3

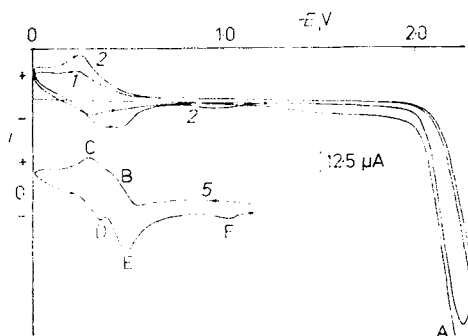Cyclic voltammograms of $3 \cdot 10^{-3}$M ClPh in DMF/0·1M TEAP. Sweep rates are given in the figure

FIG. 4

Cyclic voltammogram of $1·5 \cdot 10^{-3}$M diphenylmercury in DMF/0·1M TEAP. Sweep rate 0·2 V s^{-1}

waves have been assigned to adsorption of radicals formed in the first step of alkyl-mercury salts reduction[19-21].

Peak F, irreversible, is due in our opinion to reduction (3b). Its shape is typical of an adsorption peak and it is, in general, smaller than the preceding peaks. Its small size can be explained by competition of reactions (3b) and (7). After a typical CV experiment with $3-5 . 10^{-3}$M halobenzene, peaks D, E and F appear in further scans as well. However, they can be removed by applying a potential of -0.5 V and stirring the solution. At first glance disappearance of peak F seems to be sur-prising provided that its potential is more negative than -0.5 V; but it can be under-stood by the competition mentioned above, i.e. phenylmercury radical is formed and reacts following reaction (7) during microelectrolysis at -0.5 V.

The involvement of Hg in this processes was confirmed by CV using the same experimental conditions, but with a vitreous glassy carbon electrode. In several cycles with reversed scans, a single irreversible anodic peak appeared near 0.2 V, whose behaviour was similar to that described for secondary peaks (points $1.-4$. above). This peak increases with scan rate faster than $v^{1/2}$ and disappears upon phenol addition. Therefore, it could be due to reaction (9). The cathodic counterpart is absent owing to the high reactivity of the phenyl radical. (9) is the only reaction expected to produce a secondary peak at carbon electrodes.

Further experimental tests were performed by CV of phenylmercury nitrate and phenylmercury acetate using the same Hg cathode and medium. Since both salts dissociate, forming phenylmercury cation, they should present a cathodic behaviour analogous to the proposed intermediate. This did, in fact, occur (Fig. 5). By com-paring this figure and Figs $1-4$, a common pattern is observed. Fig. 5b shows how (if the starting potential for the reverse sweeps is set to -0.65 V, so avoiding ap-pearance of the peak F) peak B disappears. If sweeps up to -1 V are restored, peaks F and B reappear. This is consistent with the proposed scheme since in this case phenyl
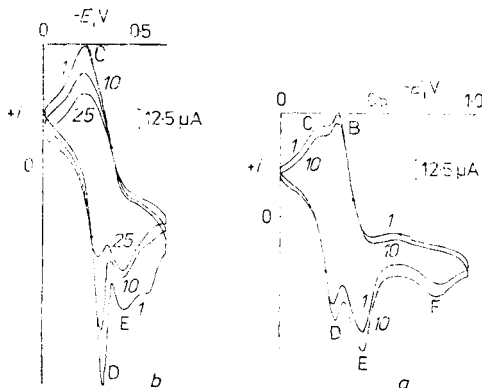

FIG. 5
Cyclic voltammograms of $1 . 10^{-3}$M di-phenylmercury nitrate in DMF/0·1M TEAP at 0.2 V s^{-1}. a Potential range: 0 to -1 V; b potential range: 0 to -0.65 V

anion is generated in peak F only, and its oxidation is observed as peak B. Fig. 5b also evidences that peak D is due to a specific adsorption. Its sharpness in the first scan was obtained by keeping the potential at 0 V for several seconds, after preceding cycles, thus increasing the concentration of phenylmercury cation near the electrode surface, due to reactions (9), (3a) and (10). In consecutive cycles currents decreased owing to reactions (7) and (3a). In this case peaks D and E relate to the reduction of phenylmercury cation in solution, but peaks B and C are, as in reduction of halobenzenes, secondary peaks due to intermediates. Thus, their decrease by a factor 20 by changing the sweep rate from 0·2 to 0·01 V s^{-1}, keeping the rest of conditions as in Fig. 5, is not surprising. It is explainable in terms of diffusion of phenyl anion away from the electrode and elimination of phenyl radical from the electrode through diffusion and/or reactions (7) and (3a). The existence of organomercury radicals in solution has been proposed in certain instances[14,21,23].

Monohalobenzenes show at the ring electrode a behaviour consistent with the exposed picture. The small anodic waves (Fig. 6) are only observed if the substrate is reduced and if the electrode is rotated. They are not observed if the ring is fixed at a potential of −0·5 V or more negative, and they are probably due to consecutive reactions (9), (3a) and (10), like peaks B and C in CV. In fact two overlapped waves can be seen for IPh experiment at thigh rotation speeds (Fig. 6a). Intermediates detected at the ring also disappear after phenol addition.

N_k values shown in Table II are small compared with N (0·20), thus indicating that the species detected are unstable in our experimental conditions. Further
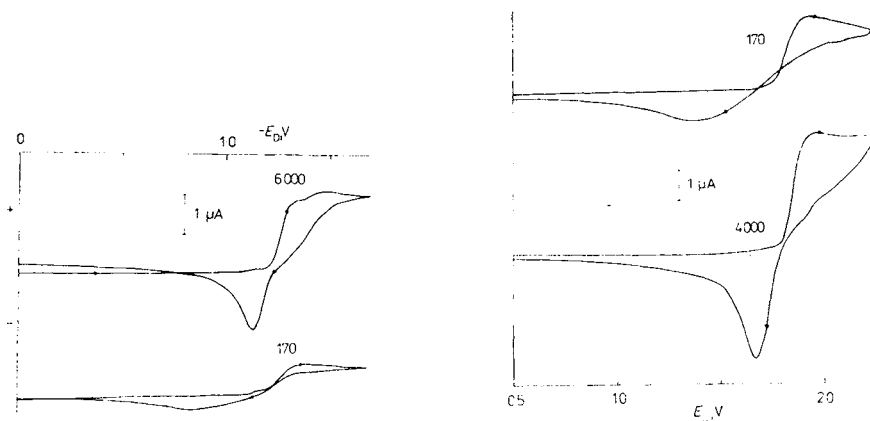

FIG. 6

Ring currents vs disk potentials at the RRDE for: a 1 . 10^{-3}M IPh and b 1 . 10^{-3}M BrPh in DMF/0·1M TEAP. Ring potential fixed at 0 V. Rotation speeds (ω, in rpm) are given in the figures. Sweep rate 0·02 V s^{-1}

evidence of this is provided by N_k decreasing upon increase of rotation speed (ω, Table II). This is qualitatively predicted for EC processes in certain conditions[17], and implies that the detected intermediate is not the radical anion, since in such a case N_k would increase with ω, approaching N at sufficiently high values of ω (ref.[22]). N_k values are especially low for IPh as compared with BrPh (Table II) and dihalobenzenes[11], thus indicating that there is a minor yield of phenyl anion in IPh reduction, i.e. the radical path and/or other competitive reactions are favored against the ionic mechanism in this case, as compared with reduction of other halobenzenes. This is consistent with the less cathodic potential needed for IPh reduction, the minor number of electrons/molecule obtained by coulometry and the smaller amount of decomposed TEAP in IPh electrolysis[2].

Cathodic peaks more or less broad are observed for IPh and BrPh in reversed scans of i_R vs E_D (Fig. 6). Their shape and behaviour indicate that they are due to the reduction of one product adsorbed at the Hg surface. They are not observed if the anodic step is not carried out before and, since in every case the area covered by the anodic wave is greater than the area covered by the cathodic peak and both areas are proportional, we believe the cathodic peaks are due to reaction (*11*). This re-action is favoured by the higher local concentration of phenylmercury cation relative to the radical after completion of oxidation (*10*), provided no more anion arrives at the ring from the disk electrode. Reaction (*7*) and equilibrium (*3a*) also favour the process since they eliminate phenylmercury radical from the electrode. So do rotation of RRDE, favouring redissolution of phenyl and phenylmercury radicals in such a way that peaks are flat at lower rotation rates due to slower cathodic redissolution.

BrPh showed an adsorption cathodic peak at about -0.5 V in voltammograms at the ring, recorded at a disk potential of -2 V. This peak matches peak E in CV. The same experiment for ClPh at a disk potential of -2.2 V showed two cathodic peaks (Fig. 7) at c. -0.75 V and -1.0 V, followed by a much higher cathodic current owing to substrate reduction. Shape and potential of the peak at -1.0 V match those of peak F in CV and, although there is not a close agreement between the first peak and peak E, it is likely that these peaks at the ring are due to reactions (*11*) and (*3b*), as in CV.

FIG. 7

Ring current vs ring potential at the RRDE for $1 . 10^{-3}$ M ClPh in DMF/0.1 M TEAP. Disk potential fixed at -2.2 V. 1 000 rpm, sweep rate 0.02 V s^{-1}
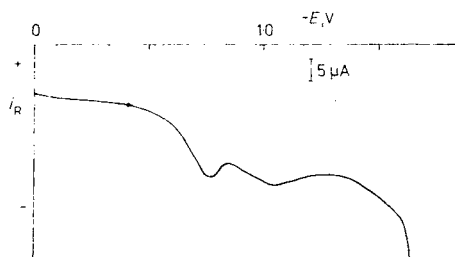
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