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ELECTROCHEMICAL STUDIES OF ORGANOMETALLIC COMPOUNDS

I. THE POLAROGRAPHY OF MERCURY DERIVATIVES OF FERROCENE, CYCLOPENTADIENYL-MANGANESE AND -RHENIUM TRICARBONYLS AND *o*-CARBORANE*

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SUMMARY

The polarographic reduction of the mercury derivatives of ferrocene, cyclopentadienylmanganese and -rhenium tricarbonyls as well as carborane has been investigated. In general, these compounds reduce in a similar manner to other organic derivatives of the type R_2Hg and RHgX investigated. The manner in which the organometallic radical R displays its specificity is discussed in detail.

INTRODUCTION

Electrochemical studies of organometallic compounds are of interest in view of the possible redox properties of these compounds and their use in solving general problems associated with the chemistry of these compounds as well as the synthetic possibilities of the electrochemical method. Thus, in recent years, a great number of papers have dealt with the polarography of organometallic compounds. The organomercury compounds R_2Hg and RHgX (where R = various hydrocarbon radicals) have been those most studied in detail. In some cases polarography has enabled data to be obtained on such important problems in the chemistry of these compounds as complex formation[1–5], stereochemistry[6] etc.

Through the use of polarography it has been possible to determine some characteristics of the hydrocarbon radical R; for example, pK_a of RH has been obtained[6,7] as has the electron affinity[8] of R. In order to obtain similar data for metallocene radicals it is necessary to investigate the reduction mechanism of the respective mercury derivatives. It might also be expected that the presence of an organometallic radical in the molecule would lead to specific electrochemical reduction. For this reason we have studied a series of mercury compounds of the type R_2Hg and RHgX, where R corresponds to ferrocenyl- or cyclopentadienylmetal tricarbonyl (M = Mn, Re). The mercury derivatives of *o*-carborane have also been investigated.

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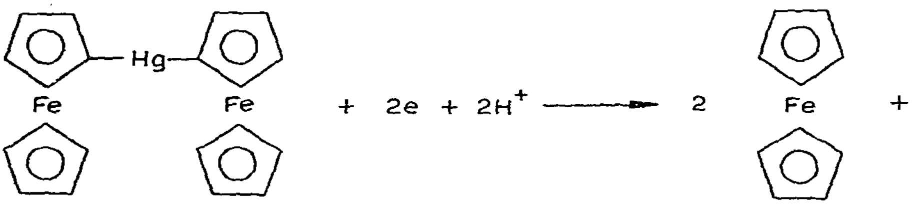
* *o*-carborane = 1,2-dicarba-closo-dodecaborane (12).

RESULTS

I. Mercury compounds of ferrocene

1. *Diferrocenylmercury.* Diferrocenylmercury (I)* is only reduced with difficulty at the dropping mercury electrode. Only in DMF with $(C_4H_9)_4NClO_4$ as the supporting electrolyte is it possible to observe the reduction wave at very negative potentials**, but under these conditions the limiting current almost coincides with the discharge current of the supporting electrolyte. In a similar fashion to other compounds of the type R_2Hg, compound (I) may be considered to reduce according to the scheme:



(1)

In CH_3CN, the polarogram of (I) has a well defined anodic wave. Its half-wave potential, $E_{\frac{1}{2}} = +0.30$ V, is in good agreement with the normal redox potential of diferrocenylmercury ($E_f^0 = 0.283$ V) observed potentiometrically[9]. Thus the anodic wave is consistent with the reversible oxidation of the iron atom in the ferrocene nucleus.

$$C_5H_5FeC_5H_4HgC_5H_4FeC_5H_5 \underset{+e}{\overset{-e}{\rightleftarrows}} C_5H_5Fe^+C_5H_4HgC_5H_4FeC_5H_5$$

2. *Ferrocenylmercury chloride $C_5H_5FeC_5H_4HgCl$ (III).* A study of the polarographic reduction of (III) showed that the best shaped wave is obtained in 90% dioxane*** where the polarogram contained two diffusion-controlled waves of about equal height. From a comparison of the wave heights and of the transfer coefficient α of the compounds (III) and (XXVII), and bearing in mind the fact that diferrocenylmercury reduces at much more negative potentials (relative to that of the second wave of ferrocenylmercury chloride), it may be concluded that $C_5H_5FeC_5H_4HgCl$ reduces according to a scheme similar to that for organomercury salts as proposed by Benesch and Benesch[10].

Introduction of substituents into the unsubstituted ferrocene ring as in compounds (II)–(VII) alters the $E_{\frac{1}{2}}$ value of the first and second waves of the ferrocenylmercury chloride. However, this effect is less than that produced by the introduction of *para* substituents into the phenyl ring (in particular with respect to $E_{\frac{1}{2}}$ for the second wave) and is in fact so small that it is not possible to make a systematic correlation analysis. The results obtained are in agreement with the well-known fact that the transmission of the electronic effect of substituents from one ferrocene ring to the

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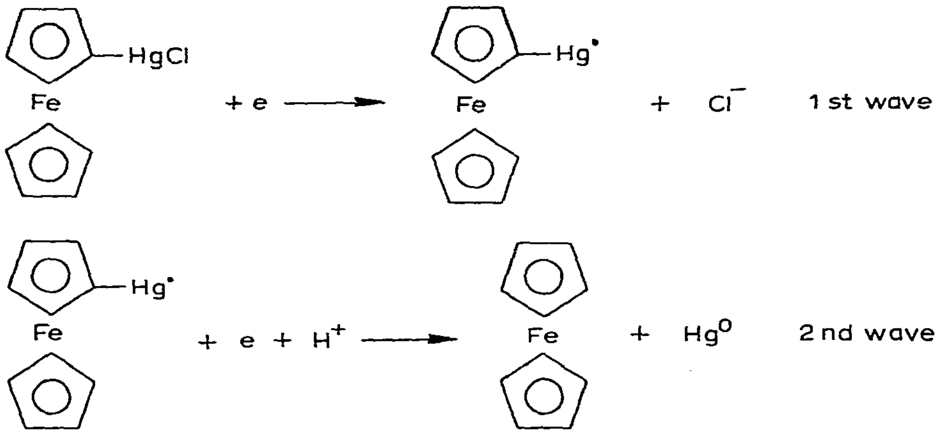
* Compounds are numbered as in Table 1.

** Under these conditions ferrocene does not give a reduction wave.

*** In other solvents investigated by the authors (DMF, CH_3CN and 70% C_2H_5OH/H_2O) the polarographic waves for (III) had a much more complex pattern (Fig. 1). It is possible that such distortion of the wave shape could be due to complicated adsorption processes involving both the depolarizer and the solvent.



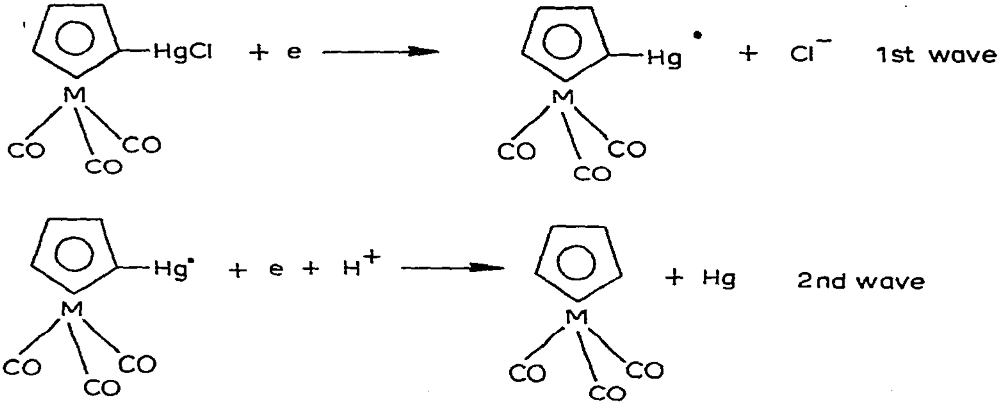
(2)

other is less when the substituent is located in the *para* position in the phenyl ring even when highly electron-deficient reaction centres are concerned[11] and that the latter can never be represented as RHg•.

II. Mercury compounds of cyclopentadienylmanganese (or -rhenium) tricarbonyl

1. *[$C_5H_4M(CO)_3]_2Hg$, M = Mn (VIII), Re (XI).* Two poorly resolved waves of about equal height are observed in the polarograms of these compounds (in DMF or CH_3CN, 0.1 *N* $(C_2H_5)_4NClO_4$) at quite negative potentials. These waves, however, cannot be assigned to reduction of the C–Hg bond in the mercury compounds as such reduction has been shown to occur in the same potential region for the initial unsubstituted complexes (IX) and (XII) (see Table 1)*.

2. *$C_5H_4M(CO)_3HgCl$, M = Mn (X), Re (XIII).* The polarograms of these compounds contain two diffuse waves of approximately equal height (in 90% dioxane, 0.1 *N* $(C_2H_5)_4NClO_4$) (see Table 1). In DMF, the observed polarogram also has two waves, but the initial part of the second wave contains a maximum which distorts its shape. From a comparison of the wave heights and the value of α for compounds (X), (XIII) and (XXVII) (the latter being reduced by a scheme similar to that proposed by



(3)

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* See also ref. 6.

TABLE 1

POLAROGRAPHIC CHARACTERISTICS OF MERCURY DERIVATIVES OF FERROCENE, CYCLOPENTADIENYLMANGANESE (OR -RHENIUM) TRICARBONYL, *o*-CARBORANE AND OTHER COMPOUNDS ($c \approx 1 \times 10^{-3}$ mol·l^{-1}, SCE, 25°, SUPPORTING ELECTROLYTE 0.1 *N* $(C_2H_5)_4NClO_4$)

No.	*Compound*	$-E_{\frac{1}{2}}(V)$	$i_d(\mu A)$	α	*Solvent*
(I)	$(C_5H_5FeC_5H_4)_2Hg$	2.68	2.90	0.22	DMF
(II)	$CH_3OC_5H_4FeC_5H_4HgCl$	0.27	1.10		90% dioxane
		1.84	1.40		90% dioxane
(III)	$C_5H_5FeC_5H_4HgCl$	0.27	1.20	0.37	90% dioxane
		1.84	1.40	0.67	90% dioxane
(IV)	$Cl{-}C_5H_4FeC_5H_4HgCl$	0.31	1.10		90% dioxane
		1.83	1.30		90% dioxane
(V)	$Br{-}C_5H_4FeC_5H_4HgCl$	0.30	1.20		90% dioxane
		1.79	1.30		90% dioxane
(VI)	$CH_3OOC{-}C_5H_4FeC_5H_4HgCl$	0.31	1.20		90% dioxane
		1.80	1.40		90% dioxane
(VII)	$CH_3COOC_5H_4FeC_5H_4HgCl$	0.34	1.20		90% dioxane
		1.78	1.40		90% dioxane
(VIII)	$[C_5H_4Mn(CO)_3]_2Hg$	2.16	3.30		DMF
		2.55	3.30		DMF
(IX)	$C_5H_5Mn(CO)_3$	2.19	1.60		DMF
		2.50	1.60		DMF
(X)	$C_5H_4Mn(CO)_3HgCl$	0.60	1.70		DMF
		1.46	1.70		DMF
		0.39	1.40	0.42	90% dioxane
		1.42	1.40	0.60	90% dioxane
(XI)	$[C_5H_4Re(CO)_3]_2Hg$	2.40	3.0	—	DMF
		2.70	2.60	—	DMF
(XII)	$C_5H_5Re(CO)_3$	2.68	3.10	—	DMF
(XIII)	$C_5H_4Re(CO)_3HgCl$	0.38	1.20	0.40	90% dioxane
		1.38	1.30	0.50	90% dioxane
(XIV)	$(H_2C_2B_{10}H_{10})_2Hg$	0.78	2.40	0.23	DMF
		2.45	3.90		DMF
(XV)	$(C_6H_5C_2B_{10}H_{10})_2Hg$	0.80	2.60	0.23	DMF
		1.97	4.30		DMF
(XVI)	$CH_3C_2B_{10}H_{10}HgCl$	0.89	2.60	0.23	DMF
		2.43	4.30		DMF
(XVII)	$C_6H_5C_2B_{10}H_{10}HgCl$	0.68	2.40		DMF
		1.93	2.60		DMF
		0.89	2.20		90% dioxane
(XVIII)	$C_6H_5C_2B_{10}H_{10}HgBr$	0.68	2.50		DMF
		1.93	2.70		DMF
(XIX)	$CH_3C_2B_{10}H_{10}HgBr$	0.72	2.50		DMF
		2.40	3.00		DMF
(XX)	$HC_2B_{10}H_{10}HgCH_3$	1.26	1.30		DMF
		2.04	2.10		DMF
		2.44	2.50		DMF

(continued)

TABLE 1 (*contd.*)

No.	*Compound*	$-E_{\frac{1}{2}}(V)$	$i_d(\mu A)$	α	*Solvent*
(XXI)	$CH_3C_2B_{10}H_{10}HgCH_3$	1.27	1.30		DMF
		2.04	2.20		DMF
		2.40	2.50		DMF
(XXII)	$C_6H_5C_2B_{10}H_{10}HgCH_3$	1.22	1.40		DMF
		2.20	5.50		DMF
(XXIII)	$H_2C_2B_{10}H_{10}$	2.38	3.60		DMF
(XXIV)	$CH_3C_2B_{10}H_{10}H$	2.35	3.60		DMF
(XXV)	$C_6H_5C_2B_{10}H_{10}H$	1.89	3.60		DMF
(XXVI)	CH_3HgCl	0.68	1.78		DMF
		2.04	1.90		DMF
(XXVII)	C_6H_5HgCl	0.35	1.30	0.50	90% dioxane
		1.78	1.40	0.63	90% dioxane

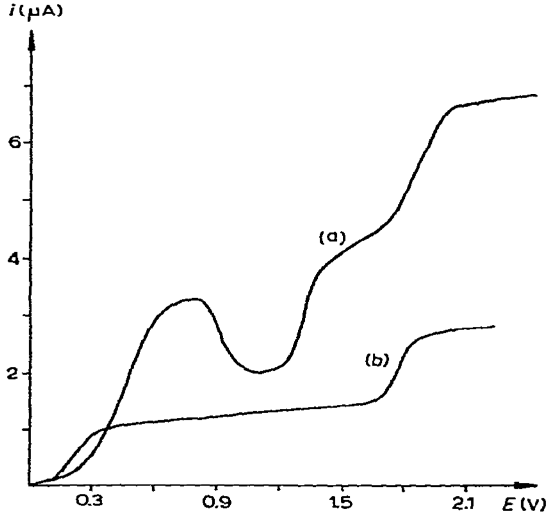


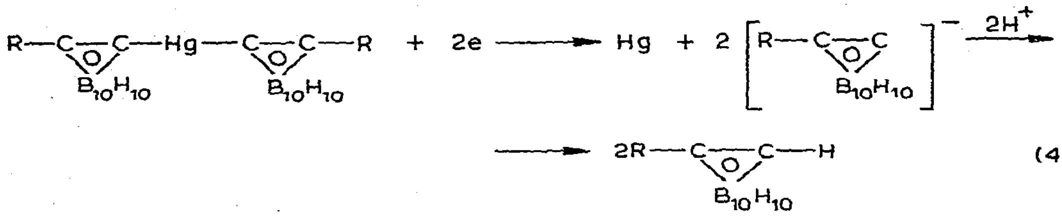
Fig. 1. Polarograms of $C_5H_5FeC_5H_4HgCl$. (a) DMF, 0.1 *N* $(C_2H_5)_4NClO_4$, $c=2\times10^{-3}$ mol·l^{-1} (b) 90% dioxane, 0.1 *N* $(C_2H_5)_4NClO_4$, $c=1\times10^{-3}$ mol·l^{-1}.

Benesch), it is possible to conclude that compounds (X) and (XIII) also reduce via a scheme common to all organomercury salts (Scheme 3). According to this scheme, the formation of $C_5H_5M(CO)_3$ is demonstrated by the observation that in the polarograms of (X) and (XIII) (preferably in DMF as the solvent) the reduction waves occur at negative potentials, the value of $E_{\frac{1}{2}}$ coinciding with that for π-$C_5H_5M(CO)_3$ measured under similar conditions (see above).

III. The o-carborane mercury compounds

1. *Symmetrical carboranylmercury compounds* $(RC_2B_{10}H_{10})_2Hg$. The polarogram of (XIV) (in DMF, 0.1 *N* Et_4NClO_4) contains two diffusion-controlled waves (see Table 1). The first wave is a two-electron wave since its height is comparable to those obtained during the reduction of other R_2Hg compounds, for example $(C_6H_5)_2$-Hg. A plot of log $i/(i_d-i)$ *versus* E gives a straight line of slope equal to 126 mV in-

dicating that the process is irreversible. Thus the first reduction step may be depicted as: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Similar products have been obtained from the chemical reduction of $(RC_2B_{10}H_{10})_2Hg$ with $LiAlH_4$ or Li in dimethoxyethane[12]. As seen from Table 1, the nature of R influences the value of $E_{\frac{1}{2}}$. When $R=CH_3$, in agreement with the electron-releasing properties of the CH_3 group, the value of $E_{\frac{1}{2}}$ shifts to more negative values; in this instance, the effect of the C_6H_5 group is very small*.

It was shown earlier[16] that the carborane nucleus is reduced at the dropping mercury electrode at rather negative potentials, the value of $E_{\frac{1}{2}}$ changing with the nature of the substituents in the carborane nucleus. In addition to the reduction wave for the C–Hg bond at negative potentials, a second wave was also observed in polarograms of dicarboranylmercury compounds investigated in this study. In each case the potential of this wave was very close to that of the respective carborane reduced under similar conditions (see Table)**. The presence of a second wave in the polarogram confirms the formation of carborane as a result of the reaction of the carboranyl anion with the solvent, thus demonstrating the relatively high basicity of the carboranyl anion.

2. *Carboranylmercury salts.* The polarogram for $RC_2B_{10}H_{10}HgX$ (DMF, 0.1 *N* Et_4NClO_4) contains two waves. Under these experimental conditions, however, the first wave is distorted by a high maximum and, in addition, a pre-wave is observed which may be adsorptive in nature. However, when 90% dioxane was employed as a solvent, the maximum disappeared and the polarogram contained two well shaped waves. The first wave is diffusion-controlled, its height being comparable to that of the two-electron wave of the dicarboranylmercury compounds. Thus, the reduction of $RC_2B_{10}H_{10}HgX$ is a two-electron step involving cleavage of the C–X and C–Hg bonds:


(5)

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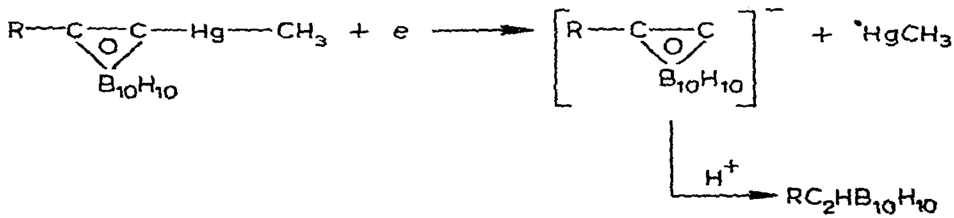
* See also refs. 13–15.

** Some differences in the value of $E_{\frac{1}{2}}$ for (XXIII)–(XXV) and in the second waves of (XIV)–(XXV) may be attributed to the so-called "inheritance effect"[17].

Introduction of a substituent into the carborane influences the value of $E_{\frac{1}{2}}$ for the first wave (see Table 1). The second wave corresponds to the reduction of the carborane nucleus in a similar manner to that of the symmetrical carboranylmercury compounds.

3. *The mixed carboranylmercury compounds* $RC_2B_{10}H_{10}HgCH_3$. Depending upon the compound, the polarogram contains three or two diffusion-controlled waves. The number of electrons participating in the first stage reduction is unity since the height of the first wave is only one-half that of the two-electron wave of $(RC_2B_{10}H_{10})_2$Hg. Since the carboranyl group is more strongly electron attractive in comparison to the methyl group, it is not unreasonable to assume that the following scheme applies for the first reduction step of compounds (XX)–(XXII):



(6)

The influence of substituents in the carborane nucleus on the $E_{\frac{1}{2}}$ values for the first wave and the complete absence of any effect upon the $E_{\frac{1}{2}}$ value for the second wave confirms the scheme proposed. The second wave for (XX) and (XXI) corresponds to the reduction of a methylmercury radical:

$$CH_3Hg\cdot + e \xrightarrow{H^+} CH_4 + Hg\cdot$$

This is confirmed by the coincidence of the $E_{\frac{1}{2}}$ values for the second waves of compounds (XX) and (XXI) with that for the second wave of CH_3HgCl (this compound was studied under similar conditions) which is known to reduce by a Benesch mechanism. The third wave observed for compounds (XX) and (XXI) corresponds to reduction of the carborane nucleus as observed for carboranylmercury compounds (XIV)–(XVI). With (XXII), the waves corresponding to reduction of the $CH_3Hg^\cdot$ radical and of phenylcarborane are common since their potentials are very close.

DISCUSSION

1. *Symmetrical organomercury compounds*

All R_2Hg compounds studied in the present work (other than $[C_5H_4M(CO)_3]_2$Hg where M = Mn, Re) reduce at the dropping mercury electrode via an irreversible two-electron step involving σ-C–Hg bond cleavage as has been observed for other R_2Hg compounds (where R = Alk, Ar)[6,7,18–22].

$$R_2Hg + 2e \rightarrow Hg\cdot + 2R^- \xrightarrow{2H^+} 2RH$$

As seen from the Table, the nature of R mainly influences the $E_{\frac{1}{2}}$ value for R_2Hg, and values of $E_{\frac{1}{2}}$ vary by more than 2V, from that for the most easily reduced compound $Hg(CN)_2$ ($E_{\frac{1}{2}} = -0.45$ V) (DMF, 0.1 N Et_4NClO_4) to that for diferrocenylmercury.

The presence of an organometallic radical R in R_2Hg gives rise to a specific polarographic pattern. For carboranylmercury compounds, in addition to the wave corresponding to reduction of the C–Hg bond, an additional wave appears at more negative potentials corresponding to reduction of the carborane nucleus. For $[C_5H_4M(CO)_3]_2Hg$, however, reduction of the $C_5H_4M(CO)_3$ radical (M = Mn, Re) probably occurs at the same potential as that of the C–Hg bond. With diferrocenylmercury, it is possible to observe an anodic oxidation wave for the ferrocene iron in the positive potential region. These characteristics may not necessarily be confined to these particular compounds, but may be common to the polarographic reduction of all R_2Hg compounds[22]. In order to understand the mechanism of the electrode reaction in the reduction of R–Hg bonds at the dropping mercury electrode, it is necessary to solve the problem of where the electronic changes associated with such a reduction are located in R_2Hg compounds. On the basis of the data available, two viewpoints can be put forward regarding this problem:

1. The electrons are transferred to the mercury atom which is positively charged as a result of the heterolytic activation[20] of the organomercury compound $R^- : Hg^{2+} : R^-$.

2. A molecule of R_2Hg is activated through a homolytic mechanism in the vicinity of an electrode with the result that in general any electronic changes associated with the molecule are located on the half-filled orbital of the $R^\bullet$ radical[22].

In our opinion, this second viewpoint regarding the mechanism of the electrode reaction is the more probable for the following reasons: (a) If mercury cyanide $Hg(CN)_2$ or other easily reduced R_2Hg compounds react at the dropping mercury electrode by the first scheme, then it is not very likely that organomercury compounds such as diphenyl- or diferrocenyl-mercury which contain covalent C–Hg bonds could react by this mechanism, for no evidence has been obtained for an equilibrium of the type $R_2Hg \rightleftharpoons 2R^- + Hg$ in any of the solvents studied. Furthermore, no reliable evidence has been obtained for a polarization of the type $R^- : Hg^{2+} : R^-$. (b) The second mechanism is also favoured by the fact that a large number of reactions involving symmetric mercury compounds proceed by a homolytic mechanism[23,24]. (c) If mechanism 2 applies, then it would be expected that the $E_{\frac{1}{2}}$ values for compounds of the type R_2Hg should vary as the electron affinity of the hydrocarbon radical R varies;

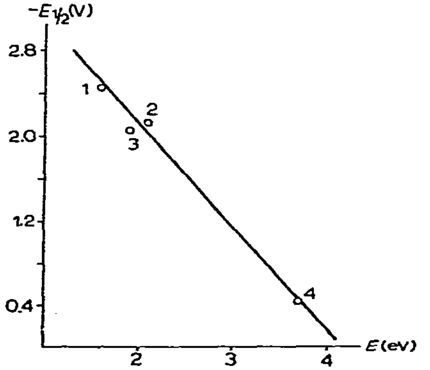


Fig. 2. A plot of the $E_{\frac{1}{2}}$ value of R_2Hg (in DMF, 0.1 N Et_4NClO_4) *versus* the electron affinity of the $R^\bullet$ radical. 1, $R = C_6H_5$; 2, $R = C_3H_5$; 3, $R = C_6H_5CH_2$; 4, R = CN.

in other words, there should be an approximately linear change in the $E_{\frac{1}{2}}$ value of R_2Hg and the $E_{\frac{1}{2}}$ of the second wave of RHgX (reduction of the $RHg^{\bullet}$ radical)*.

Figure 2 shows such a plot for the $E_{\frac{1}{2}}$ values obtained and it can be seen that a good linear relationship is observed between the $E_{\frac{1}{2}}$ value for R_2Hg and E. Thus on the basis of the data presented it is not unreasonable to assume that the mechanism involving homolytic activation of the $R^{\bullet}\ {}^{\bullet}Hg^{\bullet}\ {}^{\bullet}R$ molecule is the more probable.

2. *Organomercury salts*

As mentioned above, polarographic reduction waves in 90% dioxane exhibit the best pattern, being undistorted by maxima or pre-waves. The results obtained show that for all the RHgX compounds investigated (where R = ferrocenyl, $C_5H_4M(CO)_3$, M = Mn, Re) reduction occurs by the Benesch scheme similar to that observed for other RHgX (R = aryl, alkyl) compounds[10].

$$RHgX + e \rightarrow RHg^{\bullet} + X^- \quad \text{1st wave}$$

$$RHg^{\bullet} + e \xrightarrow{+H^+} RH + Hg \quad \text{2nd wave}$$

Carboranylmercury halides provide an exception for they reduce at the dropping mercury electrode via a two-electron step. This behaviour may be attributed to the strong electron-attracting properties of the carboranyl group which result in the first and second waves combining to form a single wave. The possibility of a one-step two-electron reduction process for some RHgX compounds has been commented upon elsewhere[22]. The mechanism of the polarographic reduction of organomercury salts will be discussed in the second paper in this series.

3. *Mixed organomercury compounds*

The compounds RHgR′, where R and R′ are alkyl or aryl, are unstable and inclined to decompose even at room temperature to give a mixture of two symmetric compounds R_2Hg and R'_2Hg. But when R = carboranyl, such compounds are stable and do not disproportionate even in the melt[12].

The presence of σ-bonded Hg–C in these compounds makes them similar to the symmetrical organomercury compounds. However the chemical behaviour of Hg–R and Hg–carboranyl bonds is considerably different[12]. The study of such compounds is also important from the viewpoint of carborane chemistry as well as from that of understanding the various factors which influence the polarographic reduction of mixed organomercury compounds, a subject which has not been studied up to date.

It has been found that mixed carboranylmercury compounds, unlike other derivatives of this type which have been investigated, reduce in a stepwise manner similar to the behaviour of organomercury salts (when R = alkyl or aryl). Due to the strong electron attraction exerted by the carboranyl group, the first stage corresponds to the reduction of the Hg–C (carboranyl) bond, while reduction of the $CH_3Hg^{\bullet}$ radical occurs in the second stage. The half-wave potential of the first step occurs at a more negative potential than that for the reduction of the respective bond in symmetrical compounds. This may be explained in terms of the polarity of the Hg–C (carboranyl)

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* Details are given in ref. 27.

bond which results from the electron-attractive effect of the carboranyl nucleus, an effect which decreases upon electron donation from the methyl group via the mercury atom[25].

In conclusion, it should be pointed out that the extent to which the $E_{\frac{1}{2}}$ value changes in both R_2Hg and RHgX compounds agrees with the electron-releasing or electron-attracting properties of the attached groups, and this may provide a method for obtaining a qualitative comparison of the properties of these groups. Thus a comparison of the value of $E_{\frac{1}{2}}$ for dicarboranylmercury and other R_2Hg compounds shows that in the former case reduction occurs at a much less negative potential than with diphenylmercury and that it is also close to the value[12] for the reduction of $(C_6F_5)_2Hg$. This provides evidence for the strong electron-attracting effect of the carboranyl group which is apparently similar to that of the pentafluorophenyl one. This result is in good agreement with the data obtained by other methods[21]. The shift in the $E_{\frac{1}{2}}$ value for diferrocenylmercury towards more negative potentials relative to the value for C_6H_5HgCl is a result of the electron-releasing effect of the ferrocenyl group. Similarly, the shift of the $E_{\frac{1}{2}}$ value for the second wave of $C_5H_4M(CO)_3HgCl$ (when M = Mn, Re), to more positive potentials with respect to that of C_6H_5HgCl, supports the electron-attracting effect of the $C_5H_4M(CO)_3$ group relative to the C_6H_5 group, while the somewhat less negative potential of $C_5H_4Re(CO)_3$ in comparison to $C_5H_4Mn(CO)_3$ demonstrates the greater electron-attracting properties of the former.

EXPERIMENTAL

The polarograms were recorded on an electronic polarograph of type PE-312. The cathode was a dropping mercury electrode provided with a forced dropping device ($m = 1.53$ mg·s^{-1}, $t = 0.37$ s). Outer aqueous saturated calomel electrodes were used as the anode and a comparison electrode. The exact cathode potential was registered by means of a PPTV-I potentiometer. Measurements were carried out in a thermostatted cell at 25±0.1°, absolute DMF and 90% aqueous dioxane being used as solvents. DMF was purified by storage over K_2CO_3 followed by distillation in vacuo, while dioxane was purified by the procedure described elsewhere[26]. The supporting electrolyte throughout was 0.1 *N* $(C_2H_5)_4NClO_4$. All the compounds investigated were synthesized using known methods and had satisfactory elemental analyses and melting points.

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