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Oxidation of Mercury Electrodes in the Presence of Phenyl–Mercury, –Lead and –Bismuth Organometallic Compounds in Dichloromethane

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Abstract

Oxidation processes observed at mercury electrodes in the presence of Ph_2Hg, Ph_3Bi, Ph_3BiCl_2, Ph_4Pb, Ph_3PbCl, Ph_3PbOAc (OAc = acetate), Ph_2PbCl_2 and $PhPb(OAc)_3$ have been examined. The data obtained, in conjunction with other reports available in the literature, suggest that the majority of organometallic species exhibit oxidation processes at mercury electrodes which involve oxidation of the mercury electrode and alkyl or aryl exchange. In the case of R_4M (M = Pb, Sn), R_3Bi, R_2Cd (R = aryl or alkyl group), pathways involving transfer of the R group to the electrode and formation of cationic and radical intermediates are proposed. In the case of R_2Hg, mercury rich cationic organomercury complexes are produced. If a halide or acetate group is present and the central metal is not mercury, then formation of a mixed metal–mercury organometallic complex and HgX_2 appears to be the favoured pathway. As in the case of the reduction studies at mercury electrodes, products formed after the charge transfer process tend to be reactive and may interact with the electrolyte, electrode and solvent.

Introduction

Reduction processes have been reported on numerous occasions for aryl– and alkyl–mercury–tin, and –lead compounds. For example, Pasciak and Gmoch have recently reviewed [1] the reduction of organomercury compounds at mercury electrodes and it has been concluded that both RHgX and R_2Hg compounds (R = aryl or alkyl; X = Cl, Br, acetate, etc.) may be reduced in complex processes involving adsorption and specific interaction with the mercury electrode. Reduction processes for R_3PbX, R_2PbX_2, $RPbX_3$ and their tin analogues at mercury electrodes are also complicated and involve interaction with the mercury electrode [2–4]. In contrast, apart from a report of the reduction processes for triphenylbismuth, triphenylbismuth dichloride, diphenylbismuth chloride and related compounds [5], the electrochemical synthesis of organobismuth compounds [6] and other brief reports containing electrochemical data [7, 8], virtually nothing is known about the electrochemistry of organobismuth compounds.

Recently, we have described a series of oxidation processes that are observed at mercury electrodes in the presence of alkyl–mercury, –cadmium, –lead and –tin compounds [9, 10]. Each of these processes involve alkyl exchange with the mercury electrode and the formation of organomercury compounds. Since alkyl–lead and –tin compounds are widely used industrial chemicals and are environmentally sensitive, the oxidation processes have formed the basis of specific analytical methods for the determination of Me_4Pb and Et_4Pb in gasoline [11] and tributyltin oxide in antifouling paint [12].

In the present study, oxidation processes in dichloromethane observed at mercury electrodes in the presence of the aryl–organometallic compounds Ph_2Hg, Ph_4Pb, Ph_3PbCl, $Ph_3Pb(OAc)$, Ph_2PbCl_2, $PhPb(OAc)_3$, Ph_3Bi and Ph_3BiCl_2 are reported. This combination of compounds has enabled the influence of aryl as opposed to alkyl substitution, the effect of halide or acetate substitution and the influence of a metal with different oxidation states to be examined. In combination with data available in earlier studies, the new information enables a systematic account to be provided of the general principles of oxidation processes at mercury electrodes observed in the presence of organometallic compounds. Relationships with the widely reported reduction processes also emerge from this comprehensive survey.

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Experimental

The organometallic compounds, solvents and electrolytes were obtained from commercially available sources and purified where necessary.

The electrochemical experiments were undertaken with either a conventional EG and G PAR Model 174 Polarographic Analyzer (polarography) or Model 173 Potentiostat with a Model 179 digital coulometer (controlled potential electrolysis). Solutions were degassed with nitrogen to remove oxygen and all experimental data were obtained at (20 ± 1) °C. Working electrodes were either a dropping mercury electrode (polarography) or a mercury pool electrode (controlled potential electrolysis). The reference electrode was Ag/AgCl (saturated LiCl in dichloromethane) which was regularly calibrated by measurement of the reversible half-wave potential, $E_{1/2}$, for oxidation of 5×10^{-4} M ferrocene (Fc) in dichloromethane. The $E_{1/2}$ value of the Fc/Fc^+ redox couple was +0.48 V versus the Ag/AgCl reference electrode. The auxiliary electrode was platinum wire (polarography) or platinum gauze separated from the test solution by a salt bridge (controlled potential electrolysis). Other experimental details are as described elsewhere [9, 10].

Results and Discussion

1. Diphenylmercury (Ph_2Hg)

At low concentrations of diphenylmercury, Ph_2Hg (less than 5×10^{-5} M), d.c. and differential pulse polarograms at the dropping mercury electrode (Fig. 1(a)) exhibit a well defined oxidation process at a potential of about 0.75 V versus Ag/AgCl, which is near to the mercury oxidation limit in dichloromethane. As the concentration of Ph_2Hg is increased, a maximum is observed in d.c. polarograms (Fig. 1(b)). Additionally, a small sharp non-faradaic response occurs over a very narrow potential range at +0.49 V versus Ag/AgCl in both d.c. (insert in Fig. 1(b)) and differential pulse polarograms. Cyclic voltammograms over the potential range near 0.49 V versus Ag/AgCl (insert in Fig. 1(b)) exhibit typical tensammetric type behaviour associated with an adsorption–desorption process. Several workers have reported that Ph_2Hg is strongly adsorbed over a wide potential range on mercury surfaces [13, 14]. The faradaic process at around 0.8 V versus Ag/AgCl is consistent with an oxidation process occurring in the adsorbed state. Consequently, the tensammetric process at 0.49 V versus Ag/AgCl can be attributed to a rearranged form of adsorbed Ph_2Hg. Reutov and Butin [13] have written a review on the formation of adsorbed organometallic compounds on mercury surfaces. A range of 'organic calomels' (R_2Hg_2) and other organometallic compounds are assumed to be formed [13, 14].

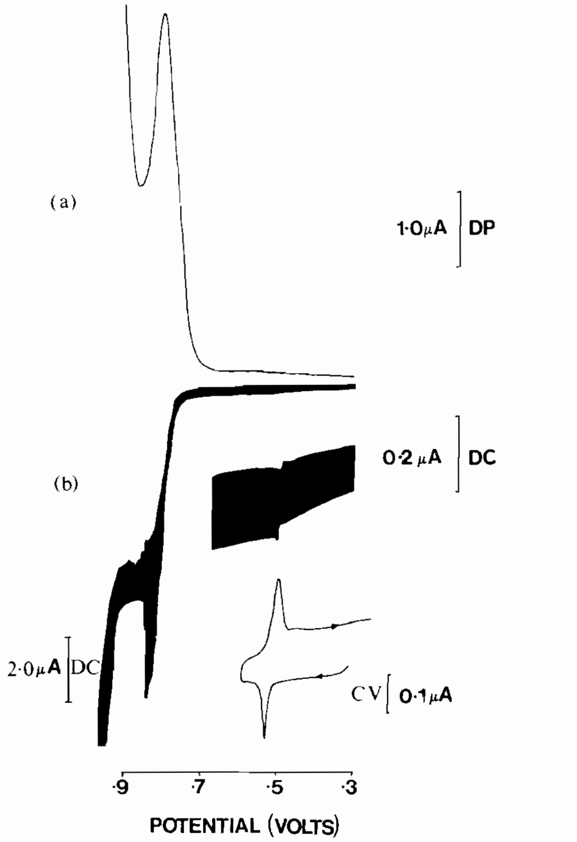

Fig. 1. Oxidation processes observed in dichloromethane (0.1 M Bu_4NClO_4) at the dropping mercury electrode (drop time = 0.5 s, T = 20 °C) in the presence of Ph_2Hg. (a) Differential pulse (DP) polarogram for 5×10^{-5} M Ph_2Hg at a pulse amplitude of 50 mV; (b) DC polarogram for 5×10^{-4} M Ph_2Hg; inserts are an expanded scale DC polarogram over part of the potential range and a cyclic voltammogram (CV) to enable the tensammetric response at 0.49 V vs. Ag/AgCl to be observed (scan rate = 500 mV s^{-1}) at a slowly growing mercury electrode.

The nature of cyclic voltammograms is very dependent on the switching potential. If the potential is switched just beyond the oxidation peak and prior to the potential at which oxidation of the mercury electrode occurs, then a large and well defined reduction process is observed on the reverse scan at +0.3 to +0.4 V versus Ag/AgCl (Fig. 2(a)). However, if the switching potential occurs at more positive potentials (Fig. 2(b)) which includes the potential for oxidation of the mercury electrode, then the cyclic voltammograms are much more complicated. A small reduction process observed at −0.5 V versus Ag/AgCl on the reverse scan at negative potentials (not shown in Fig. 2) can be attributed to the formation of $PhHg^+$ (presumably as a perchlorate from the electrolyte or chloride from the solvent). PhHgOAc, PhHgCl and $PhHgClO_4$ are all reduced in this potential region. The reaction proposed previously [15]

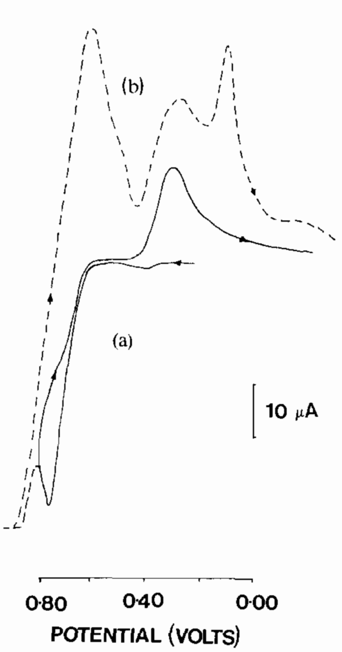

Fig. 2. Cyclic voltammogram obtained at a slowly growing mercury electrode in the presence of 5×10^{-4} M Ph_2Hg in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C. (a) Potential switched just prior to onset of mercury electrode oxidation process, (b) potential switched slightly into mercury electrode oxidation region.

$$Ph_2Hg + Hg \longrightarrow 2PhHg^+ + 2e^- \qquad (1)$$

can therefore only be a minor reaction pathway on the voltammetric timescale and the major product on the voltammetric timescale which can be reduced at +0.3 to +0.4 V versus Ag/AgCl must be a novel species.

Controlled potential electrolysis experiments at mercury pool electrodes are difficult to quantify coulometrically because of the proximity of the mercury electrode oxidation process to the process of interest (see Figs. 1 and 2). d.c. and differential pulse polarograms (Fig. 3) after electrolysis at a mercury pool electrode exhibit two reduction processes centred at about +0.4 and −0.5 V versus Ag/AgCl. The wave at −0.5 V versus Ag/AgCl is attributable to formation of PhHgCl which is now observed as a major product on the long timescale of controlled potential electrolysis. The presumably initially formed $PhHgClO_4$ must react with the solvent or impurities to form PhHgCl. The reduction process in the region of +0.4 V versus Ag/AgCl is complex with considerable adsorption accompanying the charge transfer process. Interestingly, the relative concentrations of PhHgCl ($PhHg^+$) (−0.5 V versus Ag/AgCl) and the other product (+0.4 V versus Ag/AgCl) are in the reverse order to short timescale voltammetric experiments at a slowly growing mercury electrode.

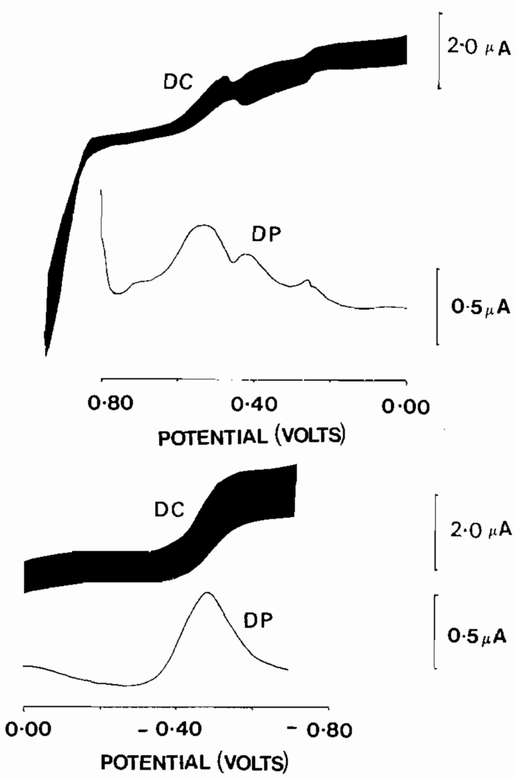

Fig. 3. d.c. (DC) and differential pulse (DP) polarograms obtained after controlled potential oxidative electrolysis in dichloromethane (0.1 M Bu_4NClO_4) at a mercury pool electrode in the presence of 5×10^{-4} M Ph_2Hg (drop time = 0.5 s, pulse amplitude = −50 mV, T = 20 °C).

Controlled potential reductive electrolysis at a potential of +0.3 V versus Ag/AgCl, at a potential where the unidentified mercury compound can be reduced, regenerates Ph_2Hg. This result suggests that the product is a mercury rich phenylmercury cation which can be reduced to Ph_2Hg and (presumably) elemental mercury.

d.c. and differential pulse polarographic monitoring of the reaction of Ph_2Hg with both $Hg_2(ClO_4)_2$ and $Hg(ClO_4)_2$ suggest that these reactions generate a compound which gives rise to the same reduction process at +0.4 V versus Ag/AgCl as seen after oxidative controlled potential electrolysis. However, additional reduction processes in the potential range 0.2 to 0.6 V versus Ag/AgCl (different, depending on whether mercury(I) or mercury(II) perchlorate are used) are observed indicating that a range of compounds is produced by reaction of Ph_2Hg with mercury(I) or mercury(II) perchlorate salts. Controlled potential reduction at potentials more positive than 0.0 V versus Ag/AgCl of the solutions prepared by reaction of Ph_2Hg with mercury salts leads to regeneration of Ph_2Hg in substantial yield confirming the formation of mercury rich derivatives of Ph_2Hg.

The above data suggest that the oxidation process observed at mercury electrodes in the presence of Ph_2Hg occurs via two distinctly different pathways. One pathway is the previously proposed pathway [15] given in eqn. (1). An alternative pathway generating mercury rich cations has not been completely characterized as a range of products may be formed. The simplest reaction which can be proposed is

$$Ph_2Hg + xHg \longrightarrow [Ph_2Hg_{x+1}]^{2+} + 2e^- \qquad (2)$$

The reduction wave at +0.4 V versus Ag/AgCl observed after oxidative controlled potential electrolysis therefore would correspond to the reduction step

$$[Ph_2Hg_{x+1}]^{2+} + 2e^- \longrightarrow Ph_2Hg + xHg \qquad (3)$$

When $x = 2$, eqn. (2) leads to the formulation of $[Ph_2Hg_3]^{2+}$ and this formulation is used in subsequent discussion for simplicity. It is probable that a labile equilibrium mixture of complexes is formed.

Chemical reactions of Ph_2Hg with $HgCl_2$, $Hg(OAc)_2$ and Hg_2Cl_2 as quantified by polarographic monitoring can be interpreted [16]

$$Ph_2Hg + Hg(OAc)_2 \longrightarrow 2PhHgOAc \qquad (4)$$

$$Ph_2Hg + HgCl_2 \longrightarrow 2PhHgCl \qquad (5)$$

$$Ph_2Hg + Hg_2Cl_2 \longrightarrow 2PhHgCl + Hg \qquad (6)$$

In dichloromethane, reactions with species containing the relatively weakly coordinating perchlorate ion as monitored in a polarographic cell involve similar reaction pathways

$$Ph_2Hg + Hg(ClO_4)_2 \longrightarrow 2PhHgClO_4 \qquad (7)$$

$$Ph_2Hg + Hg_2(ClO_4)_2 \longrightarrow 2PhHgClO_4 + Hg \qquad (8)$$

However, reactions of the kind

$$Ph_2Hg + Hg_2(ClO_4)_2 \longrightarrow [Ph_2Hg_3](ClO_4)_2 \qquad (9)$$

$$Ph_2Hg + Hg + Hg(ClO_4)_2 \longrightarrow [Ph_2Hg_3](ClO_4)_2 \qquad (10)$$

appear to occur in parallel with reactions (7) and (8). Whether perchlorate is a coordinating ligand or an inert anion is unknown.

Addition of $[Hg(Me_2SO)_6](O_3SCF_3)_2$ to Ph_2Hg has been reported [17] to occur according to reaction 10 (Me_2SO omitted for simplicity)

$$Hg(O_3SCF_3)_2 + Ph_2Hg \longrightarrow 2PhHgO_3SCF_3 \qquad (11)$$

Mercuric triflate as the dimethyl sulfoxide complex is soluble in CH_2Cl_2 and unlike the insoluble and nonsolvated $Hg(ClO_4)_2$ salt, reacts rapidly. Polarographic monitoring of the reaction of Ph_2Hg and mercuric triflate obviously occurs in the presence of elemental mercury (from the electrode). Under these conditions both the mercury rich compound(s) and $PhHgO_3SCF_3$ are formed. That is, the reaction

$$Hg + Hg(O_3SCF_3)_2 \longrightarrow Hg_2(O_3SCF_3)_2 \qquad (12)$$

can lead to the formation of the same products when reactions with either $Hg(O_3SCF_3)_2$ or $Hg_2(O_3SCF_3)_2$ are monitored in a polarographic cell.

Addition of $Hg_2(NO_3)_2$ produces a mixture of $PhHgNO_3$ and what is designated as $[Ph_2Hg_3](NO_3)_2$ and therefore parallels the behaviour of perchlorate or triflate salts of mercury. In contrast, reactions with mercury acetate and chloride produce PhHgOAc and PhHgCl exclusively, which suggests that the coordinating strength of the ligand is important in determining the relative proportions of the two kinds of complexes formed during the course of reaction with mercuric and mercurous salts.

In analogous studies on Me_2Hg it has been postulated that the species $[Me_2Hg_3]^{2+}$ is formed [13] during the course of the oxidation process observed at mercury electrodes. The Ph_2Hg case is more complex, in that a wider range of species appear to be formed.

Arene complexes of the kind $[Hg(C_6H_6)]^{2+}$ and $[Hg(C_6H_6)_2]^{2+}$ can be formed by reaction of C_6H_6 with Hg^{2+} in liquid SO_2 [18, 19]. Arene complexes are also formed by reaction with Hg_2^{2+} [20]. It would be plausible to postulate that proton abstraction from the solvent has occurred in this work to generate arene complexes. However, the fact that reduction of the new complexes regenerates Ph_2Hg and mercury via a reduction process of the kind given in eqn. (3) and not benzene and mercury seems to rule out this possibility.

The formation of cationic organomercury salts in an aprotic organic solvent via oxidation of the mercury electrode in the presence of R_2Hg has parallels with products obtained in other reactions. For example, Grdenić *et al.* [20] have demonstrated that 'basic phenyl mercuric nitrate' prepared by reactions of Ph_2Hg with $Hg(NO_3)_2$ is actually $[(PhHg)_2OH]NO_3$. Subsequently, Nicholson and Whitton [21] have showed that reaction of PhHgOH or $(PhHg)_2O$ with strong acids such as HBF_4 or HNO_3 produces the $[(PhHg)_2OH]^+$ cation which has been characterized by an X-ray structure of the hydrate $[(PhHg)_2OH][BF_4]\cdot H_2O$. ^{199}Hg NMR data in DMSO or in acidified water suggest that the bis-oxonium structure observed in the solid state is maintained as the favoured species in solution in equilibria involving the phenylmercuric group. In the case of the methyl system, a range of equilibria [22, 23] are available between various species as in eqns. (13) and (14)

$$2MeHgOH \longrightarrow (MeHg)_2O + H_2O \qquad (13)$$

$$3MeHgOH \longrightarrow [(MeHg)_3O)]^+ + OH^- + H_2O \qquad (14)$$

Evidence for $[MeHgOH_2]^+$ and $[(MeHg)_2OH]^+$ is also available [24], although only the tris(methylmercuric)oxonium cation has been isolated [23–25]. Related species include $[(MeHg)_2O(HgR)]^+$ (R = Et, Pr, Ph) [26]. Thus, cationic aryl and alkyl mercury complexes are not unknown. Unfortunately, in the electrochemical experiment in dichloromethane, products of electrolysis have not been able to be isolated and characterized because removal of the solvent appears to favor decomposition pathways. It is highly likely that an equilibrium mixture of a range of species may have been formed and removal of the solvent alters the nature of the species detected via disproportionation and other reactions.

2. *Phenyllead Compounds*

Oxidation processes at mercury electrodes in the presence of tetraphenyllead (Ph_4Pb) have been described previously in dichloromethane [9, 15]. The mechanism was characterized by an initial one electron transfer involving the exchange of a phenyl group to the mercury electrode. Diphenylmercury formed rapidly at the electrode surface. Free radical reactions with the solvent lead to the formation and subsequent electrolysis of tri- and di-phenyllead chloride compounds during controlled potential electrolysis experiments. A number of parallel reaction pathways are available for the triphenyllead radical formed in the initial electron transfer reaction and the resultant electrochemical behaviour is irreversible and complex [9, 15].

Figure 4(a) shows a d.c. polarogram recorded at positive potentials in the presence of triphenyllead chloride in dichloromethane. A well defined oxidation process (labelled process I) is observed with a half-wave potential ($E_{1/2}$ value) of +0.55 V versus Ag/AgCl. This is followed by a very small wave at slightly more positive potentials which is clearly resolved in differential pulse polarograms. The overall d.c. limiting current varies linearly with concentration and is diffusion controlled over the range 10^{-5} M to 5×10^{-4} M. Two reduction processes (at −0.46 and −1.57 V versus Ag/AgCl) are observed in polarograms recorded at negative potentials for Ph_3PbCl in dichloromethane. These processes (not shown in Fig. 4) have been observed in other media where the first process has been shown to involve the transfer of one electron per molecule of Ph_3PbCl [2–4, 26–29]. Comparison of the d.c. polarographic limiting currents per unit concentration for the first reduction wave and for oxidation process I in dichloromethane indicates that process I involves the transfer of one electron per Ph_3PbCl molecule on the d.c. polarographic time scale.

Cyclic voltammograms (Fig. 4(b)) of Ph_3PbCl in dichloromethane recorded at a slowly growing dropping mercury electrode, indicate that process I exhibits some degree of chemical reversibility (see peak I^{red}) at scan rates ≥200 mV s^{-1}. At a scan rate of 100 mV s^{-1}, process I^{red} is barely evident. The initially formed product is apparently not very stable as evidenced by the presence of a range of processes on the reverse (reduction) scan direction of cyclic voltammograms (Fig. 4b).

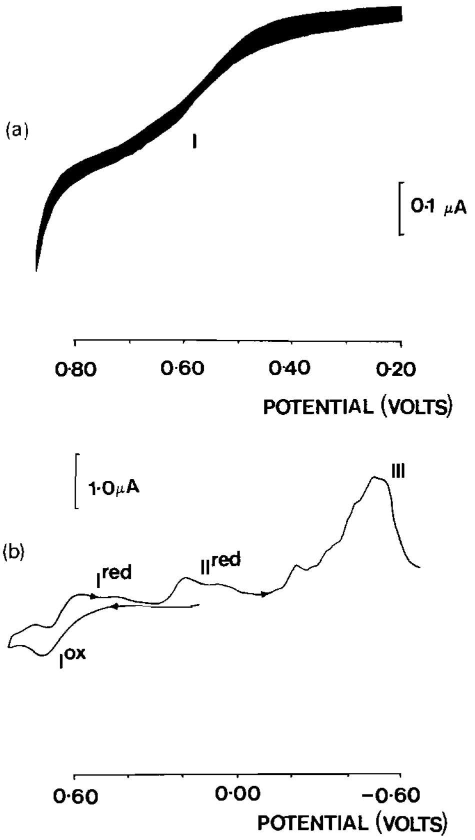

Fig. 4. d.c. polarogram (drop time = 0.5 s) and (b) cyclic voltammogram (scan rate = 200 mV s^{-1}) obtained at mercury electrodes in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C in the presence of 2.2×10^{-4} M Ph_3PbCl.

The potential region of reduction processes observed in the reverse scan in Fig. 4(b), labelled II^{red}, consists of two incompletely resolved waves at 0.2 and 0.05 V versus Ag/AgCl. The species giving rise to the major response at +0.20 V versus Ag/AgCl is unknown. The smaller peak is consistent with the formation of mercuric chloride which is reduced at around 0.05 V versus Ag/AgCl. The complex reduction processes occurring at negative potentials of Fig. 4(b) (region III) on the reverse scan in cyclic voltammograms of Ph_3PbCl may be attributed to reduction processes for Ph_3PbCl (present in bulk solution), and Ph_2PbCl_2 and $PhHg^+$ which are formed at the electrode surface. Reduction processes for PhHgX, ($X = Cl^-$, OAc^- or ClO_4^-) occur in the potential region III in d.c. polarograms of authentic solutions of these compounds in dichloromethane as noted earlier.

Exhaustive controlled potential oxidative electrolysis at a mercury pool electrode for a solution of Ph_3PbCl in dichloromethane set at a potential on the limiting current plateau for process I was complete after the transfer of (1.5 ± 0.1) electrons per Ph_3PbCl molecule as determined by coulometry. Care was taken to set the electrolysis potential at a value which avoids electrolysis of diphenyllead dichloride which is a product formed during electrolysis. A small amount of grey precipitate was formed during the course of the controlled potential electrolysis experiment which contained inorganic lead as $PbCl_2$. Differential pulse polarograms recorded during the course of the electrolysis (Fig. 5) show the response observed at mercury electrodes in the presence of Ph_2PbCl_2, and typified by the inverse differential pulse peak at +0.58 V versus Ag/AgCl (see later). Polarographic responses attributable to the formation of mercuric chloride were not observed during the monitoring of the bulk electrolysis experiments in contrast to short timescale cyclic voltammetric experiments where this was a minor product.

A mechanism for the electrochemical reactions can be proposed as follows:

$$2Ph_3PbCl + 2Hg \rightleftharpoons [Ph_3Pb{-}Hg{-}PbPh_3]^{2+} + HgCl_2 + 2e^- \qquad (15)$$

$$Ph_3PbCl + HgCl_2 \longrightarrow Ph_2PbCl_2 + PhHgCl \qquad (16)$$

$$[Ph_3Pb{-}Hg{-}PbPh_3]^{2+} + 3HgCl_2 \longrightarrow Ph_2PbCl_2 + 4PhHgCl + Pb^{2+} \qquad (17)$$

$$Ph_2PbCl_2 + Hg \longrightarrow \text{products} + ye^- \text{ (see later)} \qquad (18)$$

The polarography of the oxidation process at mercury electrodes in the presence of Ph_3PbCl resembles that described elsewhere for Me_3PbCl [12]. However, the rate of chemical reactions after the initial one electron process is faster. Coulometric data indicate that eqn. (16) is the primary reaction pathway for $HgCl_2$ during bulk electrolysis of Ph_3PbCl.

The oxidation processes observed at mercury electrodes in the presence of Ph_2PbCl_2 are extremely complex. The d.c. polarogram (Fig. 6(a)) shows a well defined one electron oxidation process (designated process I) with an $E_{1/2}$ value of about +0.15 V versus Ag/AgCl followed by a complex non-faradaic process (designated process II) at more positive potentials (+0.60 V versus Ag/AgCl). The differential pulse polarogram exhibits an inverse peak current at potentials corresponding to the non-faradaic process (Fig. 6(b). This 'negative dip' was used to identify Ph_2PbCl_2 as a product of electrolysis with Ph_3PbCl at the mercury pool electrode. On the reverse scans cyclic voltammograms (irreversible process) show no evidence of formation of $HgCl_2$ around 0 V versus Ag/AgCl.

Controlled potential electrolysis experiments in the presence of Ph_2PbCl_2 at a mercury pool electrode

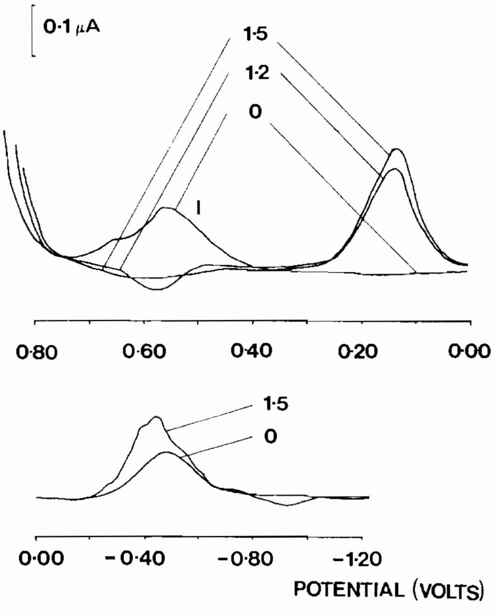

Fig. 5. Differential pulse polarograms recorded after the transfer of 0.0, 1.2 and 1.5 electron equivalents during oxidative, controlled potential electrolysis in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 20 °C at a mercury pool electrode in the presence of 2.2×10^{-4} M Ph_3PbCl.

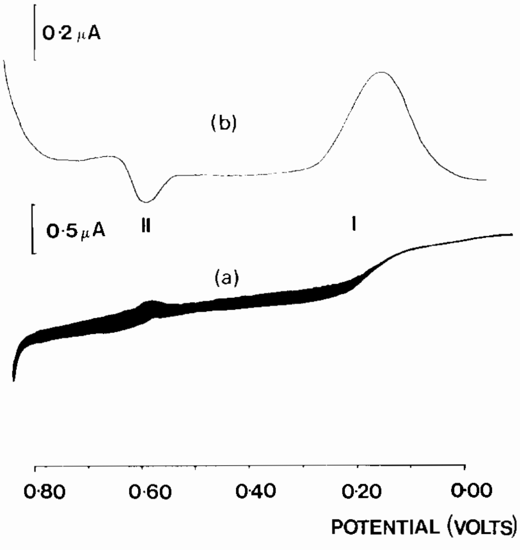

Fig. 6. d.c. polarogram (drop time = 0.5 s) in the presence of 4.6×10^{-4} M Ph_2PbCl_2 and (b) differential pulse polarogram (drop time = 0.5 s, pulse amplitude = 50 mV) in the presence of 3.5×10^{-4} M Ph_2PbCl_2 in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 20 °C.

were complete after transfer of slightly less than one electron per molecule (0.8 ± 0.1) and provided evidence for formation of a wide range of unidentified products as indicated by monitoring by polarography during the course of electrolysis. As in the case of Me_2PbCl_2 and Et_2PbCl_2 [12] the process can be described by the following equations

$$2R_2PbCl_2 + 2Hg \rightleftharpoons [R_2ClPb{-}Hg{-}PbClR_2]^{2+} + HgCl_2 + 2e^- \qquad (19)$$

$$R_2PbCl_2 + HgCl_2 \longrightarrow \text{products} \qquad (20)$$

$$[R_2ClPb{-}Hg{-}PbClR_2]^{2+} + HgCl_2 \longrightarrow \text{products} \qquad (21)$$

For R = Ph reactions (20) and (21) are fast, even on the cyclic voltammetric timescale, so that the process is irreversible and $HgCl_2$ is not seen as an intermediate. The polarography of the acetato compounds Ph_3PbOAc and $PhPb(OAc)_3$ is also complex. In the case of Ph_3PbOAc, a complex d.c. polarographic wave at 0.55 V versus Ag/AgCl is observed and appears to involve at least two unresolved processes. This is followed by a tensammetric response at 0.85 V versus Ag/AgCl similar to that observed for $Hg(OAc)_2$. Mercuric acetate is therefore assumed to be a product of the electrolysis at mercury electrodes. In the case of $PhPb(OAc)_3$, a broad d.c. polarogram with a limiting current corresponding to a one electron process is followed by the tensammetric response at 0.85 V attributable to formation of $Hg(OAc)_2$ as a product of the initial one electron oxidation.

Several general conclusions are available concerning the electrochemistry of phenyllead compounds at mercury electrodes. Substitution of a phenyl group by a halide or other anion usually shifts $E_{1/2}$ to less positive potentials than observed for the oxidation process at mercury electrodes in the presence of Ph_4Pb. The mechanism for the Ph_4Pb process appears to be distinctly different from the substituted compounds in that it involves a free radical mechanism [9, 15] whereas cationic mercury compounds are formed as reactive intermediates in the latter case via exchange processes. Substitution of phenyl for methyl as is the case with organometallic mercury compounds, leads to an increase in adsorption onto the mercury surface and an enhanced rate of attack on the initially formed cationic species by an HgX_2 species (X = halide or acetate), also formed as a product of the electrode oxidation process.

3. Triphenylbismuth (Ph_3Bi) and Triphenylbismuth dichloride (Ph_3BiCl_2)

Figure 7(a) shows a d.c. polarogram in dichloromethane in the presence of triphenylbismuth. Two oxidation processes, labelled process I and II, are observed. No reduction waves are present within the potential range available in dichloromethane. Process I is very drawn out. However, the d.c. limiting current for process I increases linearly with concentration of Ph_3Bi for concentrations over the range 5×10^{-6} to 2×10^{-4} M. Process II occurs at a similar potential

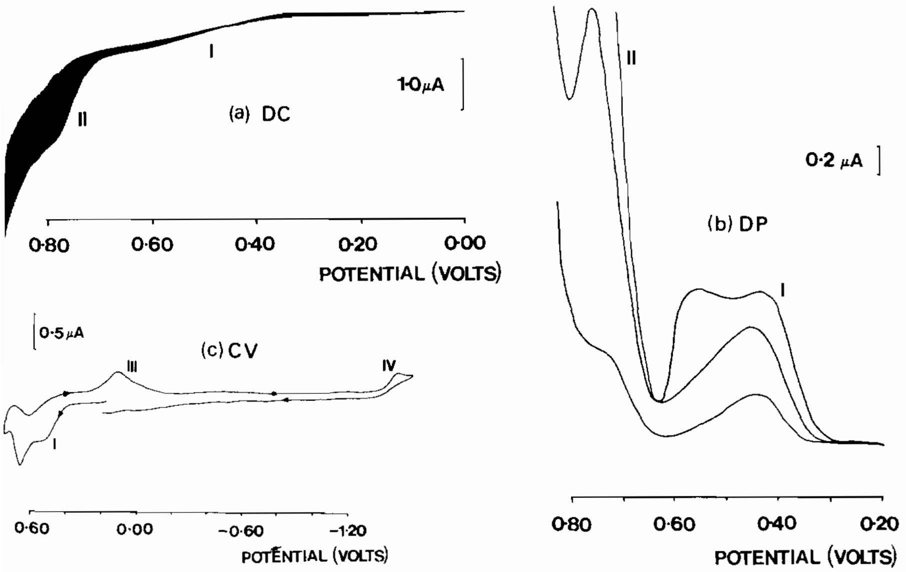

Fig. 7. Polarograms and cyclic voltammetry at mercury electrodes in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 20 °C. (a) d.c. polarogram at the dropping mercury electrode (drop time = 0.5 s) in the presence of 6.7×10^{-4} M Ph_3Bi. (b) DP polarogram at the dropping mercury electrode (drop time = 0.5 s, pulse amplitude = 50 mV) in the presence of (i) 1×10^{-4} M, (ii) 2×10^{-4} and (iii) 8×10^{-4} M Ph_3Bi. (c) Cyclic voltammogram (scan rate = 500 mV s^{-1}) at a slowly growing mercury drop electrode in the presence of 4×10^{-4} M Ph_3Bi.

to polarographic processes observed in the presence of diphenylmercury and is attributed to the generation of this compound as a product of process I.

Differential pulse polarograms recorded for different concentrations of triphenylbismuth in dichloromethane (Fig. 7(b)) confirm that process I is complicated and probably consists of at least two overlapping processes. The differential pulse polarographic peak height for process II does not increase linearly with concentration over the concentration range 10^{-6} to 10^{-4} M. In contrast, the peak heights for differential pulse polarograms of authentic solutions of diphenylmercury do increase linearly with concentration over the same concentration range. This result implies a kinetically complicated process leads to formation of Ph_2Hg.

Figure 7(c) shows a cyclic voltammogram recorded at a growing mercury drop electrode in the presence of triphenylbismuth. Process I is chemically irreversible at scan rates of up to 500 mV s^{-1}. Two new reduction processes, labelled III and IV, are observed in the reverse scan of the cyclic voltammogram. These processes are attributed to the formation of organobismuth chloride complexes and/or their mercury derivatives (see later). Process II is not readily resolved from the mercury oxidation limit in cyclic voltammetric experiments (see discussion in Ph_2Hg section), so potentials more positive than process I generally were not scanned when using this technique.

Coulometric analysis of controlled potential electrolysis experiments at a mercury pool electrode indicate that exhaustive electrolysis required the transfer of approximately one electron per molecule of triphenylbismuth. Differential pulse polarograms recorded before and after exhaustive controlled potential electrolysis are shown in Fig. 8. Process II, which is attributed to the formation of Ph_2Hg, is present both before and after controlled electrolysis experiments as would be expected if this assignment is correct. Reduction processes III and IV, observed on the reverse scans of cyclic voltammograms are also observed after the controlled potential electrolysis of process I. Apparently, short timescale experiments at the dropping mercury electrode and long timescale experiments at the mercury pool electrode lead to the formation of the same products.

The loss of phenyl groups from triphenylbismuth to form diphenylmercury during oxidation process I must follow a complex reaction pathway as proportionately greater concentrations of diphenylmercury are produced with increasing bulk concentrations of triphenylbismuth. The simplest series of equations which may be used to describe process I are shown below.

$$2Ph_3Bi + Hg \longrightarrow 2Ph_2Bi^+ + Ph_2Hg + 2e^- \qquad (22)$$

$$2Ph_3Bi + 2Hg \longrightarrow 2PhBi^{2+} + 2Ph_2Hg + 4e^- \qquad (23)$$

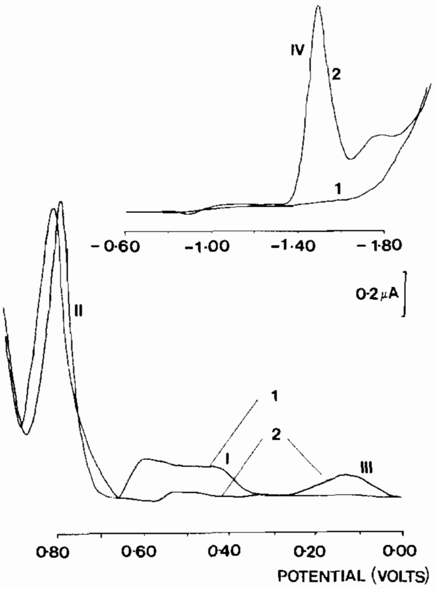

Fig. 8. Differential pulse polarograms (drop time = 0.5 s, pulse amplitude = 50 mV) recorded (1) before and (2) after exhaustive oxidative controlled potential electrolysis at a mercury pool electrode in the presence of 4.0×10^{-4} M Ph_3Bi in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 20 °C.

$$2Ph_3Bi + 3Hg \longrightarrow 2Bi^{3+} + 3Ph_2Hg + 6e^- \qquad (24)$$

The analogous radical pathway to that observed for Ph_4Pb [9, 15] probably also occurs in parallel

$$Ph_3Bi + Hg \longrightarrow Ph_2Bi\cdot + PhHg^+ + e^- \qquad (25)$$

$$2Ph_2Bi^\cdot \longrightarrow Ph_4Bi_2 \qquad (26)$$

$$Ph_2Bi^\cdot + PhHg^+ \longrightarrow Ph_2Bi^+ + PhHg^\cdot \qquad (27)$$

$$2PhHg^\cdot \rightleftharpoons Ph_2Hg + Hg \qquad (28)$$

$$2Ph_2Bi^\cdot + 2CH_2Cl_2 \longrightarrow 2Ph_2BiCl + C_2H_4Cl_2\text{, etc.}$$

The radical-dimerization pathway also forms part of the mechanism proposed for reduction of Ph_3Bi [4, 5]. The cationic complexes are expected to react with the mercury electrode to form mercury–bismuth complexes and/or the electrolyte and/or the dichloromethane solvent and/or traces of chloride impurity to produce chloride complexes. Earlier work by Devaud *et al.* [26, 29, 30] and the present authors [9, 10, 13] has shown that mercury complexes of alkyl– and aryl–lead and –tin compounds are formed during polarographic processes. Reduction process III and IV, observed after the oxidation process for triphenylbismuth may arise from formation of mercury bismuth organometallic complexes (also see subsequent discussion on Ph_3BiCl_2 reduction processes).

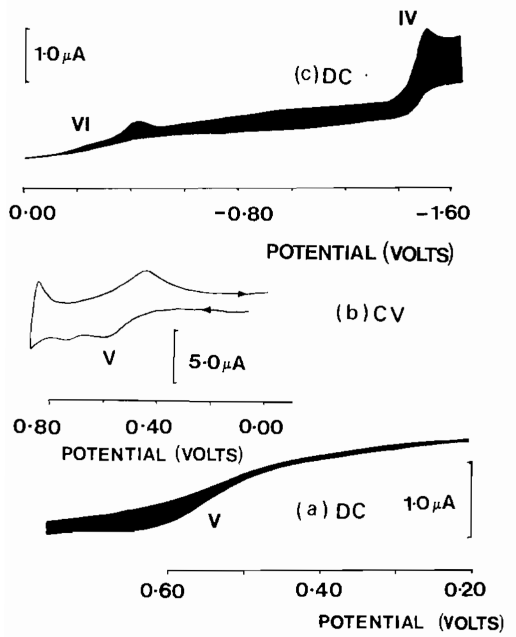

Fig. 9. d.c. polarograms and cyclic voltammograms at mercury electrodes in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 20 °C in the presence of Ph_3BiCl_2. (a) d.c. oxidation response at the dropping mercury electrode (drop time = 0.5 s) in the presence of 2.5×10^{-4} M Ph_3BiCl_2. (b) Cyclic voltammogram (scan rate = 200 mV s^{-1}) in the positive potential range at a slowly growing mercury drop electrode in the presence of 3.8×10^{-4} M Ph_3BiCl_2. (c) d.c. polarogram (drop time = 0.5 s) for reduction of 1.2×10^{-4} M Ph_3BiCl_2.

An oxidation process observed in the presence of Ph_3BiCl_2 at a mercury electrode in dichloromethane is labelled process V in Fig. 9(a). Close inspection of differential pulse polarograms of process V (not shown) shows that it is complex and consists of at least two unresolved processes. Cyclic voltammograms of process V recorded at a growing mercury drop electrode (Fig. 9(b)) show some degree of chemical reversibility at a scan rate of 200 mV s^{-1}. However, no evidence is available for formation of Ph_3Bi or $HgCl_2$ as a product of this oxidation process. Differential pulse polarograms recorded after controlled potential oxidative electrolysis of process V at a mercury pool electrode (Fig. 10) reveal two reduction processes in the positive potential region versus Ag/AgCl (Fig. 10). The origin of these processes are unknown, but the product of their reduction at the mercury pool electrode gives rise to processes which are very similar to reduction processes observed for the starting material (Fig. 9(c), 10). These processes therefore probably arise from formation of cationic mercury bismuth complexes which can be reduced to Ph_3Bi plus elemental mercury. A small amount of precipitate was observed during electrolysis experiments indicating that partial decomposition of the complexes occurs. Coulometric analysis of exhaustive oxidative electrolysis experiments indicated that 1.8 ± 0.1 electrons per molecules were transferred. Equation 29 would be an example of the class of reaction that may occur

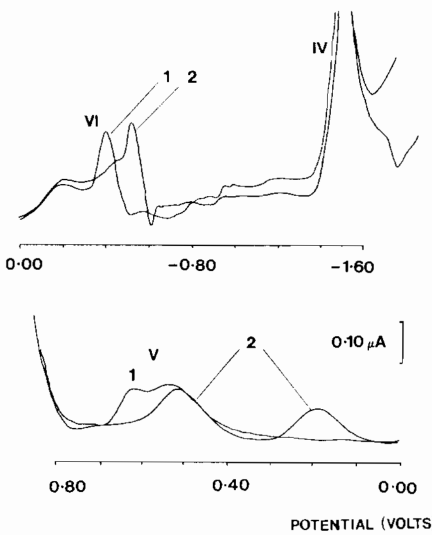

Fig. 10. Differential pulse polarograms (drop time = 0.5 s, pulse amplitude = 50 mV) recorded (1) before and (2) after exhaustive oxidative controlled potential electrolysis at a mercury pool electrode in the presence of 4.6×10^{-4} M Ph_3BiCl_2 in CH_2Cl_2 (0.1 M Bu_4NClO_4), at 20 °C.

$$
\begin{aligned}
&2Ph_3BiCl_2 + 2Hg \\
&\quad [Ph_3ClBi\text{-}Hg\text{-}BiClPh_3]^{2+} + HgCl_2 + 2e^- \\
&\qquad\qquad \downarrow \\
&\quad \text{products (further electron transfer)} \qquad (29)
\end{aligned}
$$

d.c. polarograms of triphenylbismuth dichloride in dichloromethane (Fig. 9(c)) reveal the presence of two reduction processes, labelled VI and IV, in addition to the oxidation process considered earlier. The more negative reduction process is labelled process IV since it occurs at an identical potential to reduction process IV, observed after the oxidation process observed at mercury electrodes in the presence of triphenylbismuth.

Process VI for Ph_3BiCl_2 has been described by Dessy *et al.* as a two electron reduction process in glyme [5]. This aspect of their work is now confirmed in dichloromethane. The d.c. limiting current per unit concentration for the reduction process is twice that observed for process I for triphenylbismuth which has been shown to be a one electron oxidation process. Coulometric analysis of controlled potential reductive electrolysis of process VI at a mercury pool electrode confirms the assignment of this being a two electron process. Polarograms recorded after

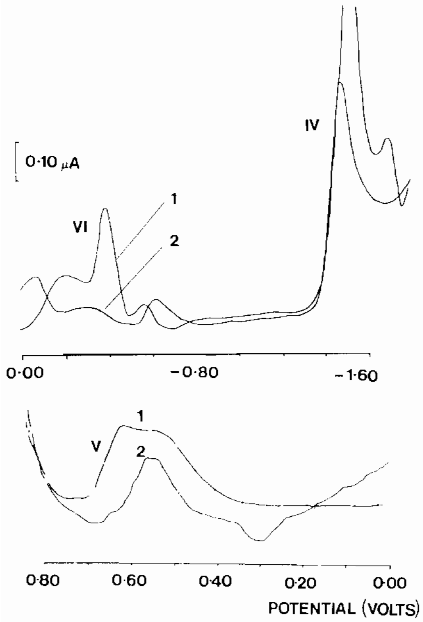

Fig. 11. Differential pulse polarograms (drop time = 0.5 s, pulse amplitude = 50 mV) recorded (1) before and (2) after exhaustive reductive controlled potential electrolysis at a mercury pool electrode of 3.8 × 10^{-4} M Ph_3BiCl_2 in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 20 °C.

the electrolysis show that process IV remains and is due to reduction of a product of process VI (Fig. 11). Process IV is also present after the oxidative electrolysis of triphenylbismuth. Since the oxidation process for Ph_3Bi involves the loss of phenyl groups from the bismuth compound to form diphenylmercury, reduction process VI for triphenylbismuth dichloride can also be assumed to probably involve the loss of phenyl groups. Polarograms recorded after controlled potential electrolysis show that diphenylmercury is not formed as a final product of reductive electrolysis of process VI. Therefore a phenylbismuthmercury compound is the likely product of process VI. Phenylmercuric chloride is reduced in the potential region of process VI at a mercury electrode under similar conditions [5] and could be an intermediate.

Process VI may initially involve reactions of the kind

$$Ph_3BiCl_2 + Hg + 2e^- \longrightarrow Ph_2BiHgPh + 2Cl^- \qquad (30)$$

$$\downarrow$$

$$\tfrac{1}{2}Ph_4Bi_2 + \text{other products}$$

which is followed by a series of further reactions, but the overall process does not appear to occur as in eqn. (31).

$$Ph_3BiCl_2 + 2e^- \longrightarrow Ph_3Bi + 2Cl^- \qquad (31)$$

The fact that process(IV) is common to both the oxidation process for Ph_3Bi and reduction of Ph_3BiCl_2 suggests that a common intermediate such as $Ph_2Bi^{\bullet}$ may be present in both the oxidation and reduction redox processes.

The electrochemical behaviour of Ph_3Bi at mercury electrodes in dichloromethane has many similarities to that of Ph_4Pb. Diphenylmercury is formed rapidly by complex, concentration dependent mechanisms in both cases and extraction of chloride from the solvent or impurities appears to occur during bulk electrolysis experiments. These phenomena are indicative of mechanisms involving phenylbismuth radical intermediates analogous to those described for phenyllead radicals.

The present work on phenyl–mercury, –lead and –bismuth compounds which extends earlier studies on organocadmium and organotin complexes [9–12, 15] leads to the conclusion that both aryl and alkyl organometallic compounds of a wide range of metals (Hg, Pb, Sn, Cd, Bi) are electroactive at mercury electrodes. In the particular case of bismuth, this applies to both oxidation state (III) and (V) complexes. Apparently, a radical exchange type mechanism involving exchange of an R group with the mercury electrode is available for complexes of the type R_4M (M = Pb, Sn), R_2Cd, R_3Bi. When a chloride or other anionic group such as acetate is present, a mixed mercury–metal cationic complex and $HgCl_2$ (HgX_2) may be produced at the electrode surface.

In the case of the parent R_2Hg compounds, a mercury rich cationic species is formed. In all cases the process involves oxidation of the mercury electrode and as is the case with reduction processes which have been reported over many years [1–8], numerous reactions accompany the charge transfer process making access to a complete characterization of the processes difficult.

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