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Polarography of Organoelementary Compounds of Non-transition Elements

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The electrochemical behaviour of many organoelementary derivatives containing a non-transition element is described. The mechanism of the electrode processes and the effect of the conditions of electrolysis are reviewed, mainly at a dropping mercury electrode. A list of 156 references is included.

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Although polarography is used fairly widely in the study of organoelementary compounds, published data have not yet been collected together. The present Review attempts to summarise and systematise very briefly the results of numerous investigations on derivatives of non-transition elements.

I. ORGANOMERCURY COMPOUNDS

These compounds are of especial interest for polarography, since they can be formed by the reaction of mercury with certain depolarisers (e.g. halogeno-derivatives, sulphur-containing compounds, certain aldehydes and ketones), as well as intermediate and final products of electrode processes, e.g. in the reduction of iodonium salts[1]. If sufficiently rapid, the formation of organomercury compounds changes substantially the character and the mechanism of the electrode process, which must therefore always be borne in mind in the study of electrode processes.

The first detailed studies of the behaviour of arylmercuric salts $RHgX$ [2,3] revealed the presence of two one-electron waves on the polarograms in 50% aqueous-ethanolic solutions, with the half-wave potential of the first wave appreciably affected by the nature of the anion X^-.[2,4] Organomercury salts are able to dissociate[5,6]:

$$RHgX \overset{K_1}{\rightleftarrows} RHg^+ + X^- . \qquad (1)$$

If an electrolyte containing a common anion X^- is present in solution, complexes are formed:

$$RHgX + X^- \overset{K_2}{\rightleftarrows} RHgX_2^- . \qquad (2)$$

Reduction of the cation RHg^+ is reversible[4]:

$$RHg^+ + e \rightleftarrows RHg^\cdot . \qquad (3)$$

The resulting radical RHg· dimerises to give an extremely unstable "organic calomel" R_2Hg_2. Formation of the latter was suggested[7,8] after comprehensive discussion of the possibilities for the cathodic reduction of organomercury salts. It has been proved by chronopotentiometric investigations[9], in particular establishment of the nature of the products of interaction of organomercury salts and their reaction with metallic mercury, and of interaction between various disubstituted mercury derivatives[10,11], as well as study of the products of the simultaneous reduction of two different organomercury salts and of reduction of a salt on an electrode covered with the adsorbed symmetrical organomercury compound[10-12].

The organic calomel is converted by disproportionation (which is probably reversible[10,13]) fairly rapidly into the symmetrical organomercury compound:

$$R_2Hg_2 \rightleftarrows R_2Hg + Hg . \qquad (4)$$

It is reduced irreversibly at the electrode[2,10,14-16]:

$$R_2Hg_2 + 2e + 2H^+ \rightarrow 2RH + 2Hg, \qquad (5)$$

corresponding to the second wave on the polarograms of organomercury salts.

Another possibility is that an organic calomel may be formed by a so called "electrochemical desorption mechanism", in which a radical formed at the electrode reacts with the initial substance and simultaneously acquires a second electron from the electrode, as well as, though less probably, by a "hydride" mechanism, in which the product RHg^- of the addition of two electrons to the initial organomercury cation at the potential of the first wave reacts with the initial cation RHg^+.[13]

The lifetime of the organic calomel R_2Hg_2 (before its disproportionation by reaction 4) decreases according to the nature of R in the sequence[12]

$C_2H_5 > \text{cyclo-}C_5H_9 > n\text{-}C_3H_7 > \text{iso-}C_3H_7 \simeq n\text{-}C_5H_{11} \gg 2,4,6\text{-}(CH_3)_3C_6H_2 > 2\text{-}C_{10}H_7 > C_6H_5 \gg CH_2 : CH$

It has been established[13] that neither the organic calomel $(RHg)_2$ nor the unsymmetrical calomel ArHgHgAlk is able to dissociate into free radicals.

The reversible character of transfer of the first electron and the accompanying chemical reactions are responsible for the form of the first wave and the influence of various factors on its parameters[4,15]. Thus if X is not a halogen, the wave in the absence of halide ions in solution is described[4] by the equation for a reversible one-electron

process followed by rapid bimolecular interaction of the electrode products in the adjacent layer of solution[16]:

$$E = \epsilon_0 - \frac{RT}{nF} \ln \frac{i^{2/3}}{i_d - i}, \quad (6)$$

where ϵ_0 is the so called characteristic potential, independent of concentration[16].

When RHgX, where X is a halogen, undergoes reduction in the absence of halide ions in solution, such ions appear at the electrode surface as a result of the electrode process (1), their concentration being greater the stronger the current. The resulting halide ions undergo reaction (2) with the initial salt RHgX, which makes the potential more negative, as occurs with bulk catalytic waves in unbuffered media, when hydroxide ions are formed provided that the wave height is still proportional to the catalyst concentration[16]. In both these cases the wave form is described by the formula

$$E = \text{const} - \frac{RT}{F} \ln K_2 - \frac{RT}{F} \ln \frac{i^{2/3}}{i_{\lim} - i},$$

where a tenfold increase in the depolariser concentration makes the half-wave potential more negative by 40 mV.

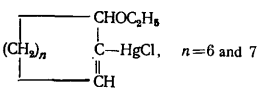
The form of the polarographic wave obtained for an organomercury halide in a solution containing excess of this halide ion is described by Eqn. (6), owing to the occurrence of reaction (2), as with bulk catalytic waves in buffered solutions. The quantity ϵ_0 becomes more negative with increase in the concentration of halogen in the solution[4]. For the ethylmercury halides the half-wave potential of the first wave becomes more negative in the sequence of derivatives Cl → Br → I.

The half-wave potential of the first reversible reduction wave of pyrid-3-ylmercuric acetate becomes less negative with lengthening of the drop period of the electrode and with increase in the depolariser concentration[15], in conformity with the Koutecký–Hanuš theory[17] for a reversible process followed by rapid dimerisation of the electrode products. In just the same way, in agreement with the theory[18] of irreversible electrode processes, for which the rate of electron transfer competes with a bimolecular reaction of the species involved in the electrochemical reaction, the half-wave potential of the second wave becomes more negative with increase in the depolariser concentration[15]. However, organomercury salts exhibit an additional shift in the half-wave potential, due to inhibition of the process by adsorbed reaction products.

The nature of the radical R influences the ease of reduction, the characteristic potential ϵ_0 (or the half-wave potential) becoming less negative with decrease in the acidity pK_a of the corresponding hydrocarbon RH.[19] However, there is no linear relation between these quantities. Negative values of ϵ_0 for the first wave of organomercury perchlorates with 0.1 *N* tetraethylammonium perchlorate as supporting electrolyte in dimethylformamide at 25°C are 0.612, 0.594, 0.613, 0.535, 0.544, and 0.370 V (s.c.e.) when R represents respectively methyl, ethyl, n-propyl, n-pentyl, phenyl, and benzyl[19].

With derivatives of phenylmercury salts not only cations of the initial compounds but also free radicals formed by electron transfer to them are adsorbed on the electrode[20]. Dimerisation of the radicals is then a surface process: i.e. the radicals undergo dimerisation when adsorbed on the electrode. The wave is then described not by Eqn. (6) but by the corresponding expression containing the square root of the current in the numerator of the antilogarithm[21]. Rate constants of surface dimerisation (or those of formation of the symmetrical compound, for it is assumed[20] that formation of an organic calomel is a very rapid reversible process, followed by the slower direct reaction (4) of the free radicals of phenylmercury and several of their derivatives with substituents in the benzene ring have been determined[20] by voltammetry with a linearly varying potential and reversal of the current. The rate constant for free phenylmercury radicals at 25°C is ~ 10^{13} cm^2 s^{-1} $mole^{-1}$. The rate of dimerisation increases or decreases on the introduction of electron-donating or electron-accepting substituents into the benzene ring, with a satisfactory correlation between the logarithm of the rate constant and the σ-parameter of the substituent[20].

cis-1-Chloromercuri-9-ethoxycyclononene and *cis*-1-chloromercuri-10-ethoxycyclodecene. When the group R in an organomercury salt RHgX is very large, the rate of dimerisation of the free radical RHg· is so slow that it ceases to influence the polarographic characteristics of the waves. This situation is probably present[22] in the reduction of these two compounds



which in 50% aqueous dioxan each give two waves, representing reduction to the free radical and its further reduction with separation of metallic mercury. The first wave is reversible, its form being described by the usual Heyrovský–Ilkovič equation for reversible waves with one transferable electron; its half-wave potential is independent of the concentration of depolariser in the solution, and both factors indicate absence of rapid dimerisation of the radicals. When a solution of these compounds in dimethylformamide is electrolysed at the temperature of liquid nitrogen, it acquires a deep yellow colour, which remains for a long time; when the solution warms up to room temperature, however, the colour characteristic of the free radicals disappears after a few minutes[22]. This is also an indication of the comparative stability of the radicals. The second wave on polarograms of these compounds is irreversible, its half-wave potential becoming more negative with increase in the depolariser concentration. For both waves these potentials depend on the pH. Although the investigators[22] speak of the diffusion nature of both waves, the first wave is appreciably lower than the second ($i_{\lim}'/i_{\lim}'' \simeq 2/3$) and has a comparatively high temperature coefficient (increasing from 2.2 to 3.8% deg^{-1} with rise in temperature from 21 to 42°C). The first wave probably has partly kinetic restriction.

trans-1-Chloromercuri-11-methoxycycloundecene and *trans*-1-chloromercuri-13-methoxycyclotridecene. These compounds have been studied under the same conditions[23] (*n* = 8 and 10 in the above general formula, with the ethoxy-group replaced by methoxyl). They each give two one-electron waves, whose limiting currents are independent of pH, while the half-wave potentials vary with pH. The first wave is reversible, and the second irreversible; free radicals appear in the first stage, and either dimerise or acquire a second electron, eliminate mercury, and form an unsaturated compound. The change from *cis*- to *trans*-isomers and the increase in size of the ring result in less negative half-wave potentials of both waves[23]. These potentials for the first waves of ring-substituted bromomercuriphenyl acetates do not correlate with the Hammett σ-constants[24]. Such correlation between the half-wave

potentials of the first waves and the nature of the substituents is absent also from other α-oxomercuric halides[24].

Fluorinated aliphatic organomercury salts. These give two waves representing reduction of the carbon–mercury bond, but in some cases more than two electrons are involved, probably owing to electrochemical cleavage of a carbon–fluorine bond[14].

Perfluorophenylmercuric bromide. In 30% aqueous methanol with 1 M sodium perchlorate as supporting electrolyte this fluorinated compound gives two waves having half-wave potentials (with a depolariser concentration of 2×10^{-4} M) of respectively −0.02 and −0.31 V (relative to an aqueous saturated calomel electrode). It has been shown galvanostatically that the first stage of reduction gives perfluorodiphenylmercury, which is able to form up to ten adsorbed layers on the electrode[25].

Pyrid-3-ylmercury chloride and acetate. In buffered aqueous solutions each of these compounds gives two one-electron diffusion reduction waves (the first of which is reversible), whose half-wave potentials become more negative at pH > 5.0 (at pH 4 these potentials are respectively 0 and −0.37 V independently of the nature of the anion). The waves are distorted by adsorption of the reaction products, so that hysteresis is observed on the polarograms[15].

2-Piperidinoethylmercuric and 2-diethylaminoethylmercuric chlorides. These compounds are reduced in two one-electron stages (whose half-wave potentials in 50% aqueous ethanol are −0.345 and −0.70 V for the former chloride, and −0.35 and −0.62 V for the latter); these potentials are appreciably more negative in dimethylformamide[26]. The reduction products are a symmetrically disubstituted mercury derivative in the first stage, and a secondary amine (piperidine or diethylamine) and ethylene in the second stage. Only traces of tertiary amines were detected among the products of electrolysis[26].

Thien-2-ylmercuric chloride. In buffered solutions this compound gives two one-electron waves (at pH < 8 the first wave is concealed by the anodic mercury-dissolution current).[15] The half-wave potentials become more negative with increase in pH; at pH > 9 that of the second wave ceases to depend on pH, its value then being $E_{\frac{1}{2}} = -0.86$ V (s.c.e.). The first wave is reversible in character, and its half-wave potential is influenced by subsequent dimerisation of the electrode products.

5-Acetylthien-2-ylmercuric bromide. In a 30% aqueous dimethylformamide solution of 1 M sodium perchlorate this compound gives three reduction waves, of which the first two (half-wave potentials −0.06 and −0.73 V s.c.e.) are one-electron diffusion waves corresponding to reduction of the organomercury moiety, and the third represents reduction of the keto-group in the acetylthiophen formed by the first two processes[27]. Galvanostatic study of the bromide shows that it forms adsorbed multilayers on the surface of the mercury electrode.

2-Methoxyethylmercuric salts. Products of the addition of mercury(II) salts to alkenes in methanol, of the type $CH_3O.CHR.CH_2.HgX$ (where X is an acid radical), behave similarly to other organomercuric salts when polarographed: they give two reduction waves on the polarograms, the first of which is reversible and corresponds to formation of the radical R′Hg· adsorbed on the mercury (its half-wave potential does not depend on the pH but is affected by the nature of the anion); the second wave is an irreversible reduction of the radical (or "calomel") to R′H with the liberation of Hg^0.[28]

2-Hydroxyethylmercuric salts. In neutral or alkaline buffered solutions these compounds HOC_2H_4HgX give two pH-independent one-electron diffusion waves with half-wave potentials of −0.45 and −1.10 V for the chloride, and −0.63 and −1.30 V for the acetate. On acidification of the solutions the height of the first wave increases at the expense of the second, so that at pH < 5 a single two-electron wave remains[29]. Preparative electrolysis at potentials corresponding to the first wave give the symmetrical bishydroxyethylmercury[30]. At those of the second wave ethanol and ethylene are formed, the proportion of the alcohol increasing when the solution is made alkaline; in acid solutions, however, the yield of ethylene approaches 100%.[29] The formation of ethanol may be due to reduction of the symmetrical bishydroxyethylmercury formed on electrolysis[30].

2-Chloromercuri-3,3,3-trifluoropropan-1-ol. In a solution of 0.1 *N* potassium chloride in 80% ethanol this compound and its ethers $CF_3CH(HgCl)CH_2OR$ give two one-electron diffusion waves (with half-wave potentials of −0.37 and −0.080 V (s.c.e.) for the propanol). On acidification the first wave grows at the expense of the second, so that in acid medium only a single wave appears with $E_{\frac{1}{2}} = -0.37$ V.[31] Electrolysis in acid medium at the potential of the first wave entails protonation of the intermediate radical with further transfer of a second electron, as a result of which the ether bond is ruptured and the alkene $CF_3CH:CH_2$ is formed. At the potential of the second wave in neutral or alkaline media carbon–mercury and carbon–fluorine bonds are broken with formation of difluoroallyl alcohol (or an ether $CF_2:CHCH_2OR$).[31]

o-Chloromercuriphenol. The usual two one-electron diffusion waves are observed in buffered aqueous solutions. With a buffer containing nitric acid (0.05 M HNO_3 + 0.45 M $NaNO_3$), however, waves of unusual character are observed owing to the very sparing solubility of the intermediate formed on the electrode by transfer of the first electron[32]: the half-wave potential of the first wave becomes more negative with increase in the depolariser concentration, owing to retardation of the process by a reaction product; and in the second wave the current in the lower part is independent of the depolariser concentration, whereas the upper part of the wave is almost rectangular, the ascending portion of the wave passing abruptly, at an angle, into a limiting-current plateau. The absence of dependence of the current in the lower part of the wave on the concentration of the starting material is attributed[33,34] to a constant surface concentration of the reactant, due to its great adsorbability and very low solubility. The equations deduced[32] for both waves and the dependence of the half-wave potential of the first wave on the depolariser concentration reproduce correctly the peculiarities of the reduction waves for *o*-chloromercuriphenol in aqueous nitric acid.

Ferrocenylmercury salts. Both these compounds and mercury salts of manganese and rhenium cyclopentadienyltricarbonyls are reduced similarly to

ordinary organomercury salts[35]. However, here two-step reduction waves (with respect to mercury), each corresponding to the transfer of one electron, can be obtained only in a 0.1 M solution of tetraethylammonium perchlorate in 90% dioxan (under these conditions neither ferrocene nor the manganese and rhenium atoms in the above compounds are involved in the electrode process). In the same medium a carboranylmercury salt gives two two-electron waves, the first corresponding to reduction to Hg^0 and carborane, and the second to reduction of the latter. As was to be expected, the introduction of substituents into the ferrocene ring system affects the half-wave potentials of both waves on polarograms of ferrocenylmercuric chloride, but the shifts are very small[35], which is consistent with the low-transmission of the induction effect of one ferrocene ring into the other.

It has recently been shown[36] that transfer of the first electron may occur either reversibly or irreversibly depending on the conditions. Thus allyl- and phenylmercuric halides give reversible waves in aqueous ethanol (1 : 1) and in ethanolic benzene (1 : 1), whereas in aqueous dimethylformamide and acetonitrile the first waves are irreversible with their half-wave potentials independent of the nature of the halide.

As already noted, the second reduction waves on polarograms of organomercury salts correspond to reduction of the "organic calomel" by reaction (5). Their half-wave potentials often depend on pH in acid media, but not in alkaline media[2]. In view of the possible reversible disproportionation (4) it might be expected that the symmetrical organomercury compounds R_2Hg formed by this reaction would be reduced at the same potentials as are the $RHg^{\cdot}$ radicals. In fact, however, the waves of symmetrical organomercury compounds are usually situated at more negative potentials than are those of R_2Hg_2. The presence of separate R_2Hg_2 and $R_2Hg^{\cdot}$ waves is due to the comparatively low rate of establishment of equilibrium (4).

The difference between the half-wave potentials for the reduction of HgR_2 and $RHg^{\cdot}$ is smaller the lower the absolute value for the former[35]. If an organomercury salt is reduced very readily, the difference between the half-wave potentials of first and second waves becomes small, so that sometimes (e.g. with carboranylmercury salts) the two waves coalesce into a single two-electron wave[35].

A linear relation exists between the half-wave potential of the second reduction wave of RHgX and the electron affinity of the radical $R^{\cdot}$. This enables the electron affinity of the radical to be estimated from polarographic data[35].

Symmetrical organomercury compounds. These are reduced irreversibly in a single stage involving two electrons[37]:

$$R_2Hg + 2e + 2H^+ \rightarrow 2RH + Hg.$$

The half-wave potential is usually unaffected by solution pH. Such an effect, i.e. preceding protonation, occurs only when R contains basic groups (e.g. carbonyl).

In some cases a symmetrical compound adsorbed on the mercury electrode reacts quite rapidly with the mercury to form free radicals $RHg^{\cdot}$ or an organic calomel[9], which are reduced at less negative potentials. Two waves are then observed on the polarograms, the second corresponding to reduction of the symmetrical compound that has not reacted with mercury[9].

The ease of reduction of R_2Hg depends on the polarity of the R–Hg bond: the more polar this bond, the more readily does reduction take place[37]. Organomercury compounds containing an α-oxo-group are reduced most easily. Thus for the reduction wave of $(C_6H_5CHCOOC_2H_5)_2$.Hg in 0.1 M sodium tetrafluoroborate in 50% aqueous methanol $E_{\frac{1}{2}} = -0.36$ V (s.c.e.), whereas the corresponding potential for dibenzylmercury under the same conditions is −1.64 V.[37] In 0.1 M tetraethylammonium perchlorate in dimethylformamide diphenylmercury gives a wave with $E_{\frac{1}{2}} = -2.21$ V (relative to 0.1 M $(C_2H_5)_4NI/Hg_2I_2$ in dimethylformamide).

The most positive value $E_{\frac{1}{2}} = -0.18$ V (s.c.e.) has been obtained for the reduction wave of mercury dicyanide in water, the wave being reversible[38], in contrast to other symmetrical organomercury compounds. Diferrocenylmercury, in contrast, is reduced at extremely negative potentials (in 0.1 M tetrabutylammonium perchlorate in dimethylformamide $E_{\frac{1}{2}} \simeq -2.68$ V aq.s.c.e.).[35]

Diphenylmercury. In tetrabutylammonium perchlorate dissolved in dimethoxyethane this compound gives a wave with $E_{\frac{1}{2}} = -3.32$ V (relative to an $Ag/AgClO_4$ (10^{-3} M) electrode). The half-wave potentials for the reduction of perchlorodiphenylmercury and perfluorodiphenylmercury under the same conditions are respectively −2.63 and −1.81 V.[14]

Perfluorodiphenylmercury. In a 1 M solution of sodium perchlorate in 30% aqueous methanol the polarograms contain one two-electron diffusion wave with $E_{\frac{1}{2}} = -1.06$ V (s.c.e.) independent of pH. The galvanostatic reduction of multilayers of perfluorodiphenylmercury adsorbed on the mercury electrode exhibits only one arrest at low current densities, but two at high current densities, the first corresponding to reduction of the first layer, and the second to reduction of the remaining layers[25]. Perfluorodiphenylmercury has been used as model compound to study the effect of the structure of the electrical double layer on the reduction of an adsorbed depolariser[39], as well as the effect of partial desorption of the depolariser on the capacitive section of the charging curve in the galvanostatic reduction of a substance adsorbed on the surface of a suspended mercury drop[40].

Bis-5-acetylthien-2-ylmercury. In a 1.0 M solution of sodium perchlorate in 30% aqueous dimethylformamide this gives two waves, the first of which ($E_{\frac{1}{2}} = -1.29$ V) corresponds to rupture of carbon–mercury bonds, and the second to reduction of the acetylthiophen formed[27].

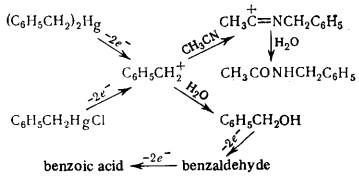
Bis-2,5-diphenyl-1,3-oxazol-4-ylmercury. With linear variation of the potential at a stationary platinum disc electrode in dimethylformamide the volt–ampère curves contain three reduction peaks[41]. With a rate of change of the potential $V = 20$ mV s^{-1} the potential of the first peak $E_p = -1.96$ V (s.c.e.) becomes more cathodic with increase in V, which indicates an irreversible chemical reaction following reversible electron transfer. The ratio of the peak current to $V^{\frac{1}{2}}$ increases with V, which is characteristic of a process with weak adsorption of the depolariser[42]. The first peak corresponds to rupture of carbon–mercury bonds; the other two peaks represent reduction of the mercury-free oxazoline derivative formed.

Bis-2-piperidinoethylmercury. In 50% aqueous ethanol this is reduced to piperidine ($E_{\frac{1}{2}} = -1.5$ V), but it gives no reduction waves in dimethylformamide[26].

The slopes of the waves (i.e. the experimental apparent transfer coefficients α_{exp}) vary greatly for different organomercury compounds. This is one reason for the absence of a strict correlation between the half-wave potentials and the Taft (or Hammett) σ-values of substituents. However, derivatives of dibenzylmercury with various substituents in the ring (when α_{exp} remains approximately constant) satisfy the correlation $E_{\frac{1}{2}}^{\frac{1}{2}} = 2\sigma\rho$ fairly well, where σ is the Hammett constant of the substituents, the factor 2 reflects the presence of two groups in both benzene rings, and $\rho = +0.49$ V.[37] A good correlation is observed also between the product $\alpha_{exp}E_{\frac{1}{2}}^{\frac{1}{2}}$ and the acid dissociation exponent pK_a of the hydrocarbon RH formed by the radical R.[19,37] It formed the basis of a proposed acidity scale for CH acids of saturated, aromatic, and unsaturated hydrocarbons, polyfluorinated and carbonyl-containing compounds, barenes, and certain other compounds[43]. However, it has been found[44] that the pK_a of CH acids correlate better with $E_{\frac{1}{2}}^{\frac{1}{2}}$ than with the product $\alpha_{exp}E_{\frac{1}{2}}^{\frac{1}{2}}$; values of pK_a have been estimated[44] for ferrocene and for the cyclopentadienyltricarbonyls of manganese and rhenium.

The polarographic method has been used to study the kinetics and the equilibria in the reaction of diphenylmercury with mercury dicyanide, bistrichloromethylmercury, and mercury bisphenylacetylide[45], as well as of diphenyl- and di-*p*-methoxybenzyl-mercury with certain symmetrical carbonyl-containing organomercury compounds in dimethylformamide solution[46].

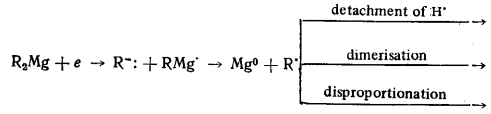
Application of a linearly varying potential to a rotating platinum anode in acetonitrile with 0.1 M sodium perchlorate as supporting electrolyte gives with organomercury compounds clear oxidation waves having half-peak potentials (with $V = 20$ V s^{-1}) of 1.28, 1.53, 1.58, 1.95, and 1.84 V (relative to silver in 0.01 *N* silver perchlorate) for n-propylmercuric chloride, benzylmercuric chloride, dibenzylmercury, phenylmercuric tetrafluoroborate, and diphenylmercury respectively. The waves are completely irreversible. The results of preparative electrolysis in acetonitrile alone and with water (10%) suggested the following schemes



i.e. the first stage always involves rupture of a carbon–mercury bond and formation of a carbonium cation. In the presence of water the process is influenced by the anions of the supporting electrolyte[47].

II. ORGANOMAGNESIUM COMPOUNDS

Dialkylmagnesium derivatives. When dissolved in dimethoxyethane these compounds R_2Mg give anodic oxidation waves having $n = 2$ (the products are R_2Hg and Mg^{2+}), but are not reduced: reduction waves (with $n = 1$) are observed only when R forms a comparatively stable carbanion[48]. Half-wave potentials for reduction (relative to the 10^{-3} M $AgClO_4$/Ag electrode) are −2.74, −2.65, and −2.50 V when R is respectively benzyl, allyl, and cyclopentadienyl. The mechanism of the process can be written[48]



Grignard reagents. Both the "natural" and the "synthetic" reagents, RMgX and $R_2Mg + MgX_2$ mixtures, give two reduction waves except with $R = CH_3$, when only one wave is observed. Coulometric electrolysis on the current plateau of both first and second waves gives $n = 1$, with the half-wave potential of the first wave close to that of MgX_2 (−2.47 V), and that of the latter lying between −2.70 and −2.80 V. The mechanism of the process was explained[48] in terms of rapid establishment of the Schlenk equilibrium

$$2RMgX \rightleftarrows MgX_2 + MgR_2 \qquad (7)$$

and reduction of MgX_2 in the first stage.

A pulsed galvanostatic study (with reversal of current) of a Grignard reagent at a magnesium electrode in diethyl ether indicates the occurrence of both cathodic and anodic processes (formation and dissolution of Mg^0). The introduction of oxygen, acetone, or bromoethane into the solution changes the form of the curves[49]. In ether and oxolan the reduction of Grignard reagents at a bright platinum cathode gives metallic magnesium; on anodic oxidation alkanes and alkenes are formed[50].

Polarisation curves have been determined for the oxidation of alkylmagnesium chlorides at rotating platinised and smooth platinum and also gold electrodes in oxolan solutions[51]. Fairly high concentrations (0.2–0.6 M) of the depolarisers were taken to ensure adequate electrical conductivity of the solution without addition of an inert electrolyte. Oxidation takes place most readily on platinised platinum, with rather greater difficulty on a gold electrode, and with the greatest difficulty on smooth platinum. The sequence of diminishing ease of oxidation of Grignard derivatives containing different groups is t-butyl > ethyl > isopropyl, vinyl > n-butyl > methyl > phenyl. The course of the reduction by these Grignard reagents in oxolan of naphthacene (at concentrations of 5×10^{-6} M and 5×10^{-4} M) to the radical-anion was followed by the determination of current–potential curves at rotating platinum and gold electrodes. The sequence of diminishing ease of oxidation of RMgCl coincides with their decreasing ability to reduce hydrocarbons[51].

Current–potential curves have been obtained at a rotating platinised platinum electrode in argon and in a mixture of argon with hydrogen at different pressures of the latter (i.e. at a hydrogen electrode) in oxolan with lithium and tetrabutylammonium perchlorates, as well as in the absence of a supporting electrolyte (for high depolariser concentrations), for several Grignard reagents and disubstituted organomagnesium compounds[52]. The oxidation of such reagents can be described by the general equation

$$2RMgCl \rightarrow R{-}R + 2e + 2MgCl^+,$$

or

$$2RMgCl \rightarrow R_{H(-1)} + RH + 2e + 2MgCl^+,$$

i.e. with dimerisation and dimutation respectively of the radicals formed ($R_{H(-1)}$ denotes an alkene formed from R).

The current observed on cathodic polarisation in argon probably corresponds to the process

$$RH + MgCl^+ + e \rightarrow RMgCl + \frac{1}{2}H_2,$$

where RH has been formed owing to decomposition of RMgCl by traces of moisture [52]. Introduction of hydrogen into the solution leads to a clear anodic wave, whose height increases with the partial pressure of hydrogen. For methylmagnesium chloride this wave probably corresponds to the process

$$CH_3MgCl + \frac{1}{2}H_2 \rightarrow CH_4 + e + MgCl^+,$$

i.e. to the oxidation of hydrogen catalysed by the Grignard reagent (the concentration of the latter far exceeds that of hydrogen), so that the height of the wave corresponds to a diffusion current of dissolved hydrogen. This anodic wave, together with the cathodic wave for the reduction of methane catalysed by $MgCl^+$, represents a redox system, in which the zero-current potential at the hydrogen electrode corresponds to the equilibrium potential of the system. Under otherwise similar conditions the latter depends on the basicity of the Grignard reagent (or, in view of the Schlenk equilibrium (7), to R_2Mg), which in turn enables the basicity of a series of Grignard reagents to be determined quantitatively from current–potential curves at a hydrogen electrode [52]. An alkylmagnesium chloride was found to be rather more basic than the bromide. In oxolan some dissociation of RMgX to RMg^+ and X^- takes place [52].

At a lead anode in 0.25 M tetrabutylammonium perchlorate in oxolan diethylmagnesium and ethylmagnesium bromide give very clear oxidation waves having half-wave potentials of −1.72 and −1.73 V (relative to Ag/0.01 M $AgClO_4$ in oxolan). The wave heights are around one-tenth of the diffusion currents and are determined by reactions with the lead electrode. Tetraethyl-lead is the final product in both cases [53]. Chemical interaction of these depolarisers with lead explains their far greater ease of oxidation on a lead than on a platinum anode [53].

III. ALUMINIUM DERIVATIVES

Sodium tetraethylaluminate. At a lead microelectrode in 0.25 M tetrabutylammonium perchlorate in oxolan this compound $NaAl(C_2H_5)_4$ gives a sharp oxidation wave with $E_{\frac{1}{2}} = -1.25$ V (relative to Ag/0.01 M $AgClO_4$ in oxolan). The height of the wave is limited by preceding chemical reaction of the depolariser and the intermediate product with the lead electrode. The final anodic oxidation products are triethylaluminium and tetraethyl-lead [53].

Triethylaluminium. Under the same conditions this compound is not oxidised at a lead electrode up to potentials at which lead dissolves (−0.6 V). [53]

Aluminium isopropoxide. At high concentrations (down to 0.1 M) in absolute propan-2-ol, with lithium chloride as supporting electrolyte, this derivative gives at a dropping mercury electrode a small kinetic cathodic wave representing discharge of hydrogen atoms with $E_{\frac{1}{2}} = -1.45$ V (relative to silver in the same solution). [54]

IV. BORON COMPOUNDS

Tetraphenylborate ion. Two oxidation peaks are obtained at a graphite anode in aqueous solutions [55,56]. The first peak corresponds to the process

$$B(C_6H_5)_4^- - 2e \rightarrow (C_6H_5)_3 + B(C_6H_5)_2^+,$$

$$B(C_6H_5)_2^+ + H_2O \rightarrow B(C_6H_5)_2OH + H^+.$$

This wave is independent of pH, and its half-peak potential $E_{p/2} = 0.216$ V (relative to a saturated NaCl–calomel electrode). The second peak represents the process

$$B(C_6H_5)_2OH - 2e + 2H_2O \rightarrow B(OH)_3 + (C_6H_5)_2 + H^+,$$

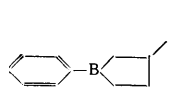
its half-peak potential depending on the pH: [56]

$$E_{p/2} = 0.92 - 0.057pH.$$

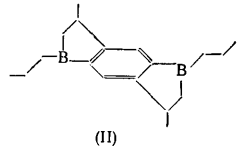
At a graphite anode two waves are obtained also in anhydrous acetonitrile and dimethylformamide with lithium perchlorate as supporting electrolyte [56]. At a platinum anode only one wave can be observed [57], but after appropriate anodic treatment of the electrode surface both oxidation waves of the tetraphenylborate ion can be observed also on platinum [58].

1,2′-Bis(diphenyl)borate ion. This gives a single two-electron wave on current–potential oxidation [59].

Dialkylborons and diarylborons. A compound such as R_2B behaves as a pseudometallic ion [60]. Its complexes with acetylacetone (AcAc) in tetrabutylammonium perchlorate in monoglyme give irreversible one-electron diffusion waves with half-wave potentials (V, relative to 1mM Ag^+/Ag electrode) of −2.16, −2.40, and −2.66 for the diphenylethynyl, diphenyl, and diethyl derivatives [60]. Electrolysis of $(C_6H_5)_2BAcAc$ at −2.48 V gave a product which, on anodic oxidation at −0.3 V, regenerates the initial compound $(C_6H_5)_2BAcAc$. Complexes of BR_2 with 1,3-diphenylpropane-1,3-dione all give two one-electron waves, with half-wave potentials of −1.60 and −2.66 V for diethylboron, and −1.90 and −2.80 V for diphenylboron [60].



(I)



(II)

Phenylborolan (I) and diborindacene (II). With 0.1 M tetrabutylammonium iodide in anhydrous dimethylformamide methyl derivatives of (I) and derivatives of (II) give reversible one-electron waves corresponding to formation of the radical-anion, with half-wave potentials respectively of −1.96 and −1.46 V (relative to the mercury at the base of the cell); the corresponding potentials for the naphthalene and anthracene waves under the same conditions are −1.94 and −1.48 V. Thus the introduction of boron facilitates appreciably transfer of an electron to the aromatic π-electron system [61]. Polarograms of diborindacene contain also a second reduction wave, representing an irreversible electrode process.

Dibutyl benzeneboronate and tetrabutyl benzene-*p*-diboronate. The products $C_6H_5B(OC_4H_9)_2$ and $(C_4H_9O)_2BC_6H_4B(OC_4H_9)_2$ of the atmospheric oxidation or the hydrolysis of the preceding compounds are also reduced under the above polarographic conditions, with half-wave potentials of −2.02 and −1.93 V respectively [61].

Barenes (carboranes). These are polyhedral aromatic systems containing boron $B_{10}H_{10}C_2RR'$. In 0.1 *N* tetraethylammonium perchlorate in dimethylformamide they give diffusion reduction waves, with half-wave potentials of −2.51 and −2.8 V (s.c.e.) for barene (*o*-barene) and neobarene (*m*-barene) respectively [62], whereas *p*-barene gives no wave [30]. Substitution of phenyl at position 1 (at a carbon atom) facilitates reduction appreciably (half-wave potentials of −1.95 and −2.45 V for 1-phenyl-*o*-barene and 1-phenyl-*m*-barene), but 3-phenyl-*o*-barene (−2.59 V) is reduced with greater difficulty than is *o*-barene itself [62]. Study of many derivatives has established that the effect of substituents on half-wave potentials is more marked with *o*- than with *m*-barenes [62]. It is noteworthy that the reduction of *o*-barene is facilitated by introduction of a 1-methyl group [62,63]. The reduction of barenes involves transfer of a single electron, probably with formation of a radical-anion [63].

C-Halogenated barenes. Polarograms obtained in dimethylformamide usually contain two waves, the first of which, representing electrochemical cleavage of the carbon–halogen bond, is double the height of the second wave. Derivatives of *o*-barene are most readily reduced, and those of *p*-barene with the greatest difficulty [63]. In contrast to the situation with halogen derivatives of benzene and benzyl, 1-chloromethyl- and 1-bromomethyl-*o*-barenes (with half-wave potentials of −2.03 and −1.21 V s.c.e.) are reduced with greater difficulty than are 1-chloro- and 1-bromo-barene respectively (−1.19 and −0.56 V). [63] 1,12-Dihalogeno-*p*-barenes give two two-electron waves representing the detachment of halogen [63]. The half-wave potentials become more negative on passing from *C*-iodo- to *C*-bromo- and *C*-chloro-derivatives of barenes. For example, values for the 1-halogenated *p*-barenes in dimethylformamide with tetradecylammonium perchlorate as supporting electrolyte are respectively −0.53, −0.99, and −2.14 V (s.c.e.). [64] It is interesting that these compounds are not reduced at a platinum electrode.

B-Halogenated barenes. These derivatives are reduced with very great difficulty, and their half-wave potentials are almost independent of the nature of the halogen. Thus for 10-halogeno-*o*-barenes in 0.1 M tetrabutylammonium bromide in dimethylformamide they are close to −2.18 V (s.c.e.). [64]

Di-*o*(and *m*)-barenylmercury. These compounds and their derivatives give reduction waves in dimethylformamide, whose half-wave potentials have been used [65] to estimate the acidity of carbon–hydrogen bonds in corresponding derivatives of *o*- and *m*-barenes. For the same purpose several dibarenylmercury derivatives (*ortho*, *meta*, and *para*) have been investigated polarographically in various solvents [66].

Phosphacarboranes. These are reduced somewhat more readily than are carboranes, the ease of reduction diminishing as with the latter in the sequence of isomers *ortho*, *meta*, and *para*. [67] For *o*-phosphacarborane in dimethylformamide with 0.1 M tetrabutylammonium perchlorate $E_{\frac{1}{2}} = -2.30$ V (s.c.e.).

Arsacarboranes. The half-wave potentials become more negative in the sequence *meta*, *para*, *ortho*. On the polarogram of the *ortho*-isomer the main wave is preceded by a prewave hump. *m*- and *p*-Arsacarboranes are reduced somewhat more readily than are the corresponding isomeric phosphacarboranes [67].

V. THALLIUM COMPOUNDS

Dialkylthallium bromide. In 30% aqueous propan-2-ol buffered to pH 7 the polarograms for the n-propyl and n-butyl derivatives R_2TlBr contain three waves of approximately the same height, the first and the third of which are diffusion waves. The first wave is preceded by an adsorption prewave [68], and corresponds to the process

$$2R_2Tl^+ + 2e \rightarrow (R_2Tl)_2$$

with half-wave potentials respectively of −0.922 and −0.895 V. Diethylthallium bromide, in contrast to its homologues, does not give prewaves on the polarograms, and its first wave ($E_{\frac{1}{2}} = -1.000$ V) corresponds to the transfer of two electrons, probably with the formation of ethylthallium(I). [68] In aqueous Britton–Robinson buffers of pH < 7 dialkylthallium bromides give a sharp one-step wave, whose half-wave potential is independent of pH and becomes more positive with growth of the alkyl chain, from −1.07 V for methyl to −0.92 V for n-pentyl. At pH > 7 a second wave is observed, and is attributed to reduction of hydrolysis products [69]. In dimethylformamide dialkylthallium bromides give four cathodic waves, the third and fourth of which become more positive on addition to the solution of phenol (as a proton donor). In excess of the donor only two waves are observed, the ratio of whose heights is 1 : 2, which corresponds to reduction to $R_2Tl\cdot$ and then to Tl^0 respectively [69]. In the absence of proton donors the primary product of one-electron reduction $R_2Tl\cdot$ either disproportionates to Tl^0 and R_3Tl or is reduced further to Tl^0. In the presence of such donors dialkylthallium cations are rapidly regenerated:

$$R_3Tl + H^+ \rightarrow R_2Tl^+ + RH\ .$$

Therefore a one-step reduction wave of R_2Tl is observed in acid aqueous solutions [69].

Trialkylthallium derivatives. In dimethylformamide such compounds are probably reduced [69] in two stages:

$$2R_3Tl + 2e \rightarrow [R_6Tl_2]^{2-},$$

$$[R_6Tl_2]^{2-} + 4e \rightarrow 6R^- + 2Tl^0.$$

Triphenylthallium(III). In dimethylformamide this gives two waves, with half-wave potentials −1.76 and −2.55 V. [69]

Diphenylthallium chloride. With 0.05 M tetraethylammonium perchlorate in dimethylformamide this gives two waves, having half-wave potentials −0.79 and −2.58 V (aq. s.c.e.) respectively [70]. After such a solution has stood over mercury for a long time (several days), however, the [first] wave falls, and a new wave ($E_{\frac{1}{2}} = -0.46$ V), corresponding to the discharge of Tl^+ ions, appears in front of it. Thus diphenylmercury may be formed at a mercury electrode not only by the cathodic reduction of diphenylthallium (see below) but also as a result of its reaction with mercury [70].

Diphenylthallium(III) cation. Polarograms obtained in aqueous phosphate buffers contain three reduction waves, the heights of the first two being proportional to the depolariser concentration and restricted by diffusion, while the third wave tends to a limit with increase in concentration[71]. The half-wave potentials of the first and third waves become more negative with increase in the diphenylthallium concentration, whereas that of the second wave becomes more positive; those of the second and third waves vary with pH, but that of the first wave does not. Electrocapillary curves obtained during the drop period indicate strong adsorption of the starting material and still greater adsorption of intermediate reduction products. On preparative electrolysis at the limiting-current potentials of all three waves 1 mole of Tl^0 is formed as an amalgam and various quantities of diphenylmercury per mole of the initial substance, accompanied on the second and third waves by benzene[71]. The primary process is transfer of a single electron:

$$(C_6H_5)_2Tl^+ + e \rightarrow Tl^{\cdot}(C_6H_5)_2.$$

The resulting radical reacts in several ways: it interacts with mercury

$$(C_6H_5)_2Tl^{\cdot} + Hg \rightarrow (C_6H_5)_2Hg + Tl^0,$$

or disproportionates in the adsorbed state on mercury, giving diphenylmercury, Tl^0 and triphenylthallium, which is rapidly hydrolysed to benzene and diphenylthallium (reduction of the latter is the reason for the > 1 electrons determined coulometrically for the first wave). The radical $(C_6H_5)_2Tl\cdot$ may also be hydrolysed to benzene and inorganic thallium derivatives, which are reduced at the dropping mercury electrode. The second wave corresponds to the transfer of one electron to the diphenylthallium radical with formation of benzene and phenylthallium(I), which reacts rapidly with mercury

$$2Tl(C_6H_5) + Hg \rightarrow (C_6H_5)_2Hg + Tl^0.$$

The third wave corresponds to the process

$$C_6H_5Tl + e \xrightarrow{H^+} C_6H_6 + Tl^0.$$

Half-wave potentials in 1 mM solution at pH 7 are respectively −0.62, −0.94, and −1.42 V (s.c.e.).[71]

Diphenylthallium derivatives. A different interpretation has been given[70] of the mechanism of reduction. Derivatives with *para*-substituents (methoxy, methyl, chloro, methoxycarbonyl) and the *m*-tolyl derivative exhibit three reduction waves in aqueous 1 M potassium acetate, the first two of which are diffusion waves, whereas the limiting current of the third wave is determined by adsorption phenomena. The first wave is regarded[70] as preceded by very rapid reaction between the thallium derivatives and mercury, to give a product that acquires an electron reversibly:

$$(C_6H_5)_2Tl^+ + Hg \underset{\rightarrow}{\overset{\text{rapid}}{\rightleftharpoons}} C_6H_5HgTl^+C_6H_5 \overset{+e}{\rightleftarrows} C_6H_5HgTl^{\cdot}C_6H_5 \xrightarrow{\text{rapid}} (C_6H_5)_2Hg + Tl^0.$$

The second wave corresponds to further reduction of $C_6H_5HgTl(C_6H_5)\cdot$ involving two electrons. However, the height of the second wave does not reach the diffusion current corresponding to the transfer of two electrons (probably because of retardation of the electrode process by substances, mainly diphenylmercury, adsorbed on the electrode). Desorption of diphenylmercury takes place at the potential of the third wave, so that the latter corresponds to reduction of depolariser that has not been reduced under the conditions of the second wave; a jump in the capacitive current due to the desorption of diphenylmercury is superimposed on the Faraday current of the third wave. This scheme of reduction is supported by the results of a chronopotentiometric study of diphenylthallium derivatives[70].

At a platinum microcathode in anhydrous dimethylformamide the diphenylthallium cation gives two irreversible diffusion waves, with half-wave potentials of −0.85 and −1.70 V (s.c.e.). The first corresponds to the transfer of one electron and the formation of diphenylthallium radicals, which disproportionate to give metallic thallium and triphenylthallium. Reduction of the latter gives the second wave, whose height is double that of the first wave[73]. The reduction of triphenylthallium yields Tl^0 and benzene. The primary products of electrolysis at −30°C are Tl^0 and $(C_6H_5)_4Tl^-$.[73]

Phenylthallium(III). Polarograms obtained in aqueous media contain an adsorption prewave and three one-electron diffusion waves. The half-wave potentials of the first and second waves are independent of depolariser concentration and of pH (−0.01 and −0.50 V (s.c.e.) respectively). That of the third wave becomes more negative with increases in both factors. Electrolysis at the limiting current of the first wave gives diphenylmercury and Tl^+; at that of the second wave Tl^0 accompanies diphenylmercury; and the third wave corresponds to reduction of phenylthallium(I) formed in the preceding stage[72]. In dimethylformamide diphenylthallium bromide and phenylthallium dichloride give two waves, the first representing reduction to Tl^0, and the second ($E_{\frac{1}{2}} = -2.55$ V) reduction of diphenylmercury[69].

VI. DERIVATIVES OF GROUP IV ELEMENTS—THE SILICON SUBGROUP

Organochlorosilanes. Reduction waves were obtained[74] in anhydrous acetone, though their reproducibility was poor. Waves that can be used for the quantitative determination of organochlorosilanes were obtained in pyridine and its aqueous mixtures[74]. The wave then corresponds to discharge of the pyridinium ion formed by solvolysis of the organochlorosilane.

Ethyltrichlorogermane. In a benzene–methanol (3 : 2) mixture with 0.1 *N* lithium chloride as supporting electrolyte a sharp three-electron diffusion wave is obtained, corresponding to detachment of all the chlorine atoms and formation of the radical $C_2H_5Ge\cdots$, which gives a polymeric product. The wave observed in acidic aqueous solutions (to pH 4.0) is distorted by strong adsorption of the initial depolariser and the reaction products; with increase in depolariser concentration the height of the wave reaches a limit (at $c > 0.5$ mM), while its half-wave potential becomes more negative. Electrocapillary and current–time curves showed that rearrangement of the adsorbed layer occurs in the lower part of the wave at −1.06 V (s.c.e.): depolariser on the electrode surface is replaced by the reaction product. In methanolic benzene neither the depolariser nor the reaction product is adsorbed on a mercury electrode[75].

Mono- and bis-trimethyl-silyl, -germyl, and -stannyl derivatives of biphenyl. Derivatives with the substituents in positions 4 or 4 and 4′ give

in anhydrous dimethylformamide reversible waves corresponding to the formation of radical-anions; the half-wave potentials lie in the range −1.94 to −2.07 V relative to the potential of the mercury at the bottom of the vessel (the supporting electrolyte is not indicated). Silicon derivatives are rather more electropositive than the germanium derivatives, while the tin derivatives are the most electronegative[76].

Bistrimethyl-silyl and -germyl derivatives of polyphenylenes. In dimethylformamide these derivatives $(CH_3)_3M[C_6H_4]_mM(CH_3)_3$ (where $m = 1$–4 and M = Si, Ge) give reversible one-electron waves, except in the case of *p*-bistrimethylgermylbenzene, which is polarographically inactive. Polyphenyl derivatives give a second one-electron wave, corresponding to formation of a dianion. The instability of the latter, leading to detachment of trimethylsilyl or trimethylgermyl groups, is responsible for the incomplete reversibility of the second wave. The half-wave potential of the first wave becomes more positive with increase in m, while the reversibility of the second wave improves[77].

In order to determine how the silyl bridge influences conjugation between two diphenylyl groups, ordinary and a.c. polarograms (with recording of the signal from the principal and second harmonics) have been obtained[78] on several compounds. The first waves correspond to reversible transfer of one electron (redox potentials E^0 given in parentheses for the first reduction waves in dimethylformamide with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte and silver in a saturated dimethylformamide solution of tetrabutylammonium iodide as reference electrode). The compounds investigated were 4-trimethylsilylbiphenyl (−1.897), 4,4′-bistrimethylsilylbiphenyl (−1.805), dibiphenyl-4-yldimethylsilane (−1.853), 4,4′-bisbiphenyl-4″-yldimethylsilylbiphenyl (−1.750), and for comparison the hydrocarbons biphenyl (−1.999), dibiphenyl-4-ylmethane (−2.019), and 4,4′-di-*p*-phenylbenzylbiphenyl (−2.024). Thus introduction of a silyl group shifts the redox potential to less negative values than for the corresponding hydrocarbon. However, comparison with the ultraviolet spectra indicated[78] that a silyl bridge largely prevents conjugation between two biphenylyl groups.

1-Naphthylpolysilanes. A study has been made[79] of the polarographic behaviour of the compounds (Ar = 1-naphthyl and Me = CH_3)—$ArSiMe_3$, $ArSiMe_2Ar$, $ArSi_2Me_5$, $Ar[SiMe_2]_2Ar$, $ArSi_3Me_7$, $Ar[SiMe_2]_3Ar$, and $ArCH_2SiMe_3$—as well as of naphthalene and 1-methylnaphthalene for comparison. With 0.05 M tetrabutylammonium iodide in dimethylformamide mononaphthyl derivatives give one reversible one-electron diffusion wave, and dinaphthyl derivatives two such waves. Half-wave potentials for the above compounds (measured by a three-electrode scheme relative to Ag/0.1 M $AgNO_3$ in dimethylformamide) are respectively (values for the second wave given in parentheses) −2.845, −2.781 (−3.038), −2.842, −2.816 (−2.983), −2.838, −2.822 (−2.924), −3.006, −2.946, and −2.964 V. Introduction of a trimethylsilyl group facilitates electron transfer to the naphthalene ring system; facilitation is still greater on introduction of a second naphthalene ring system at the end of the silyl chain. With increase in length of this chain, however, the effect of the second ring system diminishes (the half-wave potential becomes more negative), while transfer of a second electron to the second ring system is facilitated, which indicates diminished transmission of the effect through the silyl bridges[79].

1,4-Bistrimethylsilyl(and germyl) naphthalenes. These give a single reversible one-electron wave. The silicon derivatives are reduced rather more easily than are the germanium derivatives[77]. Introduction of a trimethylsilyl group into the naphthalene molecule shifts the reversible one-electron reduction wave (with 0.1 M tetrabutylammonium iodide in dimethylformamide) to less cathodic potentials (by ~ 50 and by ~ 10 mV in positions 1 and 2 respectively); reduction is still more facilitated by the introduction of two groups, reaching 150 mV with 1,4-bistrimethylsilyl derivatives. However, introduction into the naphthalene molecule of a t-butyl group (or of two such groups) impedes reduction: the maximum effect is ~ 110 mV with the 2,7-di-t-butyl derivative[80].

Iodotrialkylsilylalkanes. Cleavage of the carbon–iodine bond is somewhat facilitated by introduction of a trialkylsilyl group into an iodoalkane, although this effect may be due not only to the electronegative action of the group but also to enhanced adsorbability of the organic molecule[81]. An important consequence of such introduction is to stabilise the free radical[82] formed as intermediate in the reduction of iodo-derivatives. Such stabilisation results in division of the two-electron wave into two one-electron steps, the half-wave potentials of both of which correlate with the electronegativity of the trialkylsilyl substituent[82].

Other evidence indicates the electron-accepting properties of the trialkylsilyl group. Thus introduction of the group into the *para*-position of nitrobenzene facilitates reversible transfer of the first electron to the nitro-group (in anhydrous dimethylformamide) by ~ 100 mV.[83] Reduction of mono- and di-silanaphthenes in dimethylformamide is facilitated by 200–400 mV in comparison with naphthalene, whereas acenaphthene itself is reduced with rather greater difficulty than is naphthalene[84]. The silicon atom in 5,10-dihydro-5,5-dimethyldibenzo[*b*,*e*]silinone competes slightly[85] even with the carbonyl group, facilitating electrochemical reduction of the latter (the half-wave potential of the reversible one-electron wave in dimethylformamide is −1.64 V relative to mercury in 0.1 M tetrabutylammonium perchlorate solution).

Phenyltrimethylsilane. On reduction in anhydrous methylamine solution at a platinum cathode in the presence of lithium chloride in a cell with a diaphragm, products resulting from detachment of the trimethylsilyl group and hydrogenation of benzene are obtained. In the absence of a diaphragm the main reduction product is *p*-dihydrophenyltrimethylsilane resulting from the action of lithium methylamide formed at the anode[86].

Triphenylsilyl and triphenylgermyl chlorides. In anhydrous dimethoxyethane these compounds give a one-electron wave with half-wave potentials of −3.1 and −2.8 V relative to an $Ag/AgClO_4$ (1 mM) electrode. The products were regarded as formed by the replacement of chlorine by hydrogen atoms, but the source of the atomic hydrogen was not indicated[87].

Halogenated triphenylgermanes. In an extremely detailed study[88] 1,2-dimethoxyethane was used as solvent, with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte and silver in a saturated solution of silver nitrate in the same solvent as reference electrode

Triphenylfluorogermane. The slope suggests that the single polarographic reduction wave is reversible,

with $E_{\frac{1}{2}} = -3.1$ V and its height formally corresponding to a diffusion current with transfer of half an electron. When increasing quantities of an alcohol or water are introduced into the solution, a new wave appears and grows on the limiting-current plateau of the first wave (whose height and half-wave potential remain unaffected). The new half-wave potential is displaced to less negative values, so that in excess of these proton donors it reaches the height of the initial wave and merges with it to give a single irreversible one-electron diffusion wave.

Voltammetry with a linearly varying potential (in the absence of a proton donor) reveals only one cathodic peak, whose properties suggest that the process is irreversible. This implies that the process is in general quasi-reversible: the radical-anion formed by transfer of an electron to the initial molecule is assumed[88] to interact with another molecule of the initial compound to give an electrochemically inactive dimeric radical-anion, which explains the "half electron". The absence of an anodic peak of the radical in voltammetry with the application of triangular pulses indicates that the rate constant of formation of the dimer $[(C_6H_5)_3Ge(F)...GeF(C_6H_5)_3]^\cdot$ exceeds $10^5\ M^{-1}\ s^{-1}$. The dimer is obviously unstable, being slowly converted in solution into more stable compounds; this apparently explains the formation of a deposit of hexaphenyldigermane when the solution is allowed to stand after electrolysis.

Immediately after electrolysis bistriphenylgermyl oxide $[(C_6H_5)_3Ge]_2O$ was isolated, having been formed by reaction of the dimeric radical-anion with water or a peroxide, certain quantities of which are always present in the solvent. The anodic peak due to fluoride ions, present on current–voltage curves with reversal of potential, indicates quite rapid interactions of the dimeric radical in which fluoride ions are liberated. On the introduction of proton donors into the solution the dimeric radical-anion is protonated, after which it or a conversion product acquires a new electron, which corresponds to appearance of the new wave on the polarogram.

Triphenylchlorogermane. This gives an irreversible one-electron reduction diffusion wave having $E_{\frac{1}{2}} = -2.85$ V.[88] Addition of water or an alcohol does not affect the cathodic wave, but results in the appearance of an anodic one-electron diffusion wave. The cathodic process produces a triphenylgermyl radical and a chloride anion. The radicals dimerise to hexaphenyldigermane (the principal product of preparative electrolysis at high concentrations of the starting material), and react with peroxides to form triphenylgermyl hydroxide $(C_6H_5)_3GeOH$ and hexabiphenylyldigermyl oxide (the main product at low concentrations of the initial substance). A certain quantity of triphenylgermane is also formed on electrolysis, apparently as a consequence of abstraction of a hydrogen atom from the solvent (dimethoxyethane) by the germyl radical.

The anodic wave is due to interaction with mercury (which is absent at a platinum electrode):

$$(C_6H_5)_3GeCl \xrightarrow[Hg]{-e} (C_6H_5)_3Ge^+ + \frac{1}{2}Hg_2Cl_2,$$

$$(C_6H_5)_3Ge^+ + ClO_4^- \rightarrow (C_6H_5)_3GeOClO_3.$$

Formation of a perchlorate with a covalent bond has been proved by ultraviolet spectroscopy of the product isolated after electrolysis on the current plateau of the anodic wave. Both this product and specially prepared triphenylgermyl perchlorate give a cathodic wave with $E_{\frac{1}{2}} \simeq -1.6$ V on the polarograms, whereas the corresponding potential for the cathodic wave of the solution immediately after anodic oxidation is -0.2 V. This is regarded[88] as indicating that the germanium cation formed gives initially with the perchlorate anion an ion-pair, which is then converted into the covalent compound.

Triphenylbromogermane. This behaves similarly to triphenylchlorogermane, with the sole exception that it gives an anodic wave even in the absence of water or an alcohol[88]. Half-wave potentials are -2.63 and -0.14 V for the one-electron cathodic diffusion wave and for the anodic wave respectively.

Triphenyliodogermane. The polarograms contain two cathodic waves with half-wave potentials of -1.9 and -2.45 V (the first is kinetically restricted, and the two waves give an aggregate diffusion current with $n = 1$) and a one-electron anodic wave with $E_{\frac{1}{2}} = -0.36$ V.[88] On the addition of water to the solution the first cathodic wave grows at the expense of the second; the anodic wave also diminishes, but a new anodic wave appears and grows ($E_{\frac{1}{2}} = -0.95$ V), and was shown to be due to an anodic process involving free iodide anions. The second wave also diminishes on electrolysis at the potential of the first cathodic wave; the sole product of electrolysis is hexaphenyldigermane oxide. The second wave corresponds to detachment of an iodide anion and formation of a triphenylgermyl radical; the first is attributed[88] to the processes

$$(C_6H_5)_3GeI + H_2O \rightleftarrows [(C_6H_5)_3GeIH]^+ + OH^-,$$

$$[(C_6H_5)_3GeIH^+] + e + OH^- \rightarrow (C_6H_5)_3Ge^\cdot + I^- + H_2O.$$

In excess of water the initial substance undergoes hydrolysis with formation of an iodide anion and triphenylgermyl hydroxide.

Alkylhalogenotin derivatives. These compounds $R_{4-x}Cl_xSn$ ($x = 1-3$) have been studied by many investigators[87,89–104], but the mechanism of their reduction has not yet been finally elucidated. Their electrode behaviour is complicated by very strong adsorption on the electrode both of the initial substances and of the reaction products[94,96,97,100–104], as well as by dissociation, which is responsible for the appearance of kinetic restrictions of the current[99,100,102]. Thus for dimethyldichlorotin[100] the height of the first wave (disregarding the adsorption prewave) falls with rise in pH along a curve resembling a dissociation curve (expressing the pH dependence of the concentration or proportion of the undissociated acid). At the same time a second wave appears and grows, so that the polarographic $pK'_a = 9.05$, which exceeds the potentiometrically determined exponents for the stepwise substitution of the chloride ion by the hydroxide ion ($pK_a = 4.5$ and 8.0[100]).

It has been shown for dichlorodiethyltin as example[100] that the total wave height corresponds to the transfer of only one electron, so that the process can be represented by the scheme[87,96,98]

$$R_2SnCl_2 + e \rightleftarrows R_2Sn^\cdot Cl + Cl^-, \quad (8)$$

$$2R_2Sn^\cdot Cl \rightarrow R_2Sn(Cl)—Sn(Cl)R_2. \quad (9)$$

Addition of the electron occurs reversibly[96], with the resulting radicals dimerising on the electrode surface itself. The wave form (at low depolariser concentrations) is therefore[105] described by the equation[96]

$$E = \varepsilon_0 - 0.065 \lg \frac{i^{1/2}}{i_{\lim} - i}. \quad (10)$$

The system R_6Sn_2/R_3Sn^+ is reversible on a platinised platinum electrode in methanol alone and mixed with benzene (R = C_6H_5, CH_3, C_2H_5, C_4H_9).[106] With increase in the concentration of the depolariser (diethyldichlorotin) the wave separates into several steps[96-98], the first of which is similar in nature to a Brdička prewave (Brdička adsorption prewaves appear on polarograms with strong adsorption on the electrode of a reaction product or a complex with the initial depolariser, their height increasing with the depolariser concentration to a certain value corresponding to complete coverage of the electrode surface by a monolayer of the adsorbate, after which the prewave height remains unchanged with further increase in depolariser concentration). The appearance of two adsorption prewaves may be due[107] to layer-by-layer coverage of the surface.

A very important feature[98] of the polarographic behaviour of a dialkyldichlorotin is a gradual increase in the ratio of the total wave height to the depolariser concentration with increase in the latter, and also an increase in the number of electrons determined microcoulometrically, especially in acid media, which is attributed[98] to partial regeneration of the depolariser by the reaction

$$(R_2Sn)_2Cl_2 + 2HCl \rightarrow 2R_2SnCl_2 + H_2.$$

Other workers[61], however, assign the one-electron process (8) followed by dimerisation by (9) merely to reduction of the trialkylhalogenotin (incidentally, hexaphenylditin is formed[108] on the cathode during the electrolysis of triphenyltin chloride), whereas complete reduction of butyltrichlorotin and dibutyldichlorotin has been regarded[99] as involving respectively three and two electrons. Two-electron reduction of a dialkyldichlorotin has been assumed also in other investigations[94,100,109]. We shall now examine the behaviour of individual organotin compounds.

Trimethylchlorotin. In aqueous solutions two one-electron waves are obtained, whose heights are independent of pH, whereas the half-wave potentials become more negative with increase in pH (that of the second wave only in strongly alkaline medium).[103] An adsorption prewave precedes the second wave. With increase in depolariser concentration in an unbuffered medium the first wave divides into two steps, the first of which corresponds to reduction of the cationic form of the substance, and the second to that of trimethyltin hydroxide, which dissociates very slowly. The first wave represents formation of free radicals $(CH_3)_3Sn\cdot$, which dimerise to the water-insoluble hexamethylditin (the latter remains unreduced at a mercury electrode in oxolan up to −2.7 V). The second wave[103] is due to reduction of the radical to the anion $(CH_3)_3Sn^-$ (which then adds a proton), not to reduction of hexamethylditin; a similar process is suggested for the second wave in the reduction of triphenyltin chloride[87].

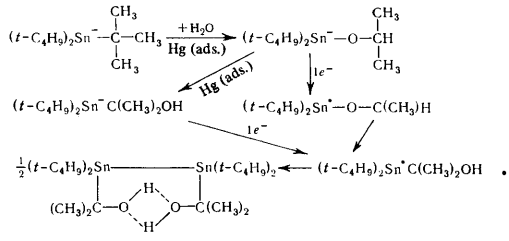
Di-t-butyltin. Very dilute solutions of the depolariser $(C_4H_9)_2Sn^{2+}$ in aqueous perchloric acid give polarograms having one diffusion reduction wave with $E_{\frac{1}{2}} = -0.55$ V, which is reversible and independent of pH.[110] Addition to the solution of increasing quantities of chloride ions shifts the wave to more negative potentials, divides it into two, and diminishes its height, conferring on it a kinetic character, and in 5 M hydrochloric acid almost completely eliminating the wave owing to the formation of a series of complexes. Studies have been made of complex formation also in buffered acetate, carbonate, and ammonium chloride solutions. Millimolar solutions of d-t-butyltin exhibit an adsorption prewave and two one-electron waves; the first stage involves formation of free radicals, which give dimeric products. The polarograms are greatly distorted by adsorption of the depolariser and especially of the electrode products. The presence of two t-butyl groups attached to tin facilitates transfer of the first electron and hinders that of the second electron in comparison with the diethyl or dimethyl derivatives, as well as stabilising considerably the four-coordinate state of tin[110].

t-Butyldiethyltin halides. With acid supporting electrolytes in 20% ethanol these give a reversible one-electron wave with an adsorption prewave; for the wave $E_{\frac{1}{2}} \simeq -1.1$ V (s.c.e.) at pH 4.6. With rise in pH the wave becomes less reversible and shifts to more cathodic potentials; a second, irreversible wave appears, lower than the first. In 1.0 *N* caustic soda the half-wave potentials are −1.45 and −1.70 V.[111] Preparative electrolysis shows that at the potential of the first wave the radicals formed dimerised to di-t-butyltetraethylditin. The same product occurs also at the potential of the second wave: the butyldiethylstannane $C_4H_9SnH(C_2H_5)_2$ formed in the second stage of the process probably reacts partly with the initial depolariser to give the dimer.

Di-t-butylethyltin bromide. The polarograms in acid solutions containing 20% of ethanol show two cathodic waves (half-wave potentials −1.05 and −1.45 V (s.c.e.) at pH 4.6) preceded by an adsorption prewave. The first, diffusion wave is reversible and corresponds to the transfer of one electron. The character of the second wave has not been established; the wave disappears on introduction of a surface-active substance into the solution. One one-electron wave occurs in alkaline medium, with $E_{\frac{1}{2}} = -1.55$ V in 1 *N* caustic soda. The waves are distorted by strong adsorption of the initial substance and the products, so that their form varies with increase in the depolariser concentration. Electrolysis yields tetra-t-butyldiethylditin.

Tri-t-butyltin. The behaviour of the cation differs appreciably[112] from that of mono- and di-t-butyl derivatives. A reversible main wave ($E_{\frac{1}{2}} = -0.6$ V at pH 1.9) and an adsorption prewave are found in acid solutions in 20% methanol. The limiting current is partly kinetic in character, although coulometric determination indicates a one-electron wave. When the solution is allowed to stand over mercury, the wave slowly diminishes, and at about −1.1 V a new wave grows to the one-electron level. Three waves are observed in alkaline medium: the sum of the first two corresponds to the transfer of one electron, and the height of the third wave also corresponds to such a process. Electrocapillary curves indicate strong adsorption of the initial depolariser and of the reaction products. Study by infrared and nuclear magnetic resonance spectroscopy of the products of preparative electrolysis suggests a general scheme involving comparatively rapid reaction between water and the depolariser adsorbed on the electrode, with elimination of a methyl group as methane and formation of an oxygen bridge; the

product, which gives a wave having $E_{\frac{1}{2}} = -0.6$ V at pH 1.9, rearranges slowly in the adsorbed state to give the compound (wave with $E_{\frac{1}{2}} = -1.1$ V):



The half-wave potentials become in general more negative with increase in the number of alkyl groups attached to tin[92,95]: no reduction waves could be observed with tetra-alkyltins[109]. With increase in the length of the alkyl substituents the half-wave potentials of the reduction waves of organotin salts become less negative[92].

Butyltrichlorotin, dibutyldichlorotin, and tributylchlorotin. These compounds have been studied also by a.c. polarography[104]. Their adsorbability on the mercury electrode increases with the number of butyl groups. Tributylchlorotin has been investigated in greatest detail; the product of its reduction on the first wave is adsorbed far more strongly than is the initial depolariser, and the second reduction step gives an unadsorbable product. The height of the peak corresponding to the second stage of reduction increases sharply with rise in temperature, which confirms its kinetic nature. The electrochemical reaction at the second stage is irreversible, and the presence of a peak on the a.c. polarograms is attributed to change in the capacity of the double layer caused by reduction of a surface-active intermediate to an inactive end-product[104]. On the addition of propan-2-ol to the aqueous solution the peak height corresponding to the first wave becomes somewhat lower, whereas the peak corresponding to the second stage of reduction shifts abruptly to more cathodic potentials without significant change in height. It is interesting that the peak potential corresponding to desorption of propan-2-ol, located in front of the peak of the second wave, varies in almost the same way. In the presence of tributylchlorotin this desorption peak drops sharply, which is attributed to competitive adsorption of two substances; the effect increases with rise in temperature.

Aquodiethyltin. Voltammetry with a linearly varying potential shows that $(C_2H_5)_2Sn^{2+}.nH_2O$ gives on reduction extremely short-lived diethyltin biradicals, which are rapidly polymerised. The lower polymers can be oxidised anodically to the initial aquodiethyltin; oxidation of the higher polymers is accompanied by loss of some of the ethyl groups[113].

Triphenyltin. With tetrabutylammonium perchlorate in dimethoxyethane the chloride gives two waves[89], the first of which (one electron, $E_{\frac{1}{2}} \simeq -1.6$ V) corresponds to the formation of radicals that are rapidly converted into a dimer, whereas the second wave, which develops at extremely negative potentials, corresponds to reduction of the dimer (hexaphenylditin) to triphenyltin anions. In aqueous solution triphenyltin fluoride gives one irreversible one-electron wave representing reduction to hexaphenylditin, which is strongly adsorbed on the electrode[101].

The most detailed study has been made[102] of the behaviour of triphenyltin (acetate and hydroxide) in buffered solutions prepared in 50 vol.% ethanol. The polarograms contain three waves over a wide pH range: the heights of the first two waves are independent of pH; the third wave becomes visible at pH 4.75, reaches its maximum height at pH 7.3, and then falls along a kind of dissociation curve with further increase in pH. The half-wave potentials of first and second waves become more negative with rise in pH (in neutral and alkaline solutions $\Delta E_{\frac{1}{2}}/\Delta pH \simeq -60$ mV), their values at pH 7 being respectively −0.62 and −0.90 V (s.c.e.); that of the third wave is independent of pH ($E_{\frac{1}{2}} = -1.35$ V). On introduction of a tetrabutylammonium salt into the solution the third wave disappears, and the second becomes more extended. The first wave was shown to be an adsorption prewave; the total height of the first two waves corresponds to a one-electron diffusion current. The second wave is reversible in character, and the third irreversible. At high depolariser concentrations the heights of the second and third waves cease to increase with concentration. The first stage involves formation of the strongly adsorbable triphenyltin radical, which is either dimerised to electrochemically inactive hexaphenylditin or reduced further (the third wave) to the triphenyltin anion (after electrolysis at the potentials of the limiting-current plateau of the third wave an anodic wave with $E_{\frac{1}{2}} = -0.4$ V appears on the polarograms of the solution, and this corresponds to oxidation of triphenylstannane $(C_6H_5)_3SnH$ to the initial triphenyltin cation; no anodic wave appears after electrolysis at the potential of the second wave).

A method has been suggested[102] for determining microquantities (down to 10^{-8} M) of triphenyltin by the accumulation of adsorbed radicals by preliminary electrolysis of the test solution at a rotating mercury-coated platinum wire (at −1.0 V (s.c.e.) for 2 min) followed by anodic oxidation of the adsorbed radicals. With increase in time of pre-electrolysis or rise in concentration of the initial compound the height of the anodic peak ceases to increase, probably owing to dimerisation of some of the triphenyltin radicals to inactive hexaphenylditin; dimerisation is not observed at low surface concentrations of the radicals.

Hexaphenylditin. In dimethoxyethane this gives a two-electron wave at −2.9 V (relative to a 1 mM $AgClO_4/Ag$ electrode), corresponding to formation of triphenyltin anions[87]. In aqueous–alcoholic medium, however, hexaphenylditin is electrochemically inactive[102].

Oxygen-containing organotin compounds. Trialkylstannyl methacrylates and ethers $R_3SnOSnR_3$ ($R = C_2H_5$, C_4H_9) in buffered aqueous solutions give two cathodic waves having half-wave potentials lying between −1.40 and −1.50 and between −1.74 and −1.78 V (s.c.e.) almost independent of the nature of the compounds, which is probably explained by their ready hydrolysis, e.g.

$$(C_2H_5)_3SnOSn(C_2H_5)_3 + H_2O \rightarrow 2(C_2H_5)_3SnOH) .$$

The first wave is rather more negative with ethyl than with butyl[114].

A polarographic method developed[115] for determining extremely small quantities (down to 3.4×10^{-7} M) of organotin compounds used as fungicides involves electrolysing the test solution in 12% hydrochloric acid at a suspended mercury drop cathode at −0.8 V (s.c.e.) for 5 min. The anodic current–potential curve for dissolution of tin from the amalgam is then recorded (rate of variation of potential 0.6 V min^{-1}), and the concentration of the

organotin compound in the initial solution is calculated from the height of the peak. The method has been tested on benzyltin trichloride, octyltin trichloride, and dibenzyltin dichloride, as well as on benzylstannic acid.

Organolead compounds. One of the earliest studies[89] recorded polarograms for triethyl-lead chloride in aqueous potassium chloride. One-electron transfer was assumed to yield a triethyl-lead radical.

Aquodiethyl-lead. This species $(C_2H_5)_2Pb^{2+}.nH_2O$ is reduced[116] with the transfer of two electrons to biradicals, which partly disproportionate

$$2\,(C_2H_5)_2Pb^{\cdot} \rightarrow (C_2H_5)_4Pb + Pb^0$$

(this is favoured by increasing the concentration of the starting material), while the rest react with mercury

$$(C_2H_5)_2Pb^{\cdot} + Hg^0 \rightarrow (C_2H_5)_2Hg + Pb^0.$$

Trialkyl-lead bromides. These compounds have been studied in 30% isopropyl alcohol[117]. Triethyl-lead bromide gives two waves, the first ($E_{\frac{1}{2}} \simeq -0.7$ V) corresponding to the transfer of one electron followed by dimerisation of the resulting radicals to hexaethyldilead. With increase in the depolariser concentration this wave is split, the first step appearing as an adsorption prewave. The second wave on the polarograms of triethyl-lead bromide, with $E_{\frac{1}{2}} \simeq -1.35$ V (s.c.e.), forms a hump, and was attributed[117] not to the reduction of hexaethyldilead but to an unestablished process involving the initial compound. A detailed study was made[109] of the behaviour of trialkyl-lead chlorides.

Triethyl-lead hydroxide. In buffered aqueous solutions this compound gives two waves independent of pH, with half-wave potentials of −0.73 and −1.50 V (s.c.e.).[118]

Hexaethyldilead. A sharp wave is obtained[119] in anhydrous ethanol with tetraethylammonium iodide as supporting electrolyte (half-wave potential lying between −1.8 and −2.0 V relative to the mercury at the base of the cell). This compound can be determined polarographically as an impurity in tetraethyl-lead, which is polarographically inactive[109].

Phenyl-lead triacetate. Three one-electron diffusion waves, with respective half-wave potentials +0.1, −0.4, and −0.8 V (s.c.e.), are obtained[120] in 20% aqueous methanol in acid medium. A slight prewave occurs at −0.9 V, owing to the increase in the capacitive current resulting from desorption of reaction products. The first two waves are reversible, and the third is irreversible. After electrolysis at the plateau potentials of first and second waves diphenylmercury and bivalent lead were obtained, resulting from slow breakdown of products—$C_6H_5Pb(COO)_2^{\cdot}$ and $C_6H_5Pb(COO)^{\cdot\cdot}$ respectively—formed on the electrode; the kinetics of the breakdown of these radicals was studied. After electrolysis at the potential of the third wave only traces of diphenylmercury were found. When the solutions had stood for a few days, the first wave had diminished and divided, while the second wave had also split, this being explained by the replacement of acetate by hydroxyl groups. The products of electrolysis of the solutions after standing included not only diphenylmercury and Pb^{2+} but also phenol and metallic lead, formed by the reaction

$$C_6H_5Pb^{2+} + H_2O \rightarrow C_6H_5OH + H^+ + \frac{1}{2}(Pb^0 + Pb^{2+}).$$

Diphenyl-lead diacetate. In buffered acid and strongly alkaline solutions containing 20% of methanol this compound gives[121] an anodic oxidation wave, two two-electron reduction waves, and a prewave, which become more negative with increase in the depolariser concentration and with rise in pH (the substance is very sparingly soluble over the pH range 5–12). Owing to variation in the diffusion coefficient the waves are rather lower in alkaline than in acid medium. At a concentration of ~ 1 mM in 1 M perchloric acid the half-wave potentials are ~ +0.1 (anodic), −0.10 (prewave), −0.40, and −0.53 V (s.c.e.). Diphenyl-lead diacetate reacts comparatively rapidly with a mercury electrode ($k = 1.55 \times 10^{-4}$ cm s^{-1}) to form diphenylmercury and Pb^{2+}, so that preparative electrolysis cannot be accomplished at a mercury cathode. An extremely unstable diphenyl-lead biradical is assumed to be formed on the first wave, and to undergo rapid dismutation to hexaphenyldilead and metallic lead (Pb^0), and also reaction with mercury to yield diphenylmercury and metallic lead. On the second reduction wave the biradical gives benzene and metallic lead[121].

Triphenyl-lead hydroxide. In buffered solutions in 20% methanol reduction takes place in two stages, whose corresponding waves are preceded by an adsorption prewave[121]. The total wave height corresponds to a diffusion process with the transfer of four electrons. For a 1 mM solution in 1 M perchloric acid the half-wave potentials are respectively −0.17 (prewave), −0.43, and −0.55 V (s.c.e.). With decrease in depolariser concentration the half-wave potential of the prewave becomes less negative, and that of the second wave more negative, while that of the first wave remains unchanged. With rise in pH the half-wave potential of the first wave remains unchanged to pH 9 and then becomes more negative, whereas that of the second wave becomes more negative to pH 5.5, and is independent of higher pH. The first wave corresponds to the transfer of one electron with formation of a triphenyl-lead radical, which reacts rapidly with mercury to give diphenylmercury and metallic lead. The main reduction products at the potential of the second wave are benzene and lead.

The anodic oxidation of triphenyl-lead hydroxide yields bivalent lead, diphenylmercury, and phenylmercury ions[121]. The polarograms are distorted by adsorption phenomena (especially strongly at high depolariser concentrations). The second wave exhibits hysteresis: waves obtained with forward and reverse variation of the polarising voltage do not coincide.

Triphenylchlorolead and diphenyldichlorolead. In dimethoxyethane these compounds react with mercury to give diphenylmercury and metallic lead[87], but the corresponding acetates do not react with mercury under the same conditions. Diphenyl-lead diacetate gives[87] two one-electron waves (half-wave potentials of −1.1 and −1.6 V relative to $Ag/AgClO_4$—1 mM in dimethoxyethane). Electrolysis at the limiting-current potential of the second wave gives a quantitative yield of diphenylmercury.

Triphenyl-lead acetate. On the first one-electron wave (−1.4 V) in dimethoxyethane this gives the triphenyl-lead radical, but electrolysis at the limiting current of this wave gave diphenylmercury, not hexaphenyldilead: i.e. reaction of these radicals with mercury is considerably more rapid than their dimerisation[87]. The second wave ($E_{\frac{1}{2}} = -2.2$ V) corresponds to the transfer of two electrons to the radical (to give a triphenyl-lead anion). The ease of addition of an electron increases in the sequence of compounds of silicon → germanium → tin → lead[87].

Hexaphenyldilead. In dimethoxyethane a two-electron wave is obtained representing formation of the triphenyl-lead anion ($E_{\frac{1}{2}} = -2.0$ V relative to 1.0 mM $AgClO_4/Ag$).[87] At a platinised platinum electrode in a mixture of methanol and benzene the $(C_6H_5)_6Pb_2/(C_6H_5)_3Pb^+$ system is reversible.[122]

VII. DERIVATIVES OF PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

Trisubstituted phosphines. Only the triaryl derivatives undergo reduction when polarographed[123-125]. With 0.09 M tetraethylammonium iodide in dimethylformamide $E_{\frac{1}{2}} = -2.670$ V (s.c.e.) for the reversible one-electron wave of triphenylphosphine. The primary product is the radical-anion[123-126]. Preparative electrolysis yields diphenylphosphine and benzene.

Benzyldiphenylphosphine. This gives a two-electron wave corresponding to detachment of the benzyl group. Reduction is facilitated appreciably by replacing the phenyl by naphthyl groups[125].

Triphenylarsine, triphenylstibine, and triphenylbismuthine. These give two-electron waves[123]. The half-wave potential for triphenylarsine in dimethylformamide is −2.790 V (aq. s.c.e.).[125]

Triphenylphosphine, diphenylphosphine, and phosphinoacetates. These compounds, especially the last group, cause the catalytic evolution of hydrogen. The catalytic waves are greatly enlarged by the addition of cobalt(II), cobalt(III), and nickel(II) salts, except to triphenylphosphine solutions. In the presence of cobalt(III) even unsubstituted phosphine PH_3 produces a catalytic hydrogen wave, which in acid solutions (pH 3–5) is visible even with 10^{-7} M phosphine[127].

Triarylphosphines, triarylarsines, and triarylstibines. Half-wave potentials have been determined for the oxidation of several of these compounds in 0.1 M lithium perchlorate in acetonitrile. Values obtained for the triphenyl derivatives were respectively 0.12, 0.43, and 0.46 V (at 25°C relative to aqueous saturated KCl–AgCl/Ag). The wave heights correspond to the transfer of one electron. Preparative anodic oxidation gave the product $[Hg(Ar_3X)_2](ClO_4)_2$, where X = P, As, Sb.[128]

Diphenyl-phosphinous, -arsinous, -stibinous, and -bismuthinous halides, acetates, and perchlorates. In dimethoxyethane these compounds give irreversible reduction waves[129]. Only one one-electron wave, with $E_{\frac{1}{2}} = -3.3$ V (relative to 1 mM $AgClO_4/Ag$), is observed for diphenylphosphinous chloride[129]:

$$(C_6H_5)_2PCl + e \rightarrow Cl^- + [(C_6H_5)_2P]^{\cdot} \xrightarrow{\text{solvent}} (C_6H_5)_2PH.$$

Diphenylarsinous bromide gives two one-electron waves, with tetraphenyldiarsenic as intermediate[129]:

$$(C_6H_5)_2AsBr \xrightarrow{e} Br^- + \frac{1}{2}(C_6H_5)_2As{-}As(C_6H_5)_2 \xrightarrow{e} (C_6H_5)As^-$$

with half-wave potentials of −0.9 and −2.7 V (relative to 1 mM $AgClO_4/Ag$). Reduction occurs in the same way with diphenylstibinous iodide (−1.0 and −2.5 V) and with diphenylbismuthinous chloride (−1.0 and −2.3 V), but the diphenylbismuth anion is unstable and decomposes with the separation of metallic bismuth[129].

Phenylphosphonous and phenylarsonous dichlorides. In dimethoxyethane these compounds are reduced in a single two-electron stage:

$$C_6H_5PCl_2 + 2e \rightarrow 2Cl^- + [C_6H_5P]^{\cdot} \xrightarrow{\text{solvent}} C_6H_5PH_2.$$

The corresponding half-wave potentials are −2.5 and −0.9 V.[129]

Triarylphosphine oxides. In dimethylformamide these compounds give one reversible one-electron wave[125,126]. They are more easily reduced than are the corresponding phosphines. Thus the half-wave potential for triphenylphosphine oxide in dimethylformamide is −2.490 V (aq. s.c.e.)[125]. This oxide is strongly adsorbed from aqueous solution on a mercury electrode, and is therefore widely used to inhibit electrode processes[130]; it exhibits inhibiting properties, though less strongly, also in aqueous–methanolic[131] and methanolic[132] solutions. A detailed study has been made[132] of the effect of the nature and concentration of an inert salt and also the presence of a depolariser (azobenzene) on the adsorption of triphenylphosphine oxide from methanolic solution on a mercury electrode.

Triphenylphosphine sulphide. This gives three waves, with half-wave potentials −2.415, −2.530, and −2.700 V (aq. s.c.e.). The process corresponds to the scheme[125]

$$(C_6H_5)_3PS + e \rightleftarrows (C_6H_5)_3PS^{\cdot-}$$

$$(C_6H_5)_3PS^{\cdot-} + e \nearrow (C_6H_5)_2PS^- + C_6H_5^- \quad \searrow (C_6H_5)_3P + S^{2-}.$$

The third, small wave on the polarograms corresponds to reduction of triphenylphosphine.

Triphenylphosphine selenide. In dimethylformamide this gives one-electron waves with half-wave potentials of −2.145 and −2.690 V.[125]

Triarylarsine oxides and sulphides. These are reduced in dimethylformamide with the production of two waves. The half-wave potentials of the first wave are less negative than with the corresponding initial triarylarsines[125].

Aryldiethylarsine oxides. In dimethylformamide these give two-electron waves corresponding to detachment of the aryl group[133]. Addition of phenol to the solution causes the wave to grow and divide, so that two two-electron waves are produced in the presence of a

fourfold to fivefold excess of phenol. The second wave then corresponds to reduction of the oxygen of the protonated species[133].

Quaternary phosphonium, arsonium, and stibonium salts. Many polarographic studies have been made of these compounds. A detailed summary will be found in Ref. 134, together with the polarographic characteristics of many phosphonium and arsonium salts in aqueous solution.

Tetraphenylphosphonium cation. Three reduction waves are obtained on the polarograms, the first corresponding to the transfer of one electron with the formation of triphenylphosphine and a phenyl radical, and the third to the reduction of phosphine[123], but the nature of the second wave was not established. Doubt has been cast on this mechanism[126]. In dimethylformamide the first wave is irreversible (according to results obtained with a Kalousek reversing switch)[126], but by analogy with the reduction of quaternary ammonium compounds[135], and on the basis of the slope of the lower part of the semi-logarithmic graph of the wave in aqueous medium[134,136], transfer of the first electron can be regarded as reversible or semi-reversible. From the inflexion in the upper part of the semi-logarithmic graph (Fig. 3 in Ref. 134) and the considerable shift in the half-wave potential to less negative values with increase in the depolariser concentration and the drop period of the electrode, it can then be supposed that electron transfer is followed by rapid bimolecular surface reaction (phosphines are strongly adsorbed on the electrode[127]) of the free radicals formed, yielding triphenylphosphine, phenyl radicals, and biphenyl, which was detected after electrolysis[124].

It has recently been shown[137] that minute quantities of hydroxide ions present in certain anhydrous media (if special measures are not taken to remove them) have a marked effect on the processes involved in the reduction of tetraphenylphosphonium salts. On polarography in dimethylformamide from which hydroxide ions (formed on storage in a glass vessel) have been specially removed the second wave on the polarogram of the tetraphenylphosphonium cation corresponds to reduction of triphenylphosphine oxide. If small quantities of hydroxide ions are present in the organic-solvent solution, the height of the second wave increases, and the limiting current of the first wave is smaller than the diffusion current corresponding to transfer of one electron, the number of electrons being less than unity by the concentration ratio $[OH^-]/[(C_6H_5)_4P^+]$ in the solution. This is due to occurrence of the very fast reactions

$$(C_6H_5)_4P^+ + OH^- \rightleftarrows (C_6H_5)_4POH, \quad (11)$$

$$(C_6H_5)_4POH + OH^- \rightarrow (C_6H_5)_4PO^- + H_2O, \quad (12)$$

followed by the comparatively slow process

$$(C_6H_5)_4PO^- \rightarrow (C_6H_5)_3PO + C_6H_5^-,$$

which under certain conditions (e.g. at very low temperatures) restricts the height of the second wave, and then the reaction

$$C_6H_5^- + H_2O \rightarrow C_6H_6 + OH^-.$$

Since dimethylformamide and acetonitrile usually contain a small quantity of water (0.1–0.2% and 0.4% respectively), the first stage of reduction (in the absence of hydroxide ions in the solution) takes place according to the scheme

$$(C_6H_5)_4P^+ + 2e + H_2O \rightarrow (C_6H_5)_3P + C_6H_6 + OH^-.$$

The hydroxide ions formed then react with a second molecule of the initial cation according to Eqn. (11), so that the height of the first wave corresponds formally to the transfer of one electron. In the preparative electrolysis of a tetraphenylphosphonium salt at the plateau potential of the first wave in dimethylformamide and acetonitrile not containing hydroxide ions, therefore, triphenylphosphine and its oxide are obtained in ~ 50% yield and benzene in 100% yield, which supports the above scheme. In conformity with this scheme the addition to dimethylformamide of formic acid, which suppresses reactions (11) and (12), raises the height of the first wave to a two-electron diffusion current. A similar but considerably smaller effect is produced by lithium ions (which combine with hydroxide ions) and also by water. The explanation for the latter[137] is that hydrated hydroxide ions are far less active than those solvated in dimethylformamide or acetonitrile.

The reversible character of transfer of the first electron to various phosphonium salts containing three phenyl groups has been shown in Ref. 138.

The half-wave potential of tetraphenylphosphonium in aqueous solution is −1.680 V (s.c.e.)[134], which becomes more negative on the successive replacement of phenyl by methyl or ethyl groups. Thus the potentials on passing from methyltriphenylphosphonium to trimethylphenylphosphonium are successively −1.862, −2.087, and −2.271 V.[134] When a phenyl group in tetraphenylphosphonium is replaced by other groups the half-wave reduction potentials become more negative in the sequence of substituents[136]

$$C_6H_5CH > (O)CH_3C_6H_4 > C(CH_3)_3 > C_6H_5 > C_2H_5 > CH_3.$$

Diphenylmethyltriphenylphosphonium cation. With 0.1 M tetraethylammonium perchlorate in acetonitrile this gives two one-electron waves[139], corresponding to formation of an ylide and its reduction respectively. Addition of phenol (a proton donor) to the solution doubles the height of the first wave and suppresses the second. With tetrabutylammonium iodide as supporting electrolyte a third wave is observed, corresponding to triphenylphosphine. With the same supporting electrolyte these three waves are present on the polarogram obtained in dimethylformamide. The process can be represented by the general scheme

$$(C_6H_5)_2CH\overset{+}{P}(C_6H_5)_3 + e \rightarrow \frac{1}{2}(C_6H_5)_2C{=}P(C_6H_5)_3 + \frac{1}{2}(C_6H_5)_3P + \frac{1}{2}(C_6H_5)_2CH_2.$$

The appearance of an ylide is attributed[139] to abstraction of a proton from the initial cation on its interaction with a very strong base—the diphenylmethyl anion—formed on the electrode by transfer of an electron to the diphenylmethyl radical, which in turn appears together with triphenylphosphine as a result of comparatively slow decomposition of the primary electrode product—the free radical formed by reversible transfer of one electron to the initial cation. In the presence of a proton donor the usual two-electron rupture of a carbon–phosphorus bond takes place.

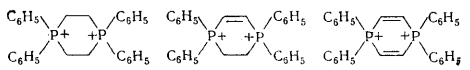
Benzyltriphenylphosphonium cation. This behaves similarly to the previous cation, giving two waves in acetonitrile with a tetra-alkylammonium salt as supporting electrolyte, and three waves in dimethylformamide or hexamethylphosphoramide with a tetrabutylammonium salt[139].

Phenacyltriphenylphosphonium cation. In acetonitrile this gives[139] three waves: the first corresponds to the transfer of one electron; the unusually low second wave was proved to represent reduction of the intermediate acetophenone (to "benzpinacone" [2,3-diphenylbutane-2,3-diol]; and the third wave, higher than the first, corresponds to reduction of the ylide and further reduction of acetophenone. The general scheme of the process is

$$(C_6H_5)\,COCH_2\overset{+}{P}(C_6H_5)_3 + e \rightarrow \frac{2}{3}\,C_6H_5COCH{=}P(C_6H_5)_3 + \frac{1}{2}\,P(C_6H_5)_3 + \frac{1}{3}\left[C_6H_5(CH_3)C(OH)-\right]_2.$$

Polymethylenebistriphenylphosphonium salts. These compounds $[(C_6H_5)_3P[CH_2]_nP(C_6H_5)_3]Br_2$ having small values of n are reduced more easily than are the usual salts. With increase in n the half-wave potential becomes more negative, from −1.195 V when $n = 1$ to ~ −1.8 V when $n = 4$–6, after which it becomes more positive again[134].

1,1,4,4-Tetraphenyl-1,4-diphosphorinium salts. These salts, those containing the corresponding dihydro- and tetrahydro-rings



and numerous derivatives have been studied in dry dimethylformamide at a dropping mercury and a platinum microelectrode[140] with the use of 0.1 M tetraethylammonium perchlorate as inert electrolyte. The diphosphoniahexane derivative gives one two-electron wave with $E_{\frac{1}{2}} = -1.84$ V (s.c.e.) at a mercury electrode. The corresponding hexene and hexadiene derivatives are reduced considerably more readily: the first waves are reversible and correspond to the transfer of one electron forming radical-cations, with half-wave potentials respectively of −0.75 and −0.56 V. An especially detailed study has been made of a 2,5-di-t-butyl-1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexa-2,5-diene salt, which gives two one-electron waves ($E_{\frac{1}{2}} = -0.723$ and −1.08 V), the first being reversible and the second not. Addition of up to 10% of water to the dimethylformamide does not affect the height of the first wave, but in the presence of traces of perchloric acid the latter grows at the expense of the second wave, so that with increase in the acid concentration a single two-electron wave remains with $E_{\frac{1}{2}} = -0.675$ V.

The transfer of two electrons is regarded[140] as yielding a hitherto unknown compound—a diphosphabenzene derivative—which possesses basic properties and can be protonated at the carbon atoms; it resembles a diylide in character. Electrochemical reduction of the initial salt in aqueous-ethanolic medium gives a product without ring cleavage—a 1,4-diphosphoniacyclohexane derivative[141]—which is considered[140] to confirm the intermediate formation of diphosphabenzene. Substitution at positions 2 and 5 in the diphosphoniacyclohexadiene ring produces a change in half-wave potential in conformity with the inductive effect of the substituents (apart from di-t-butyl). Replacement of the *P*-phenyl groups by other substituents or substitution in the phenyl rings acts similarly. The waves are better defined at a platinum electrode, since they are distorted on mercury by adsorption phenomena[140].

Triphenyltriphosphine dianion. With tetrabutylammonium perchlorate in oxolan this species $(C_6H_5P)_3^{2-}$ gives an anodic oxidation wave at −1.4 V (relative to 0.1 *N* Ag^+/Ag), the product being probably[142] pentaphenylcyclopentaphosphine and hexaphenylcyclohexaphosphine $(C_6H_5P)_5$ and $(C_6H_5P)_6$. Mainly from the electrochemical behaviour of the triphenyltriphosphine dianion it was concluded that this compound has a linear structure, not the cyclic structure assumed earlier[143].

Pentaphenylcyclopentaphosphine and hexaphenylcyclohexaphosphine. With tetrabutylammonium perchlorate (concentration not indicated) in oxolan these compounds show the same electrochemical behaviour[142], giving at a dropping mercury electrode an irreversible two-electron reduction wave with $E_{\frac{1}{2}} = -2.62$ V (0.1 *N* Ag^+/Ag reference electrode) and a semi-logarithmic graph of slope corresponding to 63 mV. Cyclic voltammetry at a spherical platinum microelectrode gives a cathodic peak with $E_{p/2} = -2.8$ V, and on reversal of polarisation three anodic peaks with −1.9, −1.4, and −1.0 V, the second anodic peak being identical with the oxidation peak of the triphenyltriphosphine dianion. It is suggested that reduction yields an unstable dianion $(C_6H_5P)_n^{2-}$ ($n = 5,6$), which rapidly decomposes, so that the anodic peaks correspond to oxidation of the products formed.

Similar electrochemical behaviour is observed also with tetraphenylcyclotetraphosphine, as well as with alkyl derivatives of polycyclophosphines[144], for which the $E_{p/2}$ of the cathodic peak correlates well with the Taft σ-constants of the alkyl groups (the $E_{p/2}$ of the phenyl derivatives also lie on the straight line obtained).

Arsonium salts. These behave like phosphonium salts, but are more easily reduced, their half-wave potentials being ~ 0.3 V more positive than those of the corresponding phosphonium derivatives[134]. One or two reduction steps are observed depending on the nature of the substituents.

Hexaphenylhexa-arsine. Like the phosphorus analogue, $(C_6H_5As)_6$ on cyclic voltammetry at a platinum electrode gives a cathodic peak with $E_{p/2} = -2.8$ V, and on anodic polarisation three oxidation peaks with −2.0, −1.5, and −1.2 V.[142] Exhaustive electrochemical reduction yields a new substance, whose reduction gives $E_{p/2} = -3.0$ V, probably neutral diarsine. The corresponding diphosphines are electrochemically inactive.

Tetramethylstibonium. In aqueous solution the polarograms contain a single irreversible two-electron wave with $E_{\frac{1}{2}} = -1.490$ V (s.c.e.), corresponding to formation of trimethylstibine and methane[145].

Trimethylphenylstibonium, dimethyldiphenylstibonium, methyltriphenylstibonium, and tetraphenylstibonium. In aqueous media these give two one-electron diffusion waves[145]. The first wave corresponds to reversible electron transfer with formation of a tetrasubstituted stibine radical, which reacts rapidly with mercury to give a trisubstituted stibine and an organomercury radical, the latter disproportionating to a disubstituted organomercury derivative. The half-wave potential of the first wave has the respective values −1.195, −0.900, −0.710, and −0.635 V (s.c.e.) for the above compounds. The second wave is irreversible.

The half-wave potentials of both waves are independent of pH over the range studied (4–12). Electrolysis on the limiting-current plateau of both waves yields a trisubstituted stibine and a hydrocarbon (benzene or methane), but formation of the latter is not a consequence of reduction of the organomercury radical (as supposed[134] from the identity of the half-wave potentials for the second wave of tetraphenylstibonium and the phenylmercury ion). This follows from the simultaneous detachment of methyl and phenyl groups on electrolysis, in different ratios at the potentials of the first and second waves. In contrast to alkylaryl-phosphonium and -arsonium ions the nature of the group split off on the cathodic reduction of tetrasubstituted stibonium ions is determined by the stability not only of the resulting hydrocarbon radical but also of the stibine derivative[145]. The second wave corresponds to transfer of an electron and then also a proton to the tetrasubstituted stibine radical, to yield a trisubstituted stibine and a hydrocarbon.

The adsorbability of methylphenylstibonium ions on a mercury electrode is considerably enhanced with increase in the number of phenyl groups.

Preparative electrolysis of a tetraphenylstibonium solution at the potential of the first-wave plateau gave only triphenylstibine and diphenylmercury (neither benzene nor biphenyl was detected among the products). The second wave on the polarograms of tetraphenylstibonium corresponds to reduction of diphenylmercury formed in the first stage[146].

Tetratolylstibonium. In aqueous solution this gives two one-electron waves, the first of which is reversible[147].

Tetraphenylbismuth cation. Unpublished results indicate[145] two one-electron waves in aqueous solution.

Pentaphenylphosphorane. With 0.1 M tetrabutylammonium iodide in dimethylformamide this gives one irreversible wave[137]. The peak potential on voltammetry (with linear variation of potential) is −2.75 V (aq. s.c.e.).

Phosphoric esters. Only a capacitive cathodic spur appears on the $dE/dt = f(E)$ oscillopolarograms obtained in 1 M aqueous potassium chloride for the esters from trimethyl to triphenyl phosphates.

Trialkyl phosphites. These give an additional spur caused by the formation of compounds with mercury[148].

Tri-*p*-nitrophenyl phosphate. Of the five reduction waves the first represents an adsorption effect, the second is a diffusion wave with the transfer of two electrons, the third is kinetic, and the fourth and fifth waves are strongly distorted maxima, whose nature has not been established. On the second wave the dianion $[(NO_2C_6H_4O)_3PO]^{2-}$ is formed, and is slowly converted by interaction with the solvent into *pp'*-dinitrobiphenyl and nitrophenyl dihydrogen phosphate $NO_2C_6H_4OPO(OH)_2$.[149]

Di-*p*-nitrophenyl hydrogen phosphate. In dimethylformamide this ester $(NO_2C_6H_4O)_2POOH$ gives three waves. The second is a diffusion wave with the transfer of two electrons and formation of a dianion converted by reaction with the solvent into *pp'*-dinitrobiphenyl and phosphoric acid[150].

Phenyl- and β-styryl-phosphonic and -phosphinic esters. In dimethylformamide these give one or two one-electron cathodic waves, the first of which is reversible[126,151]. The styrylphosphonates are reduced more readily than styrene itself by almost 0.5 V. It is interesting that the half-wave potentials are almost the same for the styrylphosphonate and a styrylphosphinate (−1.45 and −1.81 compared with −1.45 and −1.85 V relative to mercury in 0.08 M tetraethylammonium iodide).[151]

Vinylphosphonic and divinylphosphinic esters. In dimethylformamide these compounds $CH_2:CH.PO(OC_2H_5)_2$ and $(CH_2:CH)_2POOC_2H_5$ have one-step two-electron reduction waves with respective half-wave potentials of −2.02 and −1.87 V (relative to mercury in 0.08 M tetraethylammonium iodide).[126]

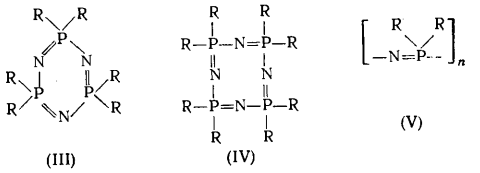
Diethyl aroylphosphonates. On reduction at a dropping mercury electrode in acetonitrile these esters $ArCO.PO(OC_2H_5)_2$ give diethyl phosphonates and benzoin. In the presence of benzoic acid diethyl α-hydroxyarylmethylphosphonates are formed[152].

Diethyl α-diazobenzylphosphonate. With 1 M lithium perchlorate in 20% aqueous dioxan this ester $C_6H_5.CN_2.PO(OC_2H_5)_2$ and its *para*-substituted derivatives give one irreversible two-electron diffusion wave ($E_{\frac{1}{2}}$ = −1.18 V (s.c.e.) for the unsubstituted ester), corresponding to replacement of the diazo-group by two hydrogen atoms[153]. The corresponding potentials of the substituted derivatives vary in conformity with the Hammett equation containing the constant $\rho = +0.098$. Under the same conditions ethyl α-diazophenylacetate gives a wave having $E_{\frac{1}{2}} = -1.17$ V: i.e. the effect of the diethoxyphosphinyl group on reduction of the diazo-group is almost the same as that of the ethoxycarbonyl group[153].

At a rotating platinum disc electrode the above phosphonates give one-electron diffusion waves, which with certain derivatives are reversible.

Acylphosphine oxides. In dimethylformamide and acetonitrile these compounds RCO.PORR' acquire the first electron irreversibly when R = CH_3 and reversibly when R = C_6H_5.[154]

Organocyclophosphazines. Compounds having a six- or eight-membered ring (III) or (IV) or the polymeric linear structure (V)



(III) (IV) (V)

($n \simeq 15$; R = C_6H_5, OC_6H_5, OCH_2CF_3, etc.) are reduced in dimethylformamide in the presence of 0.1 M tetrabutylammonium iodide, giving a one-electron first wave followed, immediately before discharge of the supporting electrolyte, by another, very indistinct wave corresponding to transfer of a second electron[155]. The size of the ring is almost without effect on the half-wave

potential of the first wave (with R = C_6H_5 structures (III) and (IV) have the values −2.65 and −2.67 V s.c.e.). Coulometric electrolysis of (III) at the limiting-current potential of the first wave showed complete regeneration of the depolariser: i.e. the first wave is catalytic in character. Cyclic voltammetry indicates the instability of the radical-anions formed on transfer of the first electron[155].

The present Review has given the principal information available on the polarographic behaviour of organoelementary compounds of non-transition elements. A brief summary of results for derivatives of transition metals can be found in the recently published Russian translation of the book by Mann and Barnes[156].

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