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Electrode reactions and electroanalysis of organomercury compounds

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Abstract. Characteristic features of mechanisms and kinetics of electrode reactions of organomercury compounds (symmetrical, non-symmetrical) and organomercury salts on a mercury electrode are analyzed. Attention is focused on the effect of coordination, adsorption and the nature and properties of intermediates on these processes as well as on the formation of organomercury derivatives in the adsorption of organic and hetero-organic compounds on a mercury electrode. The kinetics of heterogeneous chemical equilibrium 'organic calomel' – symmetrical organomercury compound in the adsorption layer and the relative stability of intermediates in the one-electron reduction of organomercury salts are discussed as well as the electrolytic hydrogen evolution catalyzed by organomercury intermediates. The problems of combined and separate electrochemical quantitation of organic and inorganic mercury compounds in natural objects are considered. The bibliography includes 396 references.

I. Introduction

Organomercury compounds (OMC) have found practical application in different fields of science and technology. At the same time, the solution of urgent problems of environmental safety requires efficient methods of their determination, analysis and destruction (detoxication).

The interest of electrochemists in OMC was aroused, on the one hand, due to the wide use of the mercury electrode, which is not always chemically inert. Many organyl halides and O-, S-, Se-, Te-, P-, N-containing compounds (*e.g.*, see Refs 1–7) and organometallic compounds [2, 8, 9] interact with mercury to form OMC as the intermediates in their adsorption and/or electrochemical reduction (ER) or oxidation (EO). This induces substantial changes in the mechanism and kinetics of electrode reactions. On the other hand, one of the most important methods in synthesizing organic and hetero-organic compounds is electrosynthesis, which involves the use of mercury electrodes.[1 – 3] Electrosynthesis is one of the methods for the preparation of certain organometallic compounds, for example, tetraalkyllead (the Nalco process).[1] However, if the synthesis of such compounds is not intended, the possibility of OMC formation should be taken into account when carrying out electrosyntheses and electroanalytical studies employing mercury electrodes.

The possibility of electrochemical preparation of organometallic compounds was first demonstrated by Tafel back in the beginning of the 20th century. He obtained diisopropylmercury upon the electrolysis of acetone solutions on a Hg cathode, which he reported as the 'unexpected formation of organometallic compounds'.[10] Until the 1950s, the electrochemical transformations of organometallic compounds (including OMC known as early as since 1852) [11] were virtually ignored due to insufficient development of electrochemical methods.

Nowadays, the trends of research in the field of electrochemistry of OMC are determined by demands of industry. At the same time, the so-called problem of environmental mercury is topical (for example, see Ref. 12). On the one hand, industry requires vast amounts of mercury (several thousand tons annually), while, on the other hand, numerous OMC pertain to the most hazardous superecotoxicants. As regards toxicity, they far surpass the majority of organo-

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metallic derivatives of heavy metals and inorganic compounds of mercury, being better soluble in oils, capable of penetrating through cell membranes and interacting with tissues of living organisms.[12,13] The high toxicity and stability of OMC (for instance, the decomposition period of Me_2Hg in the natural environment is $\sim$33 years)[14] limits their practical application, whereas the necessity to observe severe environmental standards on the environmental content of hazardous substances increases the production costs.

Organomercury compounds were the sources of electrogenerated anions,[15] the convenient precursors for preparative synthesis[10,16] and the mediators of enantioselective electrosynthesis.[17] They assisted in the production of substances the direct synthesis of which was complicated or non-selective.[18,19]

Organomercury compounds were used as medicinal drugs (*e.g.*, promesan and thiomersal preparations),[8,12,18] explosives and biochemical markers,[8,12] catalysts and initiators of polymerization and co-polymerization,[12] and also in laser engineering and microelectronics.[20] The high biocide activity is one of the most important properties of OMC.[12,18] They were successfully used as conserving agents in pharmaceutics and perfumery,[9,12,18] parts of composition of antifouling coatings for marine ships[8,12] and compositions with the high bactericide, antimoth and antimold activities.[8,9,12] It was shown[21] that polymers synthesized in the presence of organomercury initiators (for instance, Pr^i_2Hg) exhibit insectoacaricide activity. Many OMC are efficient antiseptics, fungicides, insecticides (for example, ceresan, panogen, metaphen, semesan, granosan, trimersal, aretan, *etc.*).[8,9,12] However, these compounds were only permitted for treating seeds, and the treatment should be carried out extremely carefully due to the possible incorporation of mercury into food chains (thus the defective technology exploiting granosan has resulted in the appearance of mercury in organisms of the Volga sturgeon[12]).

Mercury is a trace element of pathogenic action. In nature, under the action of specific microorganisms, it is transferred from its inorganic, often water soluble form to the oil-soluble organic form, which increases its toxicity many times. The appearance of the Minamata disease in Japan in the 1960s was explained by the action of 'organic' mercury formed by this mechanism from the wastes of soda industry.[12] Organomercury compounds can be accumulated in organisms of certain marine inhabitants especially in tiger sharks and tuna fishes.[22] The use of such OMC is limited or forbidden in the USA and several EU countries.[12]

It is commonly accepted[8,12,13] that the toxicity of OMC is caused, among other reasons, by relative ease of the C—Hg bond cleavage to form free radicals that exhibit a strong trend to coordination, for example, with amino acids, enzymes, and other vitally important compounds. Hence, the significance of studying OMC metabolism,[13] including recourse to electrochemical methods is topical.[23,24] Moreover, bearing in mind the possibility of poisoning with OMC, the interest in the development of methods of their deactivation holds.[25] Efficient physicochemical methods of OMC demercuration under mild conditions include protolysis, solvolysis,[19,26] photochemical (*e.g.*, see Refs 27–32) or microwave[33] destruction, electrochemical reduction or oxidation.[1–3]

The development of new and the improvement of the existing methods of electroanalytical determination of different forms of both inorganic mercury (Hg_2^{2+}, Hg^{2+}) and OMC (combined and separate) are topical problems. Among them, the determination of alkyl, most often, methyl derivatives, which have the common name 'monomethylmercury' and of certain phenyl derivatives attracted the keenest attention. Although several electrochemical methods for OMC determination were comprehensively analyzed in reviews[8,9] and monographs,[2,34] the interest in such studies is still high.

Indirect determination of compounds that possess low electrochemical activity (particularly, unsaturated compounds, *e.g.*, styrene, vinyl acetate, isopropenyl esters, *N*-vinylpyrrolidone, *etc.*) or mixtures (*e.g.*, styrene with α-methylstyrene) required their preliminary mercuration.[8,35–37]

Electrochemical methods *per se* or in combination with methods of quantum and theoretical organic chemistry[38–46] were successfully used in studying the structure and reactivity of organometallic compounds. The mechanism of their electrochemical transformations served as a model of certain organic reactions.[19,26] Many authors utilized the OMC electroreduction for the determination of the acidity of hydrocarbons (for details, see Refs 26, 47). In certain publications,[48–50] attention was drawn to the similarity of certain steps that accompany the reduction of organic and inorganic mercury compounds with the reactions of the mercury geochemical cycle in nature and also with the step of electrochemical adsorption of the mercury ions on pyrite surface in the mining waste treatment processes.[51]

Electrochemical studies of OMC conventionally employ polarography on the dropping mercury electrode,[52–77] linear sweep and cyclic voltammetry (LSV and CV) on the dropping mercury electrode, on the hanging mercury drop electrode or on solid electrodes,[15,36,54,78–107] chronopotentiometry,[108–125] methods of $I-t$ curves,[54,55,124,126] electrocapillary curves[36,54,60,78,79] and differential capacitance curves[118,126] and also the square-wave and pulse polarographic mehods,[53,66,78,127] methods of rotating disk electrode[92,93,126–128] and rotating ring-disk electrode.[128–132] Electroanalytic methods were often used in tandem with different physicochemical methods[53,54,66,78,118] including EPR spectroscopy, sonication, electrochemiluminescence, *etc.*[97–102,133] in combination with electrolysis at a controlled potential.[60,92–94,100,134–141] All these methods including stripping voltammetry (mainly, anodic) and electrochemical impedance were used in the electroanalytical determination of inorganic mercury and OMC.

The ER potentials for the majority of OMC studied so far and certain peculiarities of the mechanisms of their electrode reactions were discussed in reviews and monographs published no later than in the mid-1980s.[1–3,8,9,37] However, the past 15–20 years witnessed the progress in studying the mechanisms of such reactions. First of all, mention should be made of detailed studies of the electrochemical behaviour of OMC on non-mercury electrodes.[83–86,106,107] As the result, a new in principle ER mechanism, which differed from that conventionally applied to the mercury electrode, was put forward[142] as well as the mechanism of electrocatalytic evolution of hydrogen, which involved mercury intermediates.[143,144] Deepening of such studies was dictated by the demands in the development of methods for electrochemical analysis of OMC and marked by the appearance of new efficient electrode materials, modifiers as well as by modernization of the instrumental basis. The studies themselves often led

to elucidation of the OMC electroreduction mechanism.[35, 36, 78–88]

In the present review, the results of these studies including new evidence of the interaction of hetero-organic compounds with the mercury electrode are generalized.

II. General electroreduction mechanism of organomercury compounds on a mercury electrode

The electrochemical activity of organomercury salts (RHgX), symmetrical (R_2Hg) and non-symmetrical (R′HgR) (R and R′ are an organic or hetero-organic moiety) compounds is associated with the relatively low energies of the Hg–X (150–400 kJ mol^{-1}) and C–Hg (50–500 kJ mol^{-1}) bonds.[19, 145–147] The Hg–X bond may be both covalent (X = F^-, Cl^-, CNS^-, *etc.*) and virtually ionic (X = SO_4^{2-}, NO_3^-, *etc.*). For substituent X exhibiting the low affinity with respect to mercury, the salt RHgX partially dissociates in a polar solvent to afford RHg^+ and X^- (Ref. 14); RHg^+ cations [for example, $MeHg^+$ (see Ref. 148)] pertain to the softest Lewis acids. Thus in the electroreduction of OMC, the electron passed directly to the mercury atom,[67] the overall rate being determined by the positive charge on this atom, namely, the larger the charge the easier the polar bond scission.

The first comprehensive analysis of the mechanism of RHgX electroreduction on a Hg electrode was carried out for phenylmercury salts.[52] To date, this mechanism has remained for the most part generally accepted for aqueous and non-aqueous media. According to this mechanism, the electroreduction of RHgX under polarographic conditions (H_2O : EtOH = 1 : 1) proceeds in two one-electron steps:

$$RHgX + e \longrightarrow RHg^{\bullet} + X^- \quad (E^{(1)}_{1/2}), \tag{1}$$

$$RHg^{\bullet} + e \longrightarrow R^- + Hg \quad (E^{(2)}_{1/2}). \tag{2}$$

This is true not only on mercury but also on amalgam (particularly, on a mercury-covered Pt) electrodes (Fig. 1, curve *1*).[107]

Both steps depended in different manner on pH. The half-wave potential of the first reaction [$E^{(1)}_{1/2}$] was constant in the acidic region but shifted in the negative direction with an increase in pH.[52–56, 103, 104] The pH-dependence of $E^{(1)}_{1/2}$ was often associated with the nature of the buffer used[36] due to complexation of RHg^+ (see below). In a certain pH range (pH*), the first wave could split into two, which was associated with the presence in solution of comparable amounts of RHg^+ and RHgOH reduced at different potentials.[53, 84] For 5-mercuriouridine phosphates, it was shown[104] that such splitting occurs only in the presence of the chloride ions, which was associated with involvement of the latter ions in the coordination with RHg^+ (with the equilibrium constant 1.2 litre mol^{-1}).

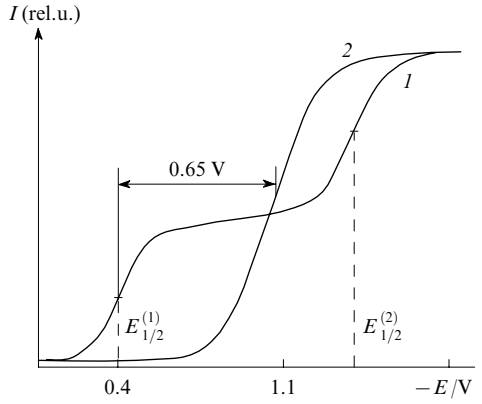


Figure 1. Polarization curves current (*I*) *vs.* potential (*E*) of the MeHgCl electroreduction on amalgam (*1*) and Pt (*2*) electrodes.[107] $E^{(1)}_{1/2}$ and $E^{(2)}_{1/2}$ are half-wave potentials of the first and second steps, respectively.

As a rule, $E^{(2)}_{1/2}$ was pH-independent in alkaline media,[36] whereas in acidic media, it shifted to more positive values. In the majority of cases, the slope of the $\partial E_{1/2}/\partial$pH-dependence was ~0.06 V,[36, 52–56] *i.e.*, close to the theoretical value for the electrode processes involving H_3O^+. It is generally accepted[52] that one of the following two reactions proceeds in acidic and neutral media (pH ⩽ 7) in the first step (corresponding to the first wave):

$$RHgX + e + BH^+ \longrightarrow RHg^{\bullet} + B + HX \tag{1a}$$

$$X^- \rightleftarrows$$

$$RHg^+ + e \longrightarrow RHg^{\bullet} \tag{1b}$$

(BH^+ is the proton donor; in acidic media, this is H_3O^+). For pH ⩾ pK_a, reaction (1c) was preceded by equilibrium (1d)

$$RHg^+ + OH^- \overset{(1d)}{\rightleftharpoons} RHgOH + e \xrightarrow{(1c)} RHg^{\bullet} + OH^-.$$

In the second step (corresponding to the second wave), the following reaction was assumed:[8, 36, 78]

$$RHg^{\bullet} + e \longrightarrow \begin{cases} \xrightarrow{BH^+} RH + Hg + B & (2a) \\ R^- + Hg \xrightarrow{BH^+} RH + Hg + B & (2b) \\ RHg^- \xrightarrow{BH^+} RH + Hg + B. & (2c) \end{cases}$$

Processes (2a) and (2b) occur in acidic and alkaline solutions, respectively.

As assumed by White[1] and proved by Butin *et al.*,[107] the process (2c) is more probable than reaction (2b), at least in anhydrous MeCN.

For a long time, the question of reversibility of the first step of RHgX electroreduction was hotly debated. This step was considered reversible if the slope of the *I*(*E*) plot , *i.e.*, the polarographic wave plotted in semilogarithmic coordinates of the Heyrovsky equation, approached 0.06 V (Refs 52, 57, 61, 62) and irreversible otherwise.[36, 53–60] As was shown later,[14] the transition from reversibility to quasi-irreversibility with the changeover of the supporting electrolyte could be associated with coordination of the supporting electrolyte anion to RHg^+. For example, in the presence of an excess of strongly coordinating anions such as I^-, Br^-, CN^-, CNS^-, S^{2-}, *etc.*, the first wave of RHgX electroreduction became reversible.[14]

On the whole, for organomercury salts, in the sequence of steps

$$RHg^+ + X(L) \overset{K_1}{\rightleftharpoons} RHgX(L) + X(L) \overset{K_2}{\rightleftharpoons} \rightleftharpoons RHgX_2(L_2) + X(L) \overset{K_3}{\rightleftharpoons} RHgX_3(L_3) \tag{3}$$

the dependence of the equilibrium constant (K_1) of the RHgX salt formation on the nature of X was as follows:[14, 36]

Anion	logK_1	Anion	logK_1	Anion	logK_1
S^{2-}	~21	I^-	8.5–10	CNS^-	5–7
CN^-	13–14	Br^-	5–7	F	1.5
OH^-	8.5–10	Cl^-	5–7	AcO^-	1.5–3.6

Usually, both K_2 and K_3

$$K_n = \frac{[RHgX_{n-1}^{-(n-1)}(L_n)]}{[RHgX_{n-1}^{-(n-2)}(L_{n-1})] \cdot [X^-(L)]} \quad (4)$$

($n = 2$ and 3 for K_2 and K_3, respectively) were substantially smaller than K_1. Note that electrochemical methods are still among the most efficient methods for the determination of these constants.[14, 104]

Using the polarographic method, it was shown [14] that as early as in the step of $PhHgClO_4$ synthesis, complexes such as $[PhHg \cdot L_n]^+ ClO_4^-$ were formed with the solvent L [L is pyridine (Py), tetrahydrothiophene (THT), dioxane, hexamethylphosphorotriamide (HMPT), $n = 1$; L is teteramethylurea (TMU), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), MeOH, MeCN; $n = 2$]. The parameters of waves for the $PhHgClO_4$ electroreduction [$E_{1/2}^{(1)}$, wave slope, *etc.*] substantially depended on the solvent nature. It was shown that the ability of a solvent to solvate the $PhHg^+$ ion (characterized by logK_1) decreased in the order

THT (10) > Py (8.1) > HMPA (6.2) > TMU (3.8) >
> DMSO (3.3) > DMF (2.8) > MeOH (1.4) >
> MeCN (1.1) > THF (0.6).

The necessity of considering the coordination of the supporting electrolyte anions with the RHg^+ cation is not the only source of ambiguity in interpretation of such data. After the addition of an electron, a bimolecular reaction could occur

$$2\,RHg^{\bullet} \underset{k'_{-1}\,(a)}{\overset{k'_1\,(very\ fast)}{\rightleftharpoons}} R_2Hg_2 \underset{k_1\,(b)}{\overset{k_{-1}\,(fast)}{\rightleftharpoons}} R_2Hg + Hg. \quad (5)$$

The parameters of reduction waves could change with concentration, which should be reflected in the polarization curve equation for the first step. In addition to the variation in the wave slope, the dimerization of radicals to form a labile intermediate such as 'organic calomel' R_2Hg_2 (or $[RHg_{ads}]_n$) should shift $E_{1/2}^{(1)}$ in the positive direction with the increase in the volume concentration of the depolarizer (c_0) and, conversely, shift $E_{1/2}^{(2)}$ in the negative direction.[36, 52–56, 123] The slope of the $\partial E_{1/2}^{(2)}/\partial \log c_0$ plot was determined by the $0.058/\alpha n_a$ ratio, where α is the transfer coefficient, n_a is the number of electrons transferred in the potential-determining step. For example, for PrHgOAc αn_a was 0.45 (Ref. 123).

Given that a reversible electron transfer step is followed by fast reversible dimerization with subsequent slower decomposition of the dimer ($k'_1/k'_{-1} \gg k_1/k_{-1}$), equilibrium (5) shifted strongly to this dimer formation. The rate constant k'_{-1} was approximately equal to 2×10^{-6} for R = Me (Ref. 93), and 3.5×10^{-5} cm s^{-1} for R = Et (Ref. 79). The rate of $RHg^{\bullet}$ dimerization depended on the nature of R and could substantially differ for different compounds, which complicated the interpretation of polarization curves. For example, for electroreduction of *trans*- and *cis*-AllHgCl (Ref. 56), the dimerization of radicals slowed down (probably due to steric hindrances) to such extent that it did not affect the characteristics of polarization curves at all. This effect was less pronounced for n-$C_6F_{13}HgI$ in DMF solutions.[89]

A clearer answer to the question of reversibility of the first step can be obtained based on the data from fast scan rate methods, *e.g.*, cyclic voltammetry or chronopotentiometry with current reversal. Figure 2 shows the charging curves of the mercury electrode in PrHgOAc solutions measured at different current densities.[123] Similar dependences were observed for other alkylmercury salts.[109] Their analysis has shown that the second wave of RHgX electroreduction (or the second faradaic delay in chronopotentiometry) corresponds to the totally irreversible step, because no signals were observed in the anodic branch of the chronopotentiogram with the current reversal. The reaction corresponding to the first delay was characterized by electron transfer with a certain degree of reversibility (Fig 3 *a*). In turn, the Tafel plots of the first step of β-NaphHgOAc (Naph is naphthyl) electroreduction consisted of two segments with slopes of 0.06 (low i) and 0.03 V (high i) (Fig. 3 *b*).[109, 111] This was rationalized [109] by the presence of the subsequent fast chemical reaction with the order varying from 1 to 2 with the increase in i. The Tafel plot for oxidation was completely irreversible; hence, the oxidized intermediate was not identical to $RHg^{\bullet}$, the primary product of reaction (1). The same conclusion was drawn for PrHgOAc,[123] namely, the different form of the Tafel plots for reactions in delay *1* and *4* and also certain irreversibility of step (5a) suggest that the original salt is not recovered in the oxidation of 'organic calomel'. On the other hand, the Tafel plot slope for delay *4* [$(\partial E_4/\partial \log i)_{E_{in}} \leqslant 0.03$ V] was too small for a strictly irreversible process and the coincidence of the Tafel plots for delays *1* and *4* can be achieved only by their extrapolation to sufficiently high current densities, *i.e.*, to $i \geqslant 10^3$ mA cm^{-2} (see Fig. 3 *a*).[123] The difference between

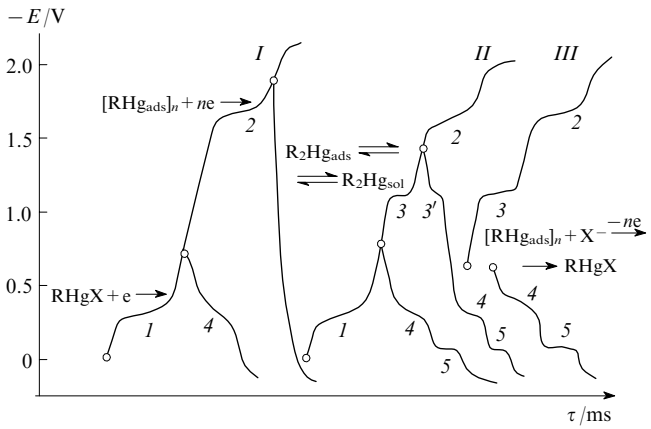


Figure 2. Chronopotentiograms (charging curves) of the mercury electrode measured under galvanostatic conditions with the current reversal in 10^{-4} M PrHgOAc solution.[123]
I is high current densities ($i \geqslant 1$ mA cm^{-2}), *II* is low current densities, *III*, $E_1 < E_{in} < E_3$; $E_{in} = 0.0$ V (*I*, *II*) and -0.6 V (*III*); (*1*–*5*) is the delay number; E_{in} is the initial potential; E_1 and E_3 are potentials of the first and the third delays, respectively.

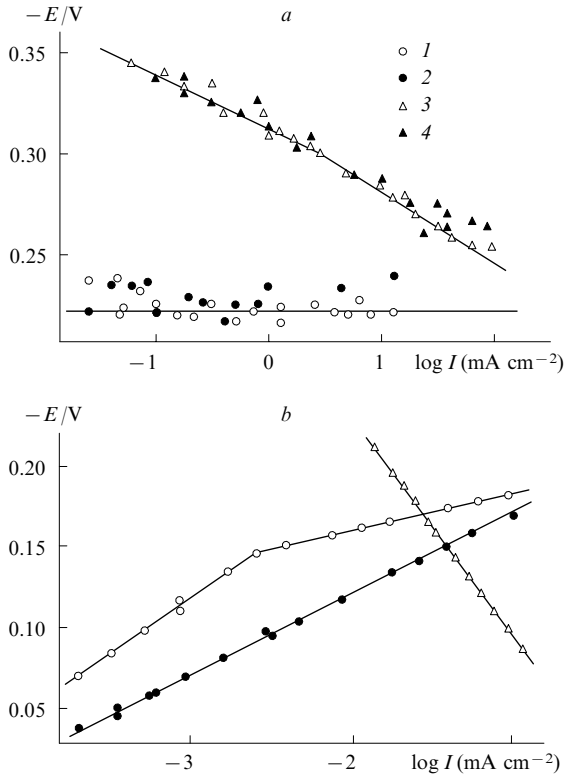


Figure 3. The Tafel plots for the reaction corresponding to the first delay (*1*, *2*) in the electroreduction of PrHgOAc (*a*) and β-NaphHgOAc (*b*), the fourth delay of oxidation of the corresponding 'organic calomels' $[RHg_{ads}]_n$ (*3*, *4*).[109, 123]

the peak potentials in voltammograms of one-electron ER and EO of cyclopropylmercury halides was considerably larger (0.3 – 0.4 V)[96] than in the above example and reached 0.5 – 0.6 V for mercuriouridine diphosphate and triphosphate,[104] *i.e.*, substantially exceeded the theoretical difference for the reversible process. Charging curves for arylmercury salts, namely, phenyl- (Ref. 110) and pentafluorophenylmercury bromides,[119] in contrast to charging curves of alkylmercury salts (see Fig. 2), contained no corresponding anodic delays, which pointed to the complete irreversibility of ER.

The value of $E^{(1)}_{1/2}$ in aqueous, water-alcohol[52, 69] or non-aqueous[69] media was independent of the nature of substituent X but depended on the nature of the background anion.[52, 69] Apparently, this was associated with a remarkable dissociation of RHgX, while the differences in $E^{(1)}_{1/2}$ for PhHgCl, PhHgBr and PhHgI in DMF solutions[66] were most probably caused by the lower degrees of dissociation of these compounds.

Both $E^{(1)}_{1/2}$ and $E^{(2)}_{1/2}$ substantially depended on the nature of R. The values of $E^{(1)}_{1/2}$ increased in the series All < Ar < Alk (Refs 67, 69), whereas $E^{(2)}_{1/2}$ increased in the series Alk < Vi < Ar (Ref. 69) (Vi is vinyl) and also increased with the shortening in the alkyl chain length and, within the series, with the increase in the electronegativity of substituents. It was shown[41] that the $E^{(1)}_{1/2}$ values also depend on the polarization effect of R groups, which can be significant for $AlkHgClO_4$, $PhHgClO_4$ and $BnHgClO_4$. Analogous conclusion also holds true for one-electron oxidation of AlkHgX.[40]

For certain RHgX salts (particularly, for R = Ph, Bn or $PhCH(CO_2H)$ (see Refs 14, 39, 74), it was shown that $E^{(1)}_{1/2}$ depends on the following factors: the redox potential (E^0), rate constants for dimerization of $RHg^{\bullet}$ [k'_1, see Eqn (5)] and formation of the $RHg^+ \cdot L$ complex (L are anions X^- or polar molecules, *e.g.*, H_2O and DMF) and the equilibrium constant of complex formation [K_1, see Eqn (3)]. Insofar as the trend of $RHg^{\bullet}$ (or $[RHg_{ads}]_n$) towards coordination was weakly pronounced, only two first factors affected the $E^{(2)}_{1/2}$ values.

The second step of RHgX electroreduction was conventionally considered[36, 52–60, 104] irreversible (Fig. 2). Complexing agents did not affect the $E^{(2)}_{1/2}$.

The reduction of the majority of RHgX salts on a mercury electrode followed the Benesch model.[52] In addition to substituted and unsubstituted organic compounds (AlkHgX, AllHgX and ArHgX), inclusion compounds also pertain to these salts [R stands for ferrocene, cyclopentadienylmetal tricarbonyls η^5-$C_5H_4M(CO)_3$ (M = Mn, Re, *etc.*) or certain carboranes].[63, 68, 106] However, numerous exceptions are known. For instance, Okamoto[64] has shown that alkynes $ArC{\equiv}CHgCl$ and $(ArC{\equiv}C)_2Hg$ (see †) were reduced at similar potentials in a single two-electron step in a H_2O – dioxane (60%) mixture with tetraalkylammonium supporting salts in the wide pH interval

$$\begin{array}{l} ArC{\equiv}CHgCl + Hg \overset{\text{fast}}{\rightleftharpoons} ArC{\equiv}CHgHgCl \xrightarrow{2e} \\ \qquad\qquad\qquad\qquad \Downarrow \\ \frac{1}{2}[ArC{\equiv}C)_2Hg + Hg] \overset{\text{fast}}{\rightleftharpoons} \frac{1}{2}(ArC{\equiv}C)_2Hg_2 \xrightarrow{e} \\ \longrightarrow ArC{\equiv}C^- + 2\,Hg + Cl^- . \end{array} \qquad (6)$$

Feoktistov and co-workers[65] used the method of hidden limiting currents and observed that 2-chloromercurio-3,3,3-trifluoropropyl acetate was reduced (similarly to vicinal dihalo alkyls[70, 71]) throughout the pH range in a single two-electron step by the mechanism of conjugated demercuration, *i.e.*, with elimination of alkene

$$\begin{array}{l} CF_3CH(HgCl)CH_2OAc + 2e \longrightarrow \\ \longrightarrow CF_3CH{=}CH_2 + Hg + Cl^- + OAc^- . \end{array} \qquad (7)$$

For other derivatives of this type, ER proceeded by this scheme only at pH $\ll$ 7 (for example, for mercurates — the addition products of $Hg(OAc)_2$ to alkenes).[36] Tomilov *et al.*[61, 62] observed pH-dependent changes in the ER mechanism of mercurioethanol salts. At pH > 7, two one-electron steps were observed and EtOH was the main electrolysis product, whereas at pH $\leqslant$ 5 the polarization curves demonstrated a single wave corresponding to the two-electron step; ethylene was produced in virtually quantitative yield. A similar two-electron wave appeared in solutions of *N*-diethylaminoethylmercury hydrochloride at pH 5 – 14.[62]

$$\begin{array}{l} R_2NCH_2CH_2Hg^+ + 2e \longrightarrow R_2NCH_2CH_2Hg^- \longrightarrow \\ \longrightarrow R_2NCH_2CH_2^- + Hg. \end{array} \qquad (8)$$

One two-electron wave was also observed in solutions of $(CF_3)_2CFHgX$ (Ref. 57) and cyclo-$C_6H_{12}HgCl$,[109] whereas the multistep ER mechanism was observed for other alicyclic OMC (cyclo-C_5H_9HgBr, cyclo-$C_7H_{13}HgBr$, *etc.*). It is

† According to certain data,[113] the $ArC{\equiv}CHgX$ salts synthesized in aqueous solutions directly in the electrochemical cell were reduced according to the Benesch mechanism.

known [109] that bis(cyclohexyl)mercury is very unstable and completely decomposes after isolation from the reaction mixture.‡ Probably, with addition of the first electron to cyclo-$C_6H_{11}HgCl$, the $RHg^{\bullet}$ radical loses its mercury atom and, at the same potential, $R^{\bullet}$ accepts the second electron. For certain carboranylmercury halides, the one-electron ER steps merged into a single step [63, 106] (probably due to the high electron affinity of the carboranyl group). Voltammetry of mercurated polyuridine derivatives Poly(U−Hg)X (Ref. 105) with the high degree of mercuration also revealed a single peak of two-electron reduction, if the time of preliminary potentiostatic stage was short. Voltammograms of 'weakly mercurated' derivatives had the conventional shape with two one-electron peaks at $E_p = -0.44$ and -0.89 V (E_p is the peak potential) as for mercurated uridine nucleotides.[104] No explanation of these differences was given.[105] However, such examples are scarce and in the majority of cases the Benesch mechanism was realized.

Attention was drawn [109] to a certain similarity between mechanisms of RHgX electroreduction and H_3O^+ discharge [the latter also afforded a dimeric product (H_2)]. For RHgX, this corresponds to the recombination process

$$2\,RHgX + 2e \overset{-2X^-}{\rightleftharpoons} 2\,RHg^{\bullet} \longrightarrow R_2Hg_2 \rightleftharpoons R_2Hg + Hg, \qquad (9)$$

mainly typical of compounds for which the irreversibility of the $RHg^{\bullet}$ dimerization at ER was proved (see above).

If the RHgX reduction rate (current) was higher than the rate of transition of R_2Hg to R_2Hg_2 but considerably lower than the rate of the reverse reaction, the recombination mechanism can be represented by a scheme

$$2\,RHgX + 2e \overset{-2X^-}{\rightleftharpoons} RHgHgR \longrightarrow R_2Hg + Hg. \qquad (10)$$

However, because this condition was not fulfilled for AlkHgX [according to Ref. 112, in Eqn (5) the ratio $k'_1/k'_{-1} \leqslant 10$], it was concluded [109] that this mechanism was valid only in the electroreduction of ArHgX. For AlkHgX, the reaction (10) with the reversible or, more likely, quasi-reversible dimerization of $RHg^{\bullet}$ [like reaction (5a)] [78, 79] with a sufficiently low equilibrium constant ($k'_1/k'_{-1} \gg k_1/k_{-1}$) was assumed to be more probable. [109] Nonetheless, as was shown above, this route is unlikely for many AlkHgX compounds and the electrochemical desorption

$$RHgX + e \overset{-X^-}{\rightleftharpoons} RHg^{\bullet} \xrightarrow{RHgX,\,e} R_2Hg_2 \rightleftharpoons R_2Hg + Hg, \qquad (11)$$

typical of the H_3O^+ discharge seems to be more realistic.

In addition to dimerization, the reaction of $RHg^{\bullet}$ with the solvent was possible, which should reduce the yield of R_2Hg_2. This way of the $RHg^{\bullet}$ loss accompanied the ER of carboxyethylmercury bromide and certain AlkHgX derivatives (Alk = Me, Et, Pr, Bu, n-C_5H_{11}, cyclo-C_5H_9).[109, 110, 123] With the increase in the electrode potential, the intermediate adsorption passed through a maximum in the ascending part of the first wave. This pointed to the product–depolarizer interaction.

The hydrogen overpotential theory [149] considers the 'hydride' mechanism according to which the RHgX electroreduction proceeds by reactions

$$RHgX + 2e \rightleftharpoons RHg^- \xrightarrow{-X^-} \begin{cases} \xrightarrow{RHg^+} RHgHgR \\ Hg + R^- \end{cases} \begin{cases} \xrightarrow{RHg^+} R_2Hg \\ \xrightarrow{BH^+} RH + B. \end{cases} \qquad (12)$$

This mechanism proved to be more probable for the ER of cyclohexylmercury chloride,[109] $ArC\equiv CHgX$ (Ref. 64) and other compound reducible in a single one-electron step.

In aqueous and non-aqueous media, symmetrical compounds R_2Hg were reduced in a single irreversible two-electron step according to the following equations:[64, 67]

$$R_2Hg + 2e + 2H^+ \longrightarrow 2\,RH + Hg\ (pH < 7), \qquad (13)$$

$$R_2Hg + 2e + 2H_2O \longrightarrow 2\,RH + Hg + 2OH^-\ (pH \geqslant 7). \qquad (14)$$

The transfer of the first proton probably followed the transfer of the first electron, because the addition of H_2O did not change the shape and the position of the reduction wave of Bn_2Hg in MeCN.[93]

Depending on the nature of substituent, the R_2Hg electroreduction may be reversible [$Hg(CN)_2$,[67, 72] $(CBr_3)_2Hg$ (Ref. 77)], quasi-reversible [di(α-carboxyethylbenzyl)mercury [67]], or, as for the majority of compounds studied so far, irreversible.[15, 67, 130] In the latter case, the ER potential varied in a sufficiently wide interval, which was first of all associated with the polarity of the C−Hg bond. The most positive potential corresponded to the reversible or quasi-reversible reduction of $Hg(CN)_2$ and α-oxoorganomercury compounds with a strongly polarized C−Hg bond (for these derivatives, carbanions R^- proved to be sufficiently stable [130]); the most negative potential corresponded to covalent compounds Alk_2Hg and Ar_2Hg.[67] The interrelation between the polarity of the C−Hg bond and the rate of R_2Hg electroreduction can be easily followed by the example of compounds of the same kind. According to the results of the above study, [67] in the series of Ph_2Hg and the corresponding halo-substituted derivatives (60% DMF−H_2O, 0.1 mol litre^{-1} Et_4NClO_4),§ the values of $-E_{1/2}$ (presented in parentheses, V *vs.* SCE) decreased synchronously as follows: Ph_2Hg (2.2) > $(C_6Cl_5)_2Hg$ (1.69) > $(C_6F_5)_2Hg$ (0.86), while αn_a cover the range from 0.6 to 0.8. The equality (or closeness) of αn_a in the series of R_2Hg derivatives (R is a substituted benzyl) implies [67] that the differences in the $E_{1/2}$ values under the condition that E^0 is independent of the nature of R were caused only by the changes in the rate constant for the R_2Hg electroreduction. This explains the adequate correlation between $E_{1/2}$ and the Hammett constants (σ) for $(XC_6H_4CH_2)_2Hg$ (X = Br, F, H, Me in different positions). Sometimes, such differences were very big. For example, for bis(β-cyanoethyl)mercury $E_{1/2} = -2.33$ V (H_2O, 0.15 mol litre^{-1} Et_4NClO_4),[1, 116] but for bis(cyanomethyl)mercury $E_{1/2} = -0.62$ V (MeCN, 0.05 mol litre^{-1} Bu_4NBF_4).[130]

Many authors tried to elucidate whether both electrons were transferred simultaneously in the R_2Hg electroreduction or only one electron was involved in the potential-determining step and the transfer rate of the second electron considerably exceeded the rate of the first step (for instance, as in the ER of certain alkyl and aryl halides [71, 150, 151]). The majority of scientists lean to the latter assumption; however,

‡ Later, its was shown [1] that the formation of this compound involves the formation of a labile intermediate $[(CH_2)_6Hg]_2$ with ring structure.

§ Throughout the present review, in describing the experimental conditions, first, the solvent composition is shown, which is followed by the supporting electrolyte composition and concentration; all potentials are expressed in Volts with respect to the saturated calomel electrode (SCE).

the polarographic method in applicable for studying fast reactions provided no answer to this question. On the other hand, even using the fast-scan pulse galvanostatic method (with the current densities up to $i \leqslant 10^4$ mA cm^{-2}), Ershler and co-workers [114] failed to observe consecutive electron transfer in the electroreduction of $(C_6F_5)_2Hg$ in the $H_2O-MeOH$ (10%) mixture. Thus, a direct proof of the consecutive nature of the OMC electroreduction requires that other methods should be invoked. Indeed, spectrophotometric studies of the pulse radiolysis products of Bn_2Hg and its fluoro derivatives [152] in THF pointed to the transient formation of quickly protonated R^- carbanions and $RHg^{\bullet}$ radicals (lifetimes <0.002 and $\sim 20-50$ ms, respectively) in reactions such as

$$R_2Hg + e \longrightarrow [R_2Hg]^{-\bullet} \longrightarrow RHg^{\bullet} + R^- . \qquad (15)$$

Radicals were lost in a second-order reaction.[152] Bregadze and co-workers [153] observed the one-electron reduction of R_2Hg (R = Ph, Bn, $PhC_2B_{10}H_{10}$) at -30 °C under the action of lithium dihydronaphthalide in THF.

It is typical that ER of non-symmetrical derivatives R′HgR usually proceeds in two one-electron steps. Dessy *et al.*[57] identified Ph_2Hg as an electroreduction product of $PhHgCCl_3$. Insofar as Ph_2Hg was reduced with considerably higher difficulty as compared with $Hg(CCl_3)_2$, the following reaction scheme was put forward:[57]

$$CCl_3HgPh + e \longrightarrow PhHg^{\bullet} + CCl_3^- \xrightarrow{BH^+} CHCl_3 + B \qquad (16)$$
$$\downarrow$$
$$\frac{1}{2}Ph_2Hg + \frac{1}{2}Hg.$$

Examples of this kind are few because many R′HgR compounds are unstable and decompose even at room temperature to R_2Hg and R'_2Hg. However, if R′ is carboranyl, these compounds do not disproportionate even in melts and are also reduced in two steps.[68] For example, the first step of $RC_2B_{10}H_{10}HgMe$ (R = Alk or H) electroreduction afforded the $MeHg^{\bullet}$ radical and the reduction potential of the latter in the second step adequately corresponded to $E^{(2)}_{1/2}$ of MeHgCl reduction, which confirmed the proposed mechanism. However, according to other data, [111] the two-electron reduction of R′HgR was also possible, for example, for $PhHgC_6F_5$.

The susceptibility of the R−Hg and R′−Hg bonds to reduction was compared in polarographic studies of the exchange reactions of R_2Hg (R = Ph, CN, CCl_3, C≡CPh, Bn, CFClCOOEt, CF_2COOEt, CH_2COOMe) compounds in DMF (0.1 mol litre^{-1} Bu_4NClO_4).[26]

$$R^1HgR^2 + R^3HgR^4 \rightleftharpoons R^1HgR^3 + R^2HgR^4 \qquad (17)$$
$$(\text{or } R^1HgR^4 + R^2HgR^3).$$

Particularly, it was shown that the exchange rate with diphenylmercury varied in the series

$$Hg(CN)_2 > Hg(CCl_3)_2 > Hg(C\equiv CPh)_2 >$$
$$> Bn_2Hg, Hg(CFClCOOEt)_2 >$$
$$> Hg(CF_2COOEt)_2, Hg(CH_2COOMe)_2;$$

moreover, no exchange was observed for the last three compounds. The authors concluded that the wider the difference in the nucleophilicity of radicals of a non-symmetrical derivative ($PhHgR'$) the higher the rate of its formation.

The electrochemical behaviour of $[R_2Hg \cdot L]$ complexes is still unclear because they are much more labile than $[RHg^+ \cdot L]$.[14] The trend of OMC towards coordination with different ligands increased in the series [154]

$$PhHgX \ll (C_6F_5)_2Hg < Hg(CN)_2 < Hg(CCl_3)_2 <$$
$$< Hg(CNS)_2 < HgX_2.$$

Complexation dramatically changed the electrochemical characteristics of OMC hindering the electroreduction and favouring the electrooxidation of R_2Hg.[75, 76] Thus bis(phenylcarboranyl)- and bis(vinylcarboranyl)mercury were not oxidized on a Pt electrode in anhydrous MeCN, but their complexes with Bipy and Py were oxidized quite easily.[75] For the ER, the opposite was true, namely, bis(carboranyl)-mercury derivatives were easily reducible,[63] whereas their complexes with Bipy proved to be electrochemically inactive.[75, 76]

Although the attempts of scientists to observe OMC solvation using different methods including electrochemical failed,[76] it deserves mentioning that for the majority of dialkyl- and diarylmercury compounds, $E_{1/2}$ values in DMF and DMSO were close but strongly differed from those in Py, MeOH and $H_2O-MeOH$ mixtures. The ability of solvents to solvate R_2Hg decreased in the series [67]

$$Py > DMSO > DMF > MeOH > H_2O.$$

The similar results were obtained for R_2Hg compounds with strongly polar groups, *e.g.*, bis(phenyl-*o*-carboranyl)-mercury and bis(methyl-*o*-carboranyl)mercury.[67, 75, 76]

Complexes $[R_2Hg \cdot L]$, where L is an inorganic anion, were less stable than those with organic ligands. As a rule, they could not be isolated; hence, only few publications dealt with the electrochemical behaviour of such complexes. Thus complexation of dicyanomercury (which, by the way, is often classified with inorganic mercury compounds) was studied by polarographic, chronopotentiometric and potentiometric methods in a classic work.[72] Insofar as the electronegativity of CN groups was sufficiently high and the C−Hg−C fragment was non-linear,[154] the strong trend of $Hg(CN)_2$ to coordination is not surprising. For the $Hg(CN)_3^-$ complex, $\log K_1$ was ~ 38.1, and $Hg(CN)_4^{2-}$ appeared in the alkaline medium (pH $\geqslant 9.5$) immediately on the electrode ($\log K_1 \approx 40.6$) or in the solution bulk in the presence of excess of cyanide ($\log K_1 \sim 40.1$); chlorides formed weak complexes such as $[Hg(CN)_2]Cl^-$ ($K_1 = 0.58 \pm 0.05$) and $[Hg(CN)_2]Cl_2^{2-}$ (Ref. 72).

The pulse galvanostatic method was used [119–122] in studying the formation of complexes of perfluorodiphenylmercury; the latter was obtained from pentafluorophenylmercuric bromide directly in the electrochemical cell. The condensed phase of this compound [120, 122] was reduced in one, two or several delays depending on the experimental conditions (Fig. 4). Based on the dependences of the potentials of first two delays of the perfluorodiphenylmercury ER on the supporting electrolyte concentration the charges of species that reacted in the first and the second delays, namely, z_1 and z_2, were determined [119, 121] as in Refs 155 and 156.

For a species reacting in the first delay, $z_1 \approx 0$, but in the second delay, in the majority of cases, a negatively charged species was reduced with the charge (z_2) dependent on the nature of the supporting electrolyte, first of all, on its anion.

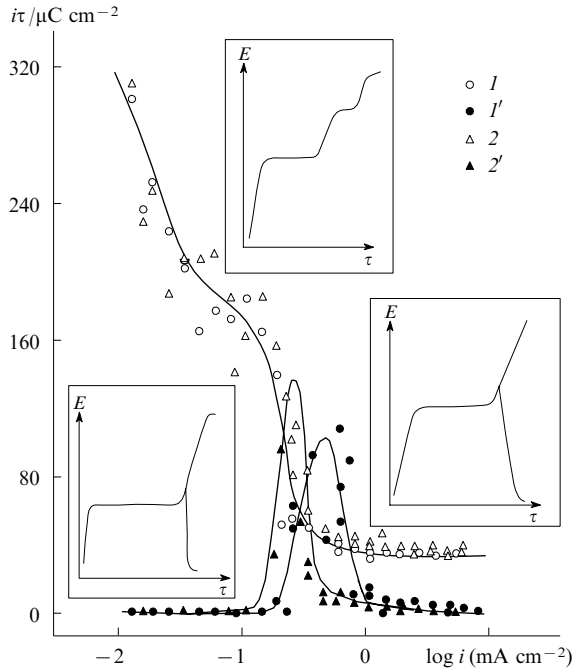


Figure 4. The lengths of the first (*1*, *2*) and the second (*1′*, *2′*) delays of the reduction of perfluorodiphenylmercury synthesized by microelectrolysis of 5×10^{-5} mol litre^{-1} pentafluorophenylmercuric bromide as a function of current density for $t_p = 2$ min.[119]
NaCl solutions in aqueous ethanol (10 vol.% EtOH) served as the supporting electrolytes. [NaCl] /mol litre^{-1}: (*1*, *1′*) 0.9; (*2*, *2′*) 0.09.

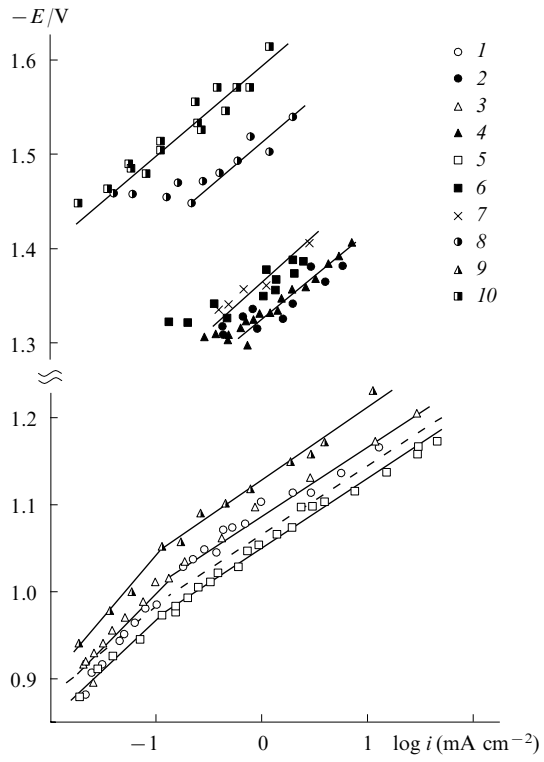


Figure 5. The Tafel plots describing electroreduction of perfluorodiphenylmercury synthesized by microelectrolysis of 5×10^{-5} mol litre^{-1} pentafluorophenylmercuric bromide.[119]
NaOAc solutions in aqueous ethanol (10 vol.% EtOH) served as the supporting electrolytes. [NaOAc] /mol litre^{-1}: (*1*–*4*) 2.7; (*5*–*7*) 0.9; (*8*) 0.09; (*9*) and (*10*) 0.009; (*1*, *3*, *5*, *9*) for the first delay; (*2*, *4*, *6*, *8*, *10*) for the second delay; dashed curve, for chemically synthesized perfluorodiphenylmercury.

This implies that the anion could enter into the composition of the reaction complex. Note that the different nature of species reacting in delays *1* and *2* follows from the considerable differences in both their potentials E_1 and E_2 and the values $(\alpha n_a)_1$ and $(\alpha n_a)_2$ (Fig. 5).[119] It is believed [119–121] that it was a complex of perfluorodiphenylmercury that was reduced in the second delay. One of its ligands was the supporting anion if $z_2 < 0$, as for instance in solutions of NaOAc ($z_2 \approx -0.7$) or NaCl ($z_2 \approx -0.4$); however, with Na_2SO_4 as the supporting electrolyte, $z_2 \approx 0$. Hence, it was concluded [119] that the AcO^- anion, in contrast to SO_4^{2-}, was the component of the reaction complex. The difference stems from the fact that the mercury atom in R_2Hg compounds is coordinatively unsaturated (its coordination number can reach 3, for example, in perfluorodiphenylmercury).[14] This is why such compounds were more susceptible to coordination with monodentate ligands, whereas the sulfate anion being a weaker coordination agent was a bidentate ligand.

Big differences between the Tafel plots measured with Na salts as supporting electrolytes, on the one hand, and Cs, K, and Et_4N salts, on the other hand, were revealed.[119] These differences were apparently associated with the changes in the surface properties of perfluorodiphenylmercury formed on the electrode as a result of specific adsorption of cations of these salts, *i.e.*, with the double layer effects.[155] The rate of electroreduction at E_1 increased in the series

$$Na^+ < K^+ < Cs^+ < Et_4N^+.$$

This effect typical of the irreversible ER of, *e.g.*, anions and alkyl halides,[157] is usually associated with the decrease in the Ψ' potential in this series as a result of specific adsorption of cations. The reaction corresponding to the second delay accelerated in the presence of specifically adsorbed cations as compared with the ER against the background of sodium salts to the greater extent than the reaction corresponding to the first delay under analogous conditions. According to these data, the transition state was localized in the vicinity of the adsorbed ion (Cs^+, K^+, Et_4N^+) and the ER of depolarizer proceeded *via* cationic bridges ('cationic catalysis' [157, 158]) or ion pairs $\{M^+ - [R_2HgX]^-\}$. The uncharged species in Na_2SO_4 solutions were treated [119, 121] as complexes with the solvent (water or ethanol). In contrast to diarylmercury, its perfluorinated analogues are stronger Lewis acids, they form adducts with different organic and inorganic bases much easier.[11, 159]

Using the Brdiczka–Wiesner model of the kinetic layer,[160] the limiting kinetic current i_k, which characterizes the stability of complexes, was assessed.[119] It was concluded that the acetate and chloride ions formed the most stable complexes with perfluorodiphenylmercury [$i_k \approx (0.05-0.15)$ mA cm^{-2}], while the sulfate and carbonate ions in solutions of caesium salts formed the most labile complexes [$i_k \approx (0.1-0.5)$ mA cm^{-2}]. The formation of a labile complex $\{[(C_6F_5)_2Hg]BH_4\}^-$ ($K_1 = 10^2$ litre mol^{-1}) in THF was observed [161] by IR spectroscopy.

A somewhat different coordination mechanism was proposed in the studies of the ER of bis(arylchalcogeno)-mercurials $(ArE)_2Hg$ (E = Se, Te) on a mercury electrode,

according to which in the first step these compounds are reduced by the two-electron mechanism, the liberated carbanion ArE^- is coordinated to $(ArE)_2Hg$ to form a triangular complex $(ArE)_3Hg^-$ and the latter is reduced at more negative (with respect to the uncoordinated form) potentials as compared with $(ArE)_2Hg$.[100, 102]

Salts of other organometallic compounds, for example, R_3SnX and R_2SnX_2 [X = Cl, Br, I; coordination number of Sn was 5 or 6 (Ref. 19)] also formed complexes with the halide ions and the solvent during the electroreduction in DMF and DMSO.[3, 162] The first chloride ion was abstracted from R_3SnCl_2 (R = Alk) in DMF at $E \approx -1$ V and from $[R_2SnCl_3]^-$ complex, at $E \approx -2$ V, whereas the complex anion $[R_2SnCl_4]^{2-}$ was inactive.[162] In the general case, the formation of heteroligand complexes, *i.e.*, with the solvent and the Cl^- ion is possible; therefore, the overall kinetic current should be determined by the competition for the position in the coordination sphere. The formation of such heteroligand complexes was also hypothesized in the case of perfluorodiphenylmercury.[119, 120]

Scheme 1 was proposed to describe the mechanism of OMC electroreduction at a mercury electrode in the general form.[121]

However, even this generalized scheme does not reflect to the full extent the details of the ER mechanism for different OMC. In particular, it does not consider the effects of the adsorption of components of the electrochemical system and also of heterogeneous equilibria such as (6) in Scheme 1 on the surface and in the bulk solution.

III. Intermediates of one-electron reduction of RHgX salts and properties of heterogeneous chemical equilibrium $R_2Hg + Hg \rightleftarrows [RHg_{ads}]_n$

Compounds with the general composition R_2Hg were obtained in the electrolysis of RHgX salts at the plateau potential of their first reduction step.[52, 57–63, 138–140] Such a method of R_2Hg synthesis was discovered and patented back in the 1920s.[1, 2, 71] According to the proposed[52] scheme, the $RHg^{\bullet}$ radical formed in the first reduction step either was reduced at more negative potentials or disproportionated to R_2Hg *via* transient metastable 'organic calomel'.

$$RHg^{\bullet}_{ads} \xrightarrow{RHg^{\bullet}} [RHgHgR] = R_2Hg + Hg \quad (18a)$$

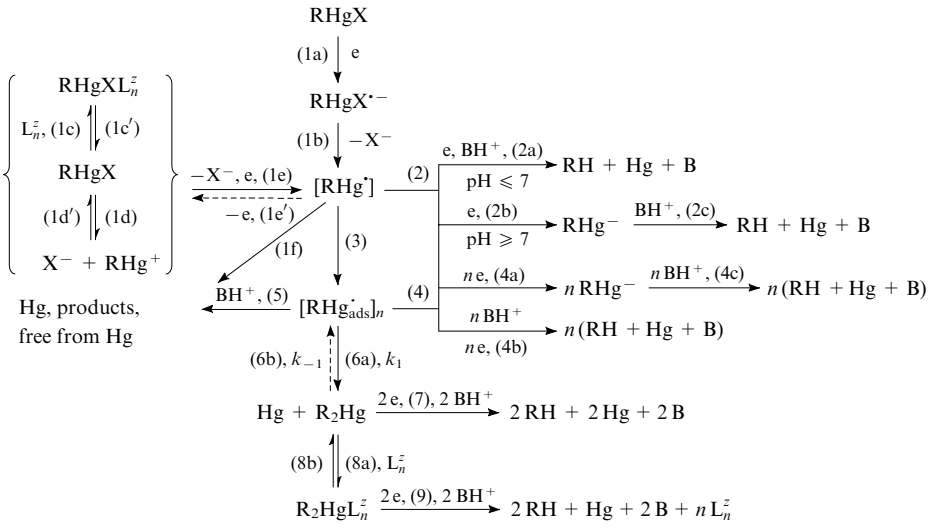
$$RHg^{\bullet}_{ads} \longrightarrow RHg^{\bullet}_{solv} \longrightarrow R^{\bullet}_{solv} + Hg \quad (18b)$$

If R_2Hg compounds formed under these conditions were electroactive, the polarization curve of electroreduction of RHgX (for example, benzylmercury halides[93, 163] or alkenylmercury[35]) demonstrated three waves. If the rate of a dismutation reaction such as (18a) was sufficiently high and R_2Hg was electrochemically more active than R_2Hg_2, the second wave corresponded to the reduction of the overall compound and the third wave corresponded to the reduction of 'organic calomel'. Such an ER mechanism was proposed for α-(bromomercurio)phenylacetic acid and its derivatives,[1, 67] n-$C_6F_{13}HgI$ (see Ref. 89) and some other compounds. As a rule, electrochemically inactive R_2Hg compounds exhibited high surface activity; at the potentials of their cathodic and anodic adsorption–desorption in polarization curves (voltammograms, chronopotentiograms), the capacitance signals were observed (see Fig. 2).

Another way of $RHg^{\bullet}$ stabilization, *i.e.*, demercuration [see reaction (18b)], was more typical of the loss of radicals in the bulk, in analogy with homolytic photo- and thermodecomposition of OMC.[19] Indeed, for $RHg^{\bullet}$, the dissociation energy $D(R-Hg)$ was lower than the mercury vaporization heat (59.1 kJ mol^{-1}) (Ref. 145) and amounted to 28 kJ mol^{-1} for $MeHg^{\bullet}$, $EtHg^{\bullet}$ and other alkylmercury radicals;[145–148] hence, this version of stabilization is correct. However, the preferableness of step (18a) more probably stemmed from the abundant evidence obtained by electrolysis at controlled potential: at the first-wave limiting current, it was R_2Hg (Refs 1 and 2) that was obtained in quantitative amounts rather than the dimer R–R. The latter was identified only occasionally and in trace amounts.[60, 93]

Reaction (18b) becomes noticeable when the radical $RHg^{\bullet}$ formed is unstable. Thus in the electroreduction of $PhHgCCl_3$ [see reaction (16)], colloidal mercury appeared even at moderate negative potentials, which was explained[57] by the decomposition of $RHg^{\bullet}$ coupled with charge transfer. Such partial decomposition of an organomercury intermediate was also typical of mercurates,[2] for instance, at potentials of the first ER step, the

Scheme 1



$HOCH_2CH_2Hg^{\bullet}$ radical could decompose to bis(β-hydroxyethyl)mercury [61, 62]

$$HOCH_2CH_2Hg^{\bullet} \xrightarrow{HOCH_2CH_2Hg^{\bullet}} (HOCH_2CH_2)_2 + Hg \quad (19a)$$

$$HOCH_2CH_2Hg^{\bullet} \longrightarrow HgOH + C_2H_4\,. \quad (19b)$$

Under these conditions, the $R_2NCH_2CH_2Hg^{\bullet}$ radical partially dimerized and simultaneously reacted with the solvent [58] to afford hydride RHgH, which also decomposed to evolve ethylene

$$R_2NCH_2CH_2Hg^{\bullet} \xrightarrow{R_2NCH_2CH_2Hg^{\bullet}} (R_2NCH_2CH_2)_2Hg + Hg \quad (20a)$$

$$R_2NCH_2CH_2Hg^{\bullet} \longrightarrow R_2NCH_2CH_2HgH \xrightarrow[-Hg]{} R_2NH + C_2H_4\,. \quad (20b)$$

Instability of such derivatives is well known,[164] namely, the rate constant for the reaction

$$RHgH \longrightarrow RH + Hg \quad (20c)$$

was from 0.02 (R = Me, Et) to 0.05 min^{-1} (R = Ph) and still higher in acidic media.[164] Obviously, this kind of reactions should compete, first of all, with steps (5) in Scheme 1, thus lowering the yield of R_2Hg.

Electrolysis of *sec*-BuHgBr afforded racemic di(*sec*-butyl)mercury.[57] Later, analogous data have appeared for other optically active derivatives of alkyl- (Ref. 96) and phenylalkylmercury.[165] The loss of optical activity was explained [57] by the radical exchange RHg···R···Hg. The one-electron reduction of PhHg*Br (Hg* is the ^{203}Hg radioactive marker) led to the formation of Ph_2Hg with the active isotope content $< 10\%$; at open circuit, no exchange was observed. This pointed to the possibility of direct exchange $RHg^{\bullet}$ – cathode in the course of electrolysis, where the reaction could proceed 'from either side' of the mercury atom in the radical (escape of the R group 'from the cage'). For example, in the ER of stereoisomeric β-chlorovinylmercuric halides,[59] the configuration of chlorovinyl groups remained unchanged. However, the latter does not rule out the possibility of exchange of the mercury atom in $RHg^{\bullet}$ with the cathode, because stereoisomeric vinyl halides were reduced to form a configurationally stable carbanion that is inverted extremely slowly.[4]

Butin and co-workers [38, 142] and other authors [83–86] have shown that on Pt (Refs 131, 132), Au, PbO_2 and GC electrodes (GC is glassy carbon),[106, 107] the RHgX salts were reduced in a single irreversible two-electron step with $E_{1/2}$ more negative than $E_{1/2}^{(1)}$ at a mercury electrode (for example, by ~ 0.7 V for MeHgCl on Pt/Hg, and also for PhHgBr, see Fig. 1). The second scan demonstrated curves almost the same as at a mercury electrode.¶ This provided grounds to conclude [107] that after the electroreduction of RHgX, mercury was deposited on platinum and other cathodes and the OMC molecules were adsorbed (more likely, chemisorbed) on this mercury layer. Then, a Hg atom was incorporated into the RHgX molecule (probably, in the same manner as in the isotopic exchange, see below) to afford non-symmetrical 'organic calomels' RHgHgX, *i.e.*, mercury promoted the RHgX electroreduction.

$$(RHgX)_{solv} \rightleftharpoons (RHgX)_{ads}\,, \quad (21)$$

$$(RHgX)_{ads} + Hg \overset{fast}{\rightleftharpoons} (RHgHgX)_{ads}\,, \quad (22)$$

$$(RHgHgX)_{ads} + e \rightleftharpoons \quad (23)$$

$$\rightleftharpoons (RHg^{\bullet}) + Hg\,[\text{or } (RHgHg^{\bullet})_{ads}] + X^-.$$

Presumably,[107] in the key step of RHgX electroreduction on mercury, non-symmetrical 'organic calomels' formed as a result of RHgX chemisorption at a mercury electrode surface and thus could be reduced [see reaction (23)] more easily than the original organomercury salt. This mechanism (below called the Butin mechanism) should be considered as fairly general. It was shown [106] that not only the C–Hg bond but also the B–Hg bond was reduced in this manner on solid electrodes. However, the voltammetric signals on such electrodes were much less pronounced as compared with the mercury electrode. Particularly, for a 'pure' microelectrode (~ 11 μm in diameter) fabricated from a carbon wire, virtually no signals were observed in monomethylmercury solutions.[85]

Naturally, the mechanism of transformations of the $RHg^{\bullet}$ radical should depend on its stability. The one-electron reduction of RHgOAc (R = Ph, Bn, n-C_6H_{13}) in the presence of CCl_4 was studied.[166] Whereas Ph- and n-C_6H_{13}HgOAc resulted mainly in RHgCl upon electroreduction at the potential of the first step, BnHgOAc afforded Bn_2Hg. Hence, disproportionation of the $BnHg^{\bullet}$ radicals was faster than their reaction with CCl_4, whereas $PhHg^{\bullet}$ demonstrated the opposite trend. Therefore, the stability of $PhHg^{\bullet}$ radicals (especially, $AlkHg^{\bullet}$) was higher than that of $BnHg^{\bullet}$. Reutov and co-workers [38, 39, 47] have shown that easily reducible and oxidizable RHgX salts form stable radicals $R^{\bullet}$ and easily undergo thermal decomposition [see reaction (18b)] with cleavage of the R–Hg bond. Moreover, the shorter the 'polarographic window' for these compounds [the difference between $E_{1/2}$ values for electrooxidation and electroreduction of RHgX (Ref. 47)] the easier their dissociation to $R^{\bullet}$ and $Hg^{\bullet}X$.

In this context, attention should be drawn to a pioneering treatise by Kraus [167] published in 1913 when the mechanism of OMC electroreduction was not even discussed. In the electrolysis of alkylmercuric halides in liquid ammonia at −70 °C, he observed the cathodic deposition of a black substance with metallic lustre that, as was demonstrated in the late 1950s,[168] exhibited no properties typical of free-radical species, for example, induced no EPR signals † and also had the crystal structure and conducted electric current. Presumably,[167–169] this solid phase represented an 'organometal'. Numeral attempts at determining its molecular mass and chemical composition failed, because this phase decomposed to R_2Hg and metallic mercury on heating to −(10–15) °C (R = Me) or to 0 to −5 °C (R = Et, Pr). The partial (R = Ph) or complete (R = Bn) decomposition started at the temperature of about −70 °C, which is qualitatively consistent with the conclusions of another study [166] on the lower stability of $BnHg^{\bullet}$ and $PhHg^{\bullet}$ as compared with $AlkHg^{\bullet}$.

¶ This is why, numerous assumptions on the identity of the electroreduction mechanism of RHgX at mercury and other electrodes (for example, at Pt) [36, 79] were probably explained by the fact that the measurements were carried out on the surface already partially covered with mercury.

† According to certain data,[127] adsorbed $AlkHg^{\bullet}$ radicals induced no EPR signals due to the fast spin exchange with the cathode mercury rather than due to their short lifetime.

In one of the studies cited,[169] as in other investigations,[57] the complete loss of optical activity was observed in the electrolysis of *sec*-BuHgBr. It was assumed [169] that the 'organometal' had the crystal lattice of mercury in which all of the C···Hg···C bonds were equivalent ‡ and the unpaired electron was delocalized in the conduction band. Naturally, the lattice stability weakened with the increase in temperature and depended on the nature of R. For example, the n-alkyl 'organometal' was more stable than the isoalkyl counterpart, which was probably caused by steric factors, because these isomers had similar C—Hg bond energies.[145]

Of special interest were the high-molecular derivatives of alkylmercury. It is known that the stability of $RHg^{\bullet}$ free radicals increases in parallel with chain elongation (for the corresponding radicals $R^{\bullet}$, the stability, conversely, decreases). A yellow precipitate formed in the one-electron reduction of *cis*-2-chloromercurio-3-ethoxycyclononene and -decene, and also of *trans*-2-chloromercurio-3-methoxycycloundecene and -tridecene at liquid nitrogen temperature;[56] moreover, as the temperature increased to room temperature, the colouring disappeared not immediately but in the course of several minutes. This precipitate gave an EPR signal (albeit poorly pronounced), which presumably pointed to its free-radical nature.

Using the high scan rate pulse galvanostatic method, the ER mechanism was studied for a series of RHgX and R_2Hg compounds.[109–125] Note that the behaviour of AlkHgX (see Fig. 2) and Alk_2Hg in the course of a current pulse proved to be very similar (albeit the first delay was absent for Alk_2Hg solutions). Charging curves of Et_2Hg unexpectedly revealed a faradaic delay in addition to the adsorption–desorption delay at *ca.* −1 V.[109,110] The faradaic delay potential coincided with $E^{(2)}_{1/2}$ of EtHgBr and the parameters of the corresponding Tafel plots also turned out to be close.[110] Moreover, it is known [1,67] that many Alk_2Hg compounds either reduced by the two-electron mechanism at very high cathodic potentials or were altogether polarographically inactive. Thus diethylmercury could not be reduced on a Hg electrode up to −2.8 V.[127] Hence, the following two conclusions can be inferred:

— upon adsorption on mercury, Et_2Hg was transformed into an electroactive substance [EtHg] analogous to the product of the first step of the EtHgBr electroreduction;

— an equilibrium between [EtHg] and Et_2Hg was established on the electrode surface.

Later, [94] it was observed that the one-electron reduction of EtI and EtBr (H_2O : EtOH = 1 : 1), like the Et_2Hg adsorption, produced one and the same ([EtHg] in Ref. 110) short-lived mercury-containing species (designated [94] as Et_{ads}) capable of the further electroreduction or electrooxidation. In Ar_2Hg chronopotentiograms, only the signals corresponding to its ER or desorption were observed.[109–111]

According to certain data,[26,170] the isotope exchange proceeded *via* the free or crypto radical state

$$R-Hg-R' + Hg^* \longrightarrow RHg-Hg^*-R' \longrightarrow RHg^*R' + Hg. \quad (24)$$

The radical $RHg^{\bullet}$ (one of the possible intermediates formed in the homolysis) proved to be extremely unstable (its lifetime did not exceed 10^{-8} s) [171] and its loss mainly occurred through demercuration [see reaction (18b)]. Hence, the very presence of its individual signals in charging curves should imply that its lifetime on the electrode was much longer than under homolytic conditions. Naturally, the stabilization of $RHg^{\bullet}$ in the adsorption layer depended on the nature of R (and the metal M for R_nM).[170] For phenyl derivatives of different metals, the degree of exchange (in %) with metallic mercury decreased in the series:

$$Ph_2Hg\ (77) > Ph_2Cd\ (53) > Ph_2Mg\ (2.9) > Ph_2Zn\ (1.6) > > Ph_3Bi\ (0.8) > Ph_4Sn, Ph_4Pb\ (0.0),$$

i.e., in parallel with the increase in the dissociation energy $D(R-M)$. For Ph_4Sn and organolead derivatives, the important role was also played by steric hindrance. For this reason, *e.g.*, in the adsorption of Alk_4Pb at a mercury electrode, no $RHg^{\bullet}$ radicals were detected.[110–112]

Hence, either the mercury electrode surface stabilizes the $RHg^{\bullet}$ radicals or the [RHg] species are not the free radicals. The latter assumption was confirmed, besides other factors, by the Tafel plots of one-electron reduction of RHgX and the electrooxidation of reaction products. The species formed during the adsorption and electroreduction of $RHgR'$ derivatives at a mercury electrode were studied [110,111] as well as the compositions of mixtures of RHgX and R′HgX; R_2Hg and R'_2Hg ($R \neq R'$) (Fig. 6).

During the adsorption of $EtHgC_6F_5$, a signal of either the direct electroreduction of this compound (curve *1*) or the reduction preceded by a slow chemical step such as reaction (22) to afford the [$EtHgC_6F_5$] species (curve *2*) was observed. The signal corresponding to the [EtHg] electroreduction was also retained.

For the co-adsorption of Et_2Hg and $(C_6F_5)_2Hg$ on the electrode, both these compounds and [Et_2Hg_2] were present on the electrode (curve *3*). The same was observed when EtHgBr was substituted for Et_2Hg (curve *4*).

The one-electron reduction of EtHgBr and C_6F_5HgBr produced $(C_6F_5)_2Hg$, Et_2Hg, [EtHg], $EtHgC_6F_5$ and [$EtHgC_6F_5$] (curves *5–8*).

The [$EtHgC_6F_5$] species could be identified with neither [EtHg] nor [C_6F_5Hg] for which $E_{1/2} \approx -(1.4-1.6)$ [110] and −0.3 V (Ref. 118), respectively, nor perfluorodiphenylmercury, which is reduced separately from the rest of species and was characterized by an delay with the ER potential ~ 0.12 V more positive than the potential of [$EtHgC_6F_5$] reduction.[118] It was assumed [111] that the considered species contained both groups (Et and C_6F_5), *i.e.*, the $EtHg^{\bullet}$ and $C_6F_5Hg^{\bullet}$, so that the $EtHg^{\bullet}$ and $C_6F_5Hg^{\bullet}$ radicals after their appearance recombined to form intermediates such as $EtHgHgC_6F_5$ ('organic calomel'). Presumably,[111] Alk_2Hg at a mercury electrode was also in equilibrium with the corresponding 'organic calomels'. The second wave in the polarograms of RHgX (in any case, its beginning, where the ER rate is still very low) was also associated with the electroreduction of R_2Hg_2 rather than of $RHg^{\bullet}$.

It is probable that the lifetimes of $RHg^{\bullet}$ (*e.g.*, see Refs 36, 54 and 60) characterize the stability of R_2Hg_2. Due to difficulties of its identification, 'organic calomel' long escaped detection, although organic chemists operated with this name for a long time. 'Organometal' is simply a one-electron reduction product of RHgX (see above), which is more stable than $RHg^{\bullet}$. Thus Casanova and Rogers [134] electrolyzed α,ω-dihaloalkanes $RHal_2$ [$R = (CH_2)_n$, $n = 4-7$, 12] and obtained products with the high mercury content and assumed them to have the R_2Hg_2 composition.

‡ Hence, the possibility of the RHg···Hg···RHg exchange follows from the very structure of the 'organometal'.

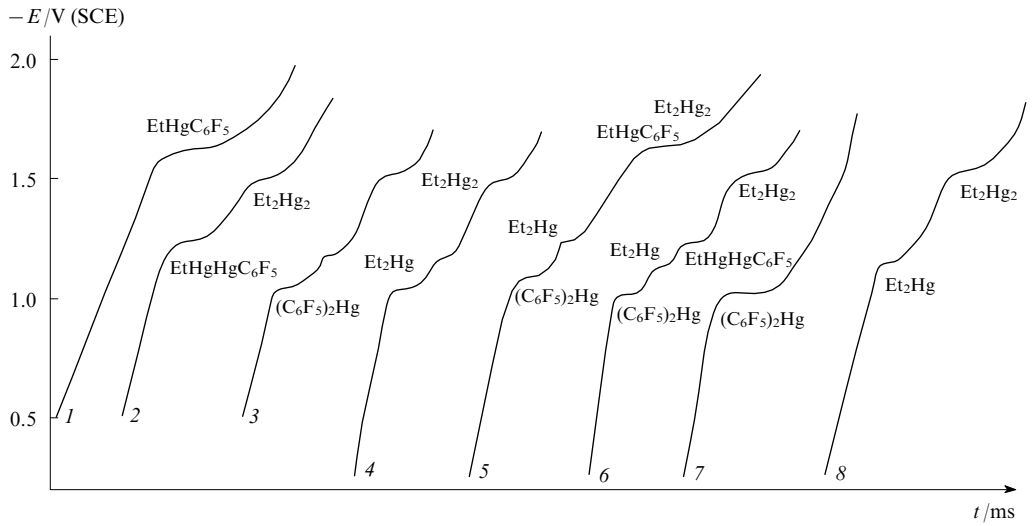


Figure 6. Chronopotentiograms of the mercury electrode in solutions of $EtHgC_6F_5$ (*1*, *2*), mixtures of $(C_6F_5)_2Hg$ and Et_2Hg (*3*), $(C_6F_5)_2Hg$ and EtHgCl (*4*), C_6F_5HgBr and EtHgCl (*5*, *6*) and also of C_6F_5HgBr (*7*), EtHgCl (*8*).[111]
KOAc solution in aqueous methanol (10 vol.% MeOH) served as the supporting electrolyte. (*1*, *5*) high, (*2*, *6*) low current densities.

However, using the methods of mass spectrometry and atomic absorption spectroscopy, it was shown[135] that, in certain cases, organomercury polymers such as $R-Hg-(RHg)_n-R$ could be formed. Bart and Peters[137] electrolyzed α,ω-diiododecane and isolated a polymer containing ~ 54% of mercury ($n \approx 5$). From their viewpoint, in this case, the monomer was the $^{\bullet}CH_2(CH_2)_9Hg^{\bullet}$ biradical. Its formation as the one-electron reduction product of CH_2I_2 was postulated by Feroci and Masragostino.[136]

Structures such as RMM′R (M = M′; M ≠ M′, where M and M′ are metals) were long known in chemistry of organometallic compounds.[26] Some of them (for example, certain Sn−Hg-[172] and Te−Te-organic compounds[99–102]) are very stable.

At the same time, it is known[160] that calomel, an inorganic derivative of 'univalent' mercury, at a mercury electrode surface is in equilibrium with mercuric chloride. Some publications reported on the synthesis and isolation of 'organic calomel' XHgHg(X′HgHg)R (where R = C═C═O; X′ = OAc; X = OAc, NO_3, ClO_4),[173] RHgHgX salts (R = 2- and 4-methylpyridyl; X = I, OAc).[18] The composition of products was inferred from their chemical properties, the elemental analysis and ^1H NMR and IR spectroscopic data. Unfortunately, attempts to grow crystals of a size sufficient for proving unambiguously the formation of RHgHgX by the X-ray diffraction method failed.[18]

Upon preparative electrolysis of acridine on a Hg cathode, diacridinyldimercury was isolated, which contained 52.9% Hg according to the data from X-ray fluorescence analysis.[174] The action of the Grignard reagent (BuMgCl) on an inorganic derivative of univalent mercury (Hg_2Cl_2) afforded a compound that was postulated to have the composition $(C_4H_9)_2Hg_2$; this succeeded to precipitate from solution.[175] These conclusions were drawn based on the results of gas chromatography in combination with mass and atomic emission spectrometry.

Insofar as in the above-mentioned cases, no $EtHgC_6F_5$ formed in the co-adsorption of Et_2Hg and $(C_6F_5)_2Hg$ (see Fig. 6, curves *3*, *4*), the dissociation of R_2Hg_2 to form $RHg^{\bullet}$ radicals is unlikely. Otherwise, the following cross-reaction could have occurred:

$$2\,Hg + (C_6F_5)_2Hg + Et_2Hg \rightleftharpoons \rightleftharpoons 2\,C_6F_5Hg^{\bullet} + 2\,EtHg^{\bullet} \rightleftharpoons 2\,C_6F_5HgHgEt. \quad (25)$$

At least for $(C_6F_5)_2Hg$ and Et_2Hg (or EtHgCl), the possibility of such dissociation (*e.g.*, see Refs 78 and 95) should not be claimed without special tests.

Taking into account the aforementioned, it can be assumed that organomercury intermediates that emerge in ER of different compounds substantially differ in their nature. In addition to 'organic calomel', the formation of other intermediates was inferred, namely, $RHgRX^-$ (Ref. 103), RHg_nR,[57,96] RHg_{ads},[60] $(RHg)_n$, $R(Hg)_n^{\bullet}$, 'adsorbed organomercury polymer'[60] or its anion,[104] RHgHgX,[107] $RHgHg^{\bullet}$ (Ref. 38), $RHgHg^+$, 'organomercury cluster',[131,138] $R_2Hg_3^{2+}$, $[R_2Hg_5Cl_2]^{2+}$ (Refs 176 and 177) and other polymercurides[104,178] and organic amalgams.[143,144,179] In any case, such intermediates could contain more than one mercury atom ($[R_mHg_{ads}]_n$ with, most probably, $n = m = 2$) and would undergo adsorption at a mercury electrode. Quantum chemical calculations suggest strong endothermicity of the process for $n > 2$.[42] Here, for the sake of simplicity, the designations $[RHg_{ads}]_n$ (or R_2Hg_2) and the term 'organic calomel' are used.

However, it should be borne in mind that 'organic calomel' as such could be formed by the following two different mechanisms, *i.e.*, with the involvement of either RHgX or R_2Hg. In the former mechanism, it forms as the result of dimerization of $RHg^{\bullet}$ radicals, the products of the first step of RHgX electroreduction (or of their reaction with RHgX, see Section II). In this case, no chemical reactions seem to occur with the mercury electrode. However, based on the results on the PhHg*Br electroreduction obtained with ^{203}Hg radioactive markers,[57] the data from electrochemical transmetallation[97–102,180–190] and also bearing in mind the fundamentally different mechanisms of RHgX electroreduction on mercury and other electrodes (see above), it can be concluded that this interaction takes place, nonetheless.

In the latter mechanism described for R_2Hg (R = Me, Et, Pr, *sec*-Bu) compounds,[109,110] bis(phenylethynyl)-mercury[113,125] and $EtHgC_6F_5$ (Ref. 111), 'organic calomel' was formed in the OMC adsorption at a mercury electrode

surface. By analogy with the isotope exchange reaction of R_2Hg compounds with metallic mercury (Hg_{met}) (Ref. 26), it was proposed [112] to describe this process by the following scheme:

1. Diffusion from the bulk of the solution (bl) to the electrode surface (M = Hg)

$$R_2Hg_{bl} \rightleftharpoons R_2Hg_{surf}.$$

2. Adsorption on the electrode

$$R_2Hg_{surf} + M_{met} \rightleftharpoons R_2Hg'M_{ads}.$$

3. Reversible exchange of M atoms in the adsorption layer

$$R_2Hg'M_{ads} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (RHgMR)_{ads} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} R_2M'Hg_{ads}.$$

4. Desorption from the mercury surface

$$R_2M'Hg_{ads} \rightleftharpoons R_2HgM_{surf} + Hg_{met}.$$

5. Diffusion from the mercury surface to the solution volume

$$R_2HgM_{surf} \rightleftharpoons R_2M_{bl} + Hg.$$

The primed symbol designates mercury atoms exchanged with the electrode material.

It was concluded [112] that the potential-determining step was step 3, *i.e.*, the chemical reaction of R_2Hg with the electrode material (more precisely, the forward and reverse reactions with rate constants k_1 and k_{-1}). The disproportionation rates (V) for different types of 'organic calomel' at a mercury electrode (Table 1) and the corresponding constants k_{-1} were assessed from the combination of experimental results [110] and published [170, 191] rates of isotope exchange for OMC. Estimation involved the use of experimental adsorption values $\Gamma_{R_2Hg_2}$ and the so-called 'break-off currents' (i_{br}),[110] *i.e.*, currents at which the competition between the disproportionation (step 3 with rate constant k_{-1}) and R_2Hg_2 electrooxidation reactions starts to appear under galvanostatic conditions.

$$RHgHgR \xrightarrow{-2e} 2\,RHg^+ \qquad (26a)$$

$$RHgHgR \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} R_2Hg + Hg \qquad (26b)$$

Examples of determination of 'break-off currents' from the $i\tau_1$ *vs.* i and $i\tau_2$ *vs.* i dependences can be found in Figs 7 and 8 (curves *1* and *2*) for R = Pr^n and Pr^i. It is seen that

Table 1. Lifetimes (τ^l) of 'organic calomel' $[RHg_{ads}]_n$, its adsorption ($\Gamma_{R_2H_2}$), demercuration rates (V) and 'break-off currents' (i_{br}) at a mercury electrode surface.

R in RHgX, R_2Hg	$10^4\,c_0$ /mol litre^{-1}	Medium, method of determination τ^l	τ^l/s	$10^{10}\,\Gamma_{R_2Hg_2}$ /mol cm^{-2}	i_{br} /mA cm^{-2}	V /mol cm^{-2} s^{-1}	Ref.
Me	1.1	$H_2O-MeOH$, (1)	–	1.3	1.10	1.1×10^{-8}	112
	4.5	H_2O, (2)	$0.02 > \tau \geqslant 0.025$ [a, b]	–	–	–	78
	–	$MeOH-H_2O$, (3)	0.2	–	–	–	9
Et	0.1	$H_2O-MeOH$, (1)	0.02 – 0.03 [c]	1.2	1.56	1.6×10^{-8}	110, 112
	$10-10^3$	EtOH, (2)	$\ll 1$ [a]	–	–	–	94
Pr	1.7	$H_2O-EtOH$, (1)	0.036 – 0.039 [a, c]	–	1.44	–	123
	10	$H_2O-MeOH$, (1)	0.06 – 0.07 [a, c]	2.3	2.04	2.1×10^{-8}	110, 112
Pr^i	2	$H_2O-MeOH$, (1)	0.02 – 0.06 [a, c]	1.7	1.24	1.3×10^{-8}	110, 112
n-$C_{10}H_{21}$	5	DMF, (2)	$\leqslant 0.0025$ [a]	–	–	–	60
n-C_5H_{11}	0.85	$H_2O-MeOH$, (1)	0.002 – 0.004 [c]	1.9	10.4	6.8×10^{-8}	110, 112
cyclo-C_5H_9	1	$H_2O-MeOH$, (1)	0.01 – 0.015 [c]	1.9	3.30	3.4×10^{-8}	110
Ph	1	$H_2O-MeOH$, (1)	$(1-2)\times10^{-4}$ (see [c])	2.2	150	1.6×10^{-6}	110, 112
β-Naph	0.6	$H_2O-MeOH$, (1)	$(2.8-6.4)\times10^{-4}$ (see [c])	2.9	100	1.0×10^{-6}	110, 112
C_6F_5	0.1	$H_2O-MeOH$, (1)	$(1-2)\times10^{-4}$	–	–	–	112
3-Py	2	H_2O, (2)	$0.01 > \tau \geqslant 0.07$ [a]	–	–	–	54
2-PEt	10	DMF, (2)	$\ll 1-2$ [a, b]	–	–	–	58
UMP	0.7	H_2O, (2)	$<4\times10^{-4}$ (see [c])	–	–	–	104
UDP, UTP	0.7	H_2O, (2)	$>0.8-1$ [b]	–	–	–	104
Poly(U)	60 [d]	H_2O, (2)	0.03 – 0.05 [b]	–	–	–	105
Bn	1	$H_2O-MeOH$, (1)	$\ll 10^{-4}$ (see [c])		$\gg 200$	$\gg 2\times10^{-6}$	110, 112
Mes	0.17	$H_2O-MeOH$, (1)	$(2.8-7.5)\times10^{-4}$ (see [c])	1.1	64	0.7×10^{-6}	110, 112
Vi	1	$H_2O-MeOH$, (1)	$(1-2)\times10^{-4}$ (see [c])	–	–	–	110
4-Me-1-C_5H_9(OMe)	1 – 2	$MeOH-H_2O$, (2)	~ 5 [a]	–	–	–	36
ECN, ECD	1.54	DMF, (4)	$1 < \tau < 10$ [a]	–	–	–	56

Notes. The following designation are taken: (1), pulse galvanostatic methods with current reversal, (2), CV, (3), chronocoulometry, (4), polarography; ECN is 3-ethoxycyclononene; ECD is 3-ethoxycyclodecene; UMP, UDP, UTP are uridine mono-, di-, triphosphates; Poly(U) stands for polyuridines in 'weakly mercurated' Poly(U – Hg)X; 2-PEt is β-piperidinoethyl. Experimental conditions: 10% $MeOH-H_2O$ + KOAc (1 mol litre^{-1}), 25 °C;[110, 112] $H_2O + HClO_4$ (0.1 mol litre^{-1}) + 0.002% Triton X100;[78] 50% $MeOH-H_2O$;[9] EtOH + Et_4NBr (0.25 mol litre^{-1}), 22 °C;[94] 10% $EtOH-H_2O$ + NaOAc (0.9 mol litre^{-1}), 25 °C;[124] DMF + Et_4NClO_4 (0.1 mol litre^{-1}) (Ref. 60); DMF or 50% $EtOH-H_2O$ + Et_4NBF_4 (0.1 mol litre^{-1}) (Ref. 58); H_2O + KCl (0.1 mol litre^{-1}), 21 °C;[104] H_2O + phosphate buffer (0.1 mol litre^{-1}) (pH 7) + NaCl (0.1 mol litre^{-1}) (Ref. 105); H_2O + NaOH (1 mol litre^{-1}) (Ref. 54); 50% $MeOH-H_2O$ + NaOH (1 mol litre^{-1}) (Ref. 36); DMF + Bu_4NI (0.2 mol litre^{-1}) (Ref. 56). [a] The value of τ^l is overestimated (a correction for depolarizer of diffusion from the bulk should be introduced); [b] the value was assessed based on the height ratio of VA peaks of the $[RHg_{ads}]_n$ electroreduction and electrooxidation; [c] determined from 'break-off currents' (or from CV curves); [d] in mg litre^{-1}.

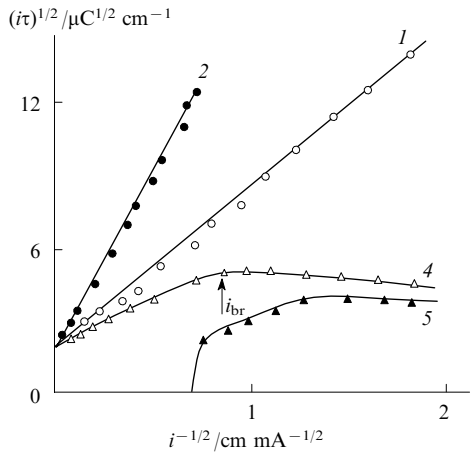


Figure 7. Dependences $(i\tau)^{1/2}$ *vs.* $i^{-1/2}$ in delays *1*, *2*, *4* and *5* (see Fig. 2, charging curves *I*, *II*) of electroreduction of 10^{-3} mol litre^{-1} PrHgOAc in 0.9 mol litre^{-1} solution of NaOAc in aqueous methanol (10 vol.% MeOH).[123]
$E_{in} = -0.15$ V, reversal potential -0.6 V.

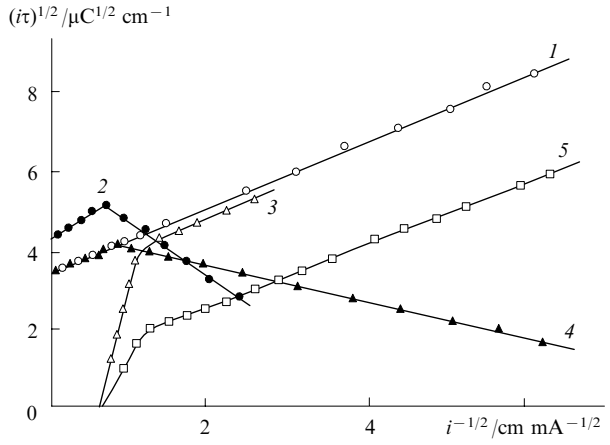


Figure 8. Dependences $(i\tau)^{1/2}$ *vs.* $i^{-1/2}$ in delays *1*–*5* (see Fig. 2, charging curves *I*, *II*) for electroreduction of 2×10^{-4} mol litre^{-1} Pr^{i}HgOAc in 1 mol litre^{-1} solution of KOAc in aqueous methanol (10 vol % MeOH).[109]
$E_{in} = -0.12$ V.

after the current was reversed between delays *1* and *2* (as in Fig. 2 *I*, *II*) at sufficiently high *i*, the time τ_1 was so small that R_2Hg was virtually absent in the monolayer up to the end of the delay. At the same time, the cathodic *1* ($i\tau_1$) and anodic *4* ($i\tau_4$) delays were equal; hence, in the first approximation, it is reasonable to neglect reaction (26b). With a decrease in the anodic current density, a moment was reached when the anodic delay started to decrease so that a break appeared in the $i\tau_4$ *vs.* *i* dependence (see Figs 7, 8). Simultaneously, in the charging curve, delay *5* corresponding to the anodic desorption of dipropylmercury appeared (see Fig. 2 *II*). In approximately the same time (current density) interval, delay *3* corresponding to the cathodic desorption of dipropylmercury emerged in the cathodic branch of the charging curve (see Fig. 2 *II*). Taking this into account, the rate of R_2Hg_2 decomposition can be equated to the 'break-off current'

$$i_{br} = k_{-1}\Gamma_{R_2Hg_2}.$$

In the cyclic voltammetry method, i_{br} was determined from the dependences of the ratio of cathodic and anodic peak heights i_c/i_a (or, more precisely, their areas Q_c/Q_a) for the same reactions on the scan rate *v*; $i = i_{br}$ when this ratio begins to deviate from unity.

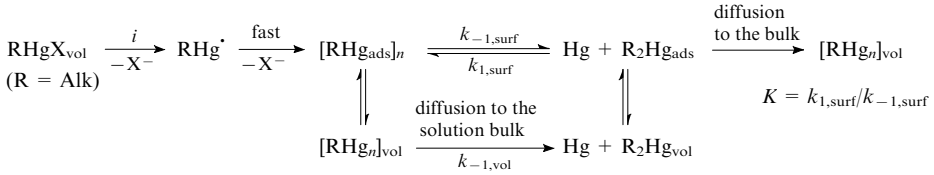
With R = Pr^{n} (Ref. 123) and cyclo-C_5H_9 (Ref. 109), the $i\tau_4$ *vs.* *i* plots were virtually horizontal for $i < i_{br}$, *i.e.*, where the decomposition of 'calomel' have already started and the adsorption of both R_2Hg and $[RHg_{ads}]_n$ already ceased to change (the overall electrode surface coverage $\theta \approx 1$). However, for the majority of RHgX salts [R = Pr^{i} (see Fig. 8), Me, Naph, Mes, *etc.*],[109,110] this dependence passed through a maximum; moreover, for R = Ar, the value of $i\tau_4$ dropped virtually to zero. This effect implies that, in addition to the oxidation of 'organic calomel', a unimolecular reaction of its decomposition occurs, which is clear evidence of the low stability of this intermediate in the bulk.

The minimum time from the beginning of the first delay (or i_c peak) to the end of delay *4* (in the CV method, these are i_c and i_a peaks, respectively) for $i = i_{br}$ corresponds to the time of the transition from $[RHg_{ads}]_n$ to R_2Hg, or the lifetime of 'organic calomel' τ^{l} in the adsorption layer. Thus for $[PrHg_{ads}]_n$, the τ^{l} value was ~ 0.04 s (see Table 1) but in the $PrHgOAc-[PrHg_{ads}]_n-Pr_2Hg$ system at $c_0 \geqslant (2-4)\times10^{-4}$ mol litre^{-1}, τ^{l} proved to increase with the increase in c_0 (probably due to the contribution of reagent diffusion).[123,125] As a result, the dependences of $i\tau_1$ and $i\tau_4$ on *i* for $i \geqslant i_{br}$ do not coincide any longer (see Fig. 7) (such coincidence was observed only for small c_0 (Ref. 123). Analogous assumptions are true for other alkylmercury salts (see Fig. 8). Therefore, only τ^{l} values unaffected by diffusion and obtained at $c_0 \leqslant (1-2)\times10^{-4}$ mol litre^{-1} should be taken as true and the data shown in Table 1 should be considered from this viewpoint.

The analysis of scarce literature data on this problem has shown that the stability of 'organic calomels' mainly depends on the nature of substituent R and, to the lesser extent, on the nature of solvent and its composition. The organomercury intermediates studied so far can conditionally be divided according to their lifetimes τ^{l} (s) into the following groups (see Table 1): alkyl ($\sim10^{-1}-10^{-3}$), aryl with alkyl substituents [Bn $\ll 10^{-4}$, Mes $(1-8)\times10^{-4}$], aryl, C_6F_5, vinyl $[(1-5)\times(10^{-4}-10^{-5})]$, hetaryl ($\sim10^{-2}-10^{-3}$), oxymercuration products of alkenes R(OMe) ($\sim1-10$).

In connection with this, integrated studies of kinetic characteristics of equilibrium (5) appear important; to date, they were accomplished by the example of the $PrHgOAc-Pr_2Hg-[PrHg_{ads}]_n$ system.[123–125] The analysis of the aforementioned delays as a function of the current density for RHgX salts as well as of photoemission data has shown that 'organic calomel' can be formed either directly from RHgX [steps (1b, e), (3) of Scheme 1] or by reaction (6a) from R_2Hg. It is heterogeneous chemical equilibrium (6) rather than the thermodynamic equilibrium that is established (see Scheme 1), where $[RHg_{ads}]_n$ irreversibly decomposed in the bulk but was in equilibrium with R_2Hg in the adsorption layer. The possible steps of such equilibrium are shown in detail in Scheme 2,[124] where *i* is the current in the potentiostatic mode, $k_{-1,surf}$ and $k_{-1,bl}$ are the rate constants of the surface and bulk decomposition and k_1 ($k_{1,surf}$) is the rate constant for the (surface) formation of 'organic calomel' from R_2Hg. For low RHgX

Scheme 2



concentrations when the $[RHg_{ads}]_n$ decomposition rate in the bulk k_{-1} ($k_{-1,bl}$) is negligibly low,

$$i = -k_1\Gamma_1 + k_{-1}\Gamma_{-1}, \quad (27)$$

where Γ_1 and Γ_{-1} are the adsorption values for Pr_2Hg and $[PrHg_{ads}]_n$. It was concluded [124] that for the determination of k_1 and k_{-1} in the adsorption layer, only the values Γ_1 and Γ_{-1} obtained at low volume concentrations of PrHgOAc should be employed together with the steady-state values of the limiting diffusion current i_d under potentiostatic conditions (Fig. 9). For low c_0, the dependence of adsorption of 'organic calomel' on current was virtually linear (Fig. 9 *a*). This implies that k_1 and k_{-1} were independent of adsorption. From their estimates found from formula (27) (Table 2), it follows that in the adsorption layer, the equilibrium was strongly shifted to Pr_2Hg. Deviation of I *vs.* Γ_{-1} dependences in Fig. 9 *a* from the straight line suggests that the equilibrium constant K decreased (see Scheme 2), *i.e.*, k_{-1} increased. Probably, with the increase in Γ_{-1}, the formal constant k_{-1} increased (Fig. 9 *b*) due to the acceleration of decomposition of 'organic calomel' in the adsorption or kinetic (bulk) layer. Next, insofar as at high electrode surface coverages with the components (Pr_2Hg and $[PrHg_{ads}]_n$), the constant k_1 was small, then the dimerization of RHg$^\bullet$ radicals formed in the one-electron reduction of RHgX, rather than reaction (6 *b*) in Scheme 1,

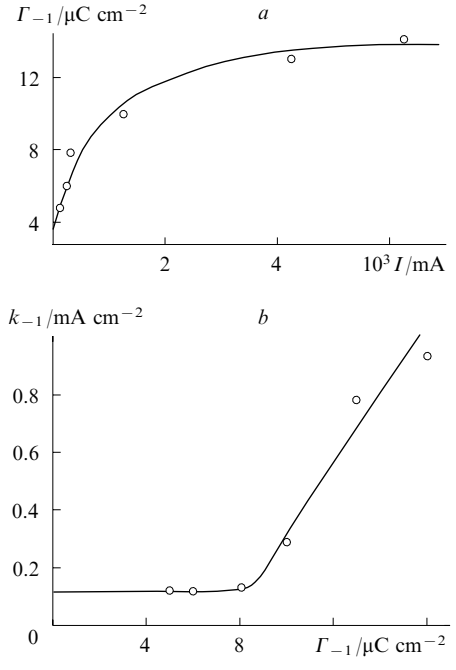


Figure 9. Dependences of steady-state adsorption Γ_{-1} for 'organic calomel' $[PrHg_{ads}]_n$ on experimental current values (*a*) and rate constants for its decomposition k_{-1} *vs.* Γ_{-1} (*b*).[124]

Table 2. Parameters of chemical equilibrium $R_2Hg + Hg \rightleftharpoons [RHg_{ads}]_n$.

R in R_2Hg, RHgX or RI	k_1/s^{-1}	k_{-1}/s^{-1}	$K = k_1/k_{-1}$	Ref.
Me	–	55 [a]	–	142
Et	~0.6	–	–	112
	0.15	–	–	112
	–	80 [a]	2×10^{-3}	142
	–	1–10 [a, b]		94
Pr^n	0.07–0.14	1.3–2.7	0.03–0.11 [a]	123
	–	–	0.01–0.05	110
	–	105 [a]	–	142
Pr^i	–	65 [a]	–	142
n-$C_{10}H_{21}$	–	–	8×10^{-6} (see [a, c])	127
Ph	40	–	–	112
	60	–	–	112
	–	8×10^3	5×10^{-3}	142
	–	1.85×10^3	–	95
C_6F_5	< 0.007	–	–	115
β-Napht	–	5×10^3	–	142
$C_6H_5C{\equiv}C$	~50	–	–	113
Bn	–	$\gg 10^4$	–	112
Mes	–	3.5×10^3	–	142

[a] The value of k_{-1} is overestimated and actually represents a sum $k_{-1,surf} + k_{-1,bl}$ (a correction for depolarizer diffusion from the bulk should be introduced); [b] data from Ref. 94 for EtI, Et_2Hg; [c] calculated based on the data.[127]

should be considered as the main source of 'organic calomel'.[124, 125]

According to the obtained results,[112] on the whole, the rate of $[AlkHg_{ads}]_n$ decomposition was the lowest (see also in Table 2) and the ratio of the rates of formation and decomposition of Ph_2Hg_2 and Et_2Hg_2 was close to 100. It was noticed that for these compounds, the rates of isotope exchange in benzene differed by about the same factor.[191] The rate of $[PhHg_{ads}]_n$ formation from Ph_2Hg that follows from these estimates (under the assumption that $\Gamma_{R_2Hg_2} \approx 10^{-10}$ mol cm^{-2}, which is reasonable for Ph_2Hg derivatives [115]), turned out to be considerably higher for Ar_2Hg as compared with Alk_2Hg. Insofar as no R_2Hg_2 formation was observed at the adsorption of Ar_2Hg too,[115] it was assumed [112] that the demercuration rate was sufficiently high.

Laviron and Roullier [95] used the method of high scan rate voltammetry to study the behaviour of several PhHg derivatives with different electrophilic and nucleophilic substituents in the benzene ring. It was shown that constants k_{-1} depend on the nature of substituents; they increased by more than two orders of magnitude in the following series ($k_{-1} \times 10^{-11}$, cm^2 mol^{-1} s^{-1}):

$$m\text{-}NO_2\ (0.7) < p\text{-Cl}\ (3.7) < p\text{-NHAc}\ (3.7) <$$
$$< p\text{-}CO_2\ (23) < H\ (185) < p\text{-}NH_2\ (443),$$

whereas a simple correlation was observed between $\log k_{-1}$ and the Hammett constants σ. The same authors arrived at a conclusion that in such systems 'organic calomel' was most probably formed through the $RHg^{\bullet}$ dimerization (see also Ref. 109). If one postulates that for the studied [95] Ph_2Hg-derivatives $\Gamma_\infty \approx 10^{-10}$ mol cm^{-2} and assumes that 'organic calomel' decomposes by the first-order reaction, based on the data from Ref. 112, then the k_{-1} estimates fit the range from 7 to 4400 s^{-1}.

The rate of 'organic calomel' decomposition increased in the presence of electron-donating substituents in the benzene ring and decreased in the presence of electron-withdrawing substituents. By the example of the series of Ph- and Bn-ethoxycarbonylbenzylmercury halides and perchlorates, Reutov *et al.*[74] have shown that electron-donating substituents increased and electron-withdrawing substituents decreased the effective positive charge on the mercury atom and favoured the delocalization of the unpaired electron in $RHg^{\bullet}$ radicals. This leads to slowing down of their dimerization.

It should be noted that in studies under discussion,[94,95,112] the constants k_1 and k_{-1} were estimated based on direct measurements by the methods of high-scan rate chronopotentiometry and cyclic voltammetry with the programmed potential control and associated with definite potential values. For example, the values k_1 and k_{-1} were assessed [94] in the following system:

$$EtX + e \xrightarrow[-X^-]{} Et^{\bullet}_{ads} \xrightarrow{Hg} \begin{array}{l} \rightleftharpoons e + EtHg^+ \\ \overset{k_{-1}}{\underset{k_1}{\rightleftharpoons}} Et_2Hg \end{array} \qquad (28)$$

as $k_1 \approx \times 10^{-5}$ cm s^{-1}, $k_{-1} \approx 1 \times 10^{10}$ cm^2 mol^{-1} s^{-1}. Here, X = I or Br, and the values of k_1 and k_{-1} pointed to the shift of equilibrium towards formation of Et_2Hg. However, if 'organic calomel' (R_2Hg_2),[111,124] rather than $Et^{\bullet}_{ads}$ was the intermediate in these steps, then Et_2Hg was formed by the first-order reaction rather than a second-order reaction. Insofar as for dialkylmercury, $\Gamma_\infty \approx (1-5) \times 10^{-10}$ mol cm^{-2} (for example, 3.3×10^{-10} mol cm^{-2} for Pr_2Hg),[124,125] then recalculation to the first-order reaction affords $k_{-1} \approx 1-10$ s^{-1}, which adequately agrees with the data for R = Et ($k_{-1} \approx 0.15-0.6$ s^{-1}) (Ref. 111) and Pr ($k_{-1} \approx 1.3-2.7$ s^{-1}) (Ref. 123) (see Table 2).

Diarylmercury compounds behaved in a somewhat different manner. Thus Ph_2Hg_2 could not be detected on the electrode surface as soon as in 0.1–0.2 ms after its generation from PhHgX (Ref. 110) (see Table 1) and no 'organic calomel' was formed in the Ph_2Hg adsorption at a mercury electrode, although, judging from the value k_1 (~ 60 s^{-1}) assessed [112] using the data of another study,[191] the rate of Ph_2Hg interaction with the electrode should exceed 4 mA cm^{-2} for $\theta \to 0$. An attempt was undertaken [115] to detect 'organic calomel' during the ER of another compound of the aryl series, namely, perfluorodiphenylmercury. It was shown [115] that the rate of the reaction of perfluorodiphenylmercury with mercury was much lower than the diffusion rate and $k_1 < 0.007$ s^{-1} at low cathodic potentials.

A different situation took place for bis(phenylethynyl)-mercury, which, in contrast to perfluorodiphenylmercury, did not accumulate on the electrode surface at potentials more negative than the potential (about -0.35 V) typical of the ER of the corresponding 'organic calomel'.[113] The original compound was electrochemically reduced by the general mechanism at *ca.* -1.1 V in a single two-electron polarographic step. However, a single delay in the chronopotentiogram, corresponding to the two-electron ER was observed only at sufficiently high current densities.[113] As i decreased, another delay appeared in the charging curve at *ca.* -0.35 V ($\sim E^{(2)}_{1/2}$ for PhC≡CHgX) and became the only one at low current densities. Thus, the transformation of R_2Hg into 'organic calomel' [see step (6) in Scheme 1] occurred with k_1 equal to ~ 50 s^{-1}.

Comparing the behaviour of Ar_2Hg and Alk_2Hg (see Table 2), it should be noted that for Ph_2Hg and Et_2Hg, not only k_{-1} but also k_1 differed by *ca.* two orders of magnitude. Moreover, the shift of equilibrium (6) in Scheme 1 also depended on the potential.[124,125] However, in many particular examples, the question of whether 'organic calomel' was produced in a reaction of the depolarizer with the electrode material or a reaction of intermediates of its electroreduction ($RX^{-\bullet}$, $R^{\bullet}$, R^+) or the both channels, still remains open.

IV. Formation of organomercury derivatives in the adsorption and electrochemical reactions of mercury-free compounds

The mechanism of OMC formation and the nature of their ER intermediates can be understood based on a comparative analysis of polarization curves for the ER of miscellaneous organic compounds at mercury, amalgam and inert (Pt, GC) [116] electrodes, especially if their adsorption and ER at mercury was accompanied by the appearance of OMC.[1–3] As was mentioned above, the commonly used mercury electrode is not always chemically inactive. Considering organohalides (RHal), their ER can be accompanied by the formation of organometallic compounds at other electrodes (Pb, Sn, In, Bi, Tl, Zn, Cd), too (for details, see, *e.g.*, Refs 1–9). This was revealed sufficiently long ago; and, moreover, in different steps of the development of OMC chemistry, the results of these studies were often used for the elucidation of the mechanism of electrode reactions for these compounds (*e.g.*, see Refs 1–7, 84–94, 127, 139–141, *etc.*).

If the electrode potential was more positive than the potential of the second step of electroreduction of RHal, then the first step could afford R_2Hg and/or RHgX. After the electrolysis, the OMC could not be isolated in some cases. However, the fact of appearance of colloidal, finely dispersed (or dropped) mercury was conventionally assumed [192–198] to be evidence of the OMC formation. Correspondingly, this type of degradation of cathodes made of different materials accompanied by the formation of organometallic compounds [2] was also observed (for instance, in the electrolysis of BuI at Zn, Hg and Sn electrodes and also at a Pb electrode where Bu_3PbI could even be isolated [198]). The indirect evidence of the involvement of the mercury electrode in the depolarizer electroreduction was believed to include the appearance of additional signals in voltammograms that were absent at other electrode and also the easier electroreduction at mercury as compared with electrocatalytically inactive electrodes [199–201] (GC, boron-doped and fluorinated boron-doped diamond electrode, see, *e.g.*, Ref. 202). It should be stressed that this is not always associated with the formation of organomercury intermediates.[203]

Analysis of abundant data made it possible to conclude [1] that compounds with a weak C—Hal bond, namely, iodides, more rarely, bromides, and very rarely, chlorides, form OMC at a mercury electrode. Insofar as mercury exhibits the maximum affinity to halogens,[204] its presence apparently favoured the scission of this bond. As a rule,[2,3] the lower the C—Hal bond energy and the larger the D(C—M) value [or D(C—Hg)] the more probable the formation of an organometallic compound. The probability of OMC formation increased with the increase in the number of halogen atoms (especially, Br and I) in its molecule. Thus according to certain data,[205] among *gem*-tri-, *gem*-di- and monohalo derivatives of ethyl fumarate and the corresponding halogenated alcohols, only ethyl 2,2,2-tribromoethyl fumarate and 2,2,2-tribromoethanol formed OMC at a mercury electrode, whereas ethyl 2,2-dichloroethyl fumarate and 2,2-dichloroethanol did not. It was shown [206,207] that behaviour of CBr_4 at the dropping mercury electrode and GC differed strongly. Thus the first wave in the CBr_4 polarogram, which was associated earlier [71] with the one-electron reduction of this compound to the radical anion, belonged in fact to its reaction product with mercury. Moreover, it was shown [206] that the polarographic behaviour of all polybromomethanes (CH_2Br_2, $CHBr_3$, CBr_4) differed in principle from that of the corresponding polychloromethanes, whereas the voltammetric behaviour of polybromometanes at GC was much the same as that of polychloromethanes. This was associated [206] with the formation of OMC on the electrode by a reaction coupled with or preceding the charge transfer to polybromomethanes. For chloroform and dichloromethane, no organometallic intermediates were detected. At the same time, the reduction of carbon tetrachloride at a lead electrode [208] included a step of formation of unstable organolead compounds by the electrocatalytic mechanism.

If the potential of the substrate ER was more positive than the potential of the second bromine atom elimination,[139,140] then both alkyl and aryl dibromides BrRBr could form OMC as the main (sometimes, side) electrolysis products at the controlled potential. Thus, whereas the ER of 1,3-dibromopropane afforded only small amounts of dipropylmercury (<1%), that of 1,3-dibromo-1-phenyl- and 1,3-dibromo-1,3-diphenylpropane resulted in OMC as the main electrolysis products.[139] It deserves mention that in DMF, their yield substantially depended on the nature of the supporting electrolyte at its concentration of 0.2 mol litre^{-1}, for example, with Et_4NBF_4, the yield was several-fold higher than with $LiClO_4$.

Polarograms of unsubstituted benzyl bromide (DMF, 0.05 mol litre^{-1} Bu_4NClO_4), its three monobromo derivatives and 3,5-dibromobenzyl bromide demonstrated a single wave corresponding to two-electron reduction.[141] However, polarograms of pentabromo-, pentachloro-, 2,3,4,6-tetrabromo- and 2,4,6-tribromobenzyl bromides demonstrates waves identical to those of the corresponding benzylmercuric bromides. It is of note that 2,6-dibromobenzyl bromide, in contrast to 3,5-dibromobenzyl bromide, was also reduced with the preliminary formation of an OMC, which is typical [141] of compounds that can form organomercury compounds even in a brief contact with the electrode. Note that dibenzylmercury was the main electrolysis product for the series of substituted alkyl and halobenzyl bromides [209–214] (see also Refs 5, 6) at the controlled potential (less negative than the potential of two-electron ER of the depolarizer [214]). The yield of dibenzylmercury substantially depended on the nature of concentrated (2 mol litre^{-1}) electrolytes [DMF; Me_4NBr, Me_4NCl, $(Me_4N)_2SO_4$] and reached maximum in LiCl. Casanova *et al.*[165] assumed that (1-bromoethyl)benzene and analogous RX compounds such as benzyl and allyl halides could also form RHgX being brought in contact with the electrode. An attempt to isolate OMC failed in this case [165] but the product obtained at the temperature below 0 °C contained mercury (see also Refs 168, 169). It was shown [211] that shaking benzyl bromide with mercury in the MeOH—H_2O (1 : 1) solution (with supporting 1 M $LiClO_4$) or shaking benzyl chloride (longer contact of the latter with mercury) afforded the corresponding mercury salts. Benzhydryl bromide in DMF also underwent a fast reaction with the mercury electrode to afford $HgBr_3^-$ even before the application of the potential. However, the corresponding chloride reacted extremely slow.[212] According to certain data,[215] 1,2-dibromo-2,4-dicyanobutane reacted easily with the mercury electrode virtually in the absence of polarization (as early as at +0.2 V) and the reaction product inhibited the subsequent reactions (see below).

Using the methods of coulometry, classical and differential pulse polarography (10% DMF—H_2O, 0.2 mol litre^{-1} AcOH—NaOAc, pH 2.6), polychlorinated fungicides, namely, *N*-(trichloromethylthio)phthalimide (Folpet), *N*-(trichloromethylthio)-1,2,3,6-tetrahydrophthalimide (Captan) and *N*-(1,1,2,2-tetrachloroethylthio)-1,2,3,6-tetrahydrophthalimide (Captafol), were studied [216] with the aim of developing methods of their electroanalytical determination. It was concluded that the transfer of the first electron (abstraction of a chlorine ion) resulted in the formation of an organomercury intermediate adsorbed on the electrode. The curves corresponding to its reduction were observed only at a mercury electrode and were absent at GC.

The possibility (and the rate) of OMC formation also depended on the electrode potential. Presumably (*e.g.*, see Refs 4, 91 and 93), the reactions of RX (halogenated allyl and benzyl derivatives, carboxylic acids, esters, perfluoroalkanes, *etc.*) with mercury to afford OMC proceeded only on the 'negatively polarized' surface and the specific adsorption of I^-, Br^-, CNS^- and other anions accelerated the reaction of alkyl and aryl halides with metallic mercury. This fact can to a certain extent be interpreted as the effect of the potential on the heterogeneous chemical reaction with mercury. The direct evidence of this effect was provided by the changes in the concentration ratio between diethylmercury and the corresponding 'organic calomel' in the adsorption layer in the region of their maximum adsorption. It was shown that on going from −0.6 to −0.8 V, the adsorption of Et_2Hg decreased and the amount of $[EtHg_{ads}]_n$ increased in proportion.[123]

The possibility of OMC formation depended not only on the nature of X in RX but also on other conditions, *i.e.*, the nature and concentration of the supporting salt, temperature, the solvent nature,[90] illumination,[210] sonication,[123] where the effect of the solvent nature was by no means restricted to solvation (complexation). The changes in the supporting electrolyte composition induced changes in the electric double layer structure, depolarizer adsorption characteristics, viscosity and protolytic equilibrium constants, which, naturally, affected the ER mechanism. Below, certain examples of this effect are shown.

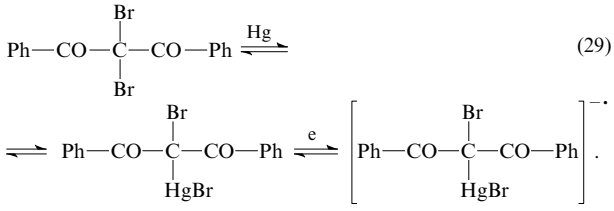
In the electroreduction of iodo- and bromobenzene at a mercury electrode in DMF in the presence of CO_2, only

small amounts of diphenylmercury were detected. Under the same conditions but in the absence of CO_2, benzene was obtained in the yield of virtually 100%.[217]

In water–ethanol solutions (50 vol.%) with supporting alkali metal, tetramethyl- and tetrabutylammonium salts, the electrolysis of iodobenzene virtually exclusively afforded benzene, too;[218] however, in tetraethylammonium solutions, diphenylmercury was also detected (up to 3%–9%). Electrolysis of AlkHal in MeCN in the presence of the tetraethylammonium cation produced organolead compounds Alk_4Pb and Alk_6Pb_2 at a Pb cathode; however, only traces of these organolead compounds were detected in tetrabutylammonium solutions.[218] In the electroreduction of 2-iodooctane in DMF, the appearance of di(*sec*-octyl)mercury in large amounts was observed; moreover, the latter was successfully isolated in much larger amounts when 0.1 M Me_4NClO_4 solution was used as the supporting electrolyte in place of Bu_4NClO_4.[219] At the same time, in ethanolic solutions under different ER conditions, no Ph_2Hg was detected for bromo- and iodobenzenes at elevated temperatures (50 °C).[94] At the same time, the yield of R_2Hg derivatives in the ER of the corresponding ethyl and butyl halides was virtually quantitative.

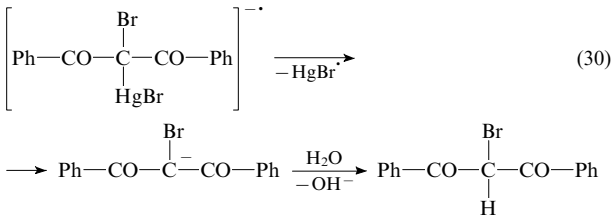
The mechanism of formation of organometallic compounds in the adsorption or the ER of a metal-free substrate still remains unclear. It was assumed[70] to include the formation of a transition complex M[IR]$^-$ (IRX is a depolarizer, R = CH_2CH_2, X = H, OMe, OH, COOH, Cl, CN; electrode M = Hg, Pb) depending on the values of D(M–I) and D(M–R), followed by its decomposition to R$^\bullet$ or RM$^\bullet$ and the reduction of the latter. The formation of a 'physical complex' [PhI–Et_4N^+], which interacts with the electrode material,[218] before electron transfer was put forward as the prime cause of the appearance of Ph_2Hg among the ER products of iodobenzene with Et_4NBr as the supporting electrolyte.

An alternative reduction mechanism of organic compounds that involves the intermediate reaction with the mercury cathode was proposed.[220] The reduction of dibenzoyldibromomethane at Hg and Pt electrodes was studied. The first step was quite conventional



(29)

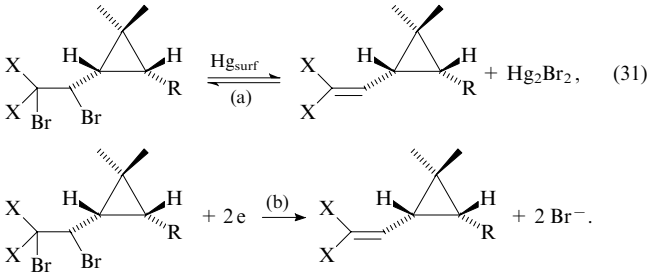
However, it is the C–Hg bond dissociation that occurs in the radical anion formed after the transfer of the first electron



(30)

rather than the Hg–X bond.[4–7] As a result, a relatively stable anion formed in which the charge was stabilized due to the electron-withdrawing effect of the second bromine atom and the negative charge delocalization over two benzoyl groups.

Bond and co-workers[221] observed that the ER of Tralomethrin and Tralocytrin, synthetic polyhalo derivatives of pyrethroid insecticides, proceeds at a mercury electrode at potentials 0.6–0.9 V more positive than at GC. Moreover, shaking these insecticides in MeCN and MeOH with metallic mercury resulted in the precipitation of mercury bromides. The reactions that occurred on the mercury surface and the ER of the mercury electrode are described by the following scheme:

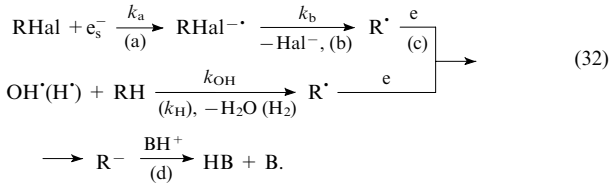


(31)

The debromination reaction similar to step (*b*) in process (31) occurred at a GC electrode but at a different potential. Insofar as the final ER products at both electrodes were similar, the process at a mercury electrode can be considered as electrocatalytic. These effects were sufficiently pronounced for the ER of 2-bromo-2-chloro-1,1,1-trifluoroethane (Halotan) at silver and mercury electrodes.[201,202] At the latter electrodes, the ER was facilitated to a maximum extent as compared with inert electrodes. This was explained[202] by the transient formation of OMC.

It is widely accepted that at cathodic potentials, it is the ER product of the depolarizer, *i.e.*, the free radical, rather than the depolarizer itself that reacts more often with the mercury electrode (*e.g.*, see Refs 5, 6). However, during the dissociative electron transfer,[150] the first electron was as a rule transferred more slowly as compared with the second electron;[5–7] moreover, the RX electroreduction wave[4,6] appeared at more negative potentials as compared with the corresponding waves of OMC and R$^\bullet$, and the latter waves were not observed.

Additional information on the nature of intermediates could be acquired using the methods that combine non-electrochemical (*i.e.*, indirect) generation of intermediates with their subsequent electrochemical studies.[222] Particularly, this approach can be exemplified by photoemission methods[156,198,222–234] where the slow heterogeneous electron transfer step was displaced by the quick homogeneous capture of the solvated (e_s^-)/hydrated (e_{eq}^-) electron by an acceptor (RH or RHal). If the rate constant (k_a) for the solvated electron capture by the acceptor [step (a) in reaction (32)] was insufficiently high, then in place of e_s^-, the photoemitted radicals OH$^\bullet$ (in aqueous solutions) or H$^\bullet$ were used in the synthesis of intermediates. As a result of the following set of reactions, free radicals R$^\bullet$ formed.



(32)

For example, for R = β-cyanoethyl,[231] Me,[227] Pr^i,[232] and Hal = Cl, Br, and especially I,[231] the chemical reaction between the radical and the mercury electrode could precede step (c) in Eqn (32). The probability of such reactions in the photoemissive transformations of intermediates (acceptors RHal were the anions of polyfluorobenzoic acids $C_6F_nH_{5-n}COO^-$, $n = 0-5$) cannot be ruled out.[234] However, for R = Ph,[231] no such reactions were observed.

The electrochemical behaviour of propyl ($Pr^{\bullet}$) (Ref. 226) and chloromethyl ($CH_2Cl^{\bullet}$) radicals generated using the laser photoemission methods [the overall reaction (32)] was studied[223, 228] at a mercury electrode to check the possibility of OMC formation in the adsorption of simple organic radicals. Figure 10 shows the Tafel plot for the $[PrHg_{ads}]_n$ electroreduction[123] and the rate constants (W) for the reduction of radicals $Pr^{\bullet}$ (Ref. 226). It is seen that ER of the radical occurred in much more negative potential range as compared with the corresponding 'organic calomel'. Nor the $Pr^{\bullet}$ oxidation was observed up to $E \leqslant 0.1$ V, *i.e.*, in the range where the 'organic calomel' $[PrHg_{ads}]_n$ itself was already oxidized (see Fig. 2). At the same time, for electroreduction of the chloromethyl radical $CH_2Cl^{\bullet}$, the Tafel dependences were much alike at Hg and GC electrodes (the deviations did not exceed 0.1 V) and virtually coincided for Hg and nanostructured carbon.[228]

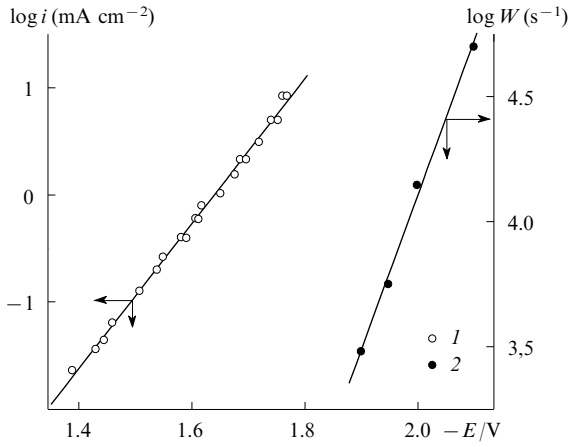


Figure 10. Dependences log i *vs.* E and log W *vs.* E for the reduction of $[PrHg_{ads}]_n$ (*1*)[123] and $Pr^{\bullet}$ (*2*)[226] at a mercury electrode.
Supporting electrolyte is 1 mol litre^{-1} solution of KOAc in aqueous methanol (10 vol.% MeOH)

It is generally accepted[141] that OMC are formed most easily from organohalides that are capable of generating relatively stable radicals (allyl,[235–237] benzyl and its derivatives,[73, 93, 141, 163, 210, 211] *etc.*); this is confirmed by numerous experimental data. However, the results of laser photoemission[223, 225] and laser photoinjection[230] methods in non-aqueous solvents (DMSO, DMF, MeCN) have shown that for sufficiently stable benzyl and benzhydryl radicals, not only the redox potentials of $R^{\bullet}/R^-$ pairs but also their redox constants[222, 225, 230] virtually coincided at mercury and gold electrodes, *i.e.*, the $R^{\bullet}$ radical does not interact with the mercury electrode. However, a reaction of this kind that involved an electrode-polarized halide was observed.[204]

Symmetrical OMC or RHgX salts were detected and/or isolated during the electroreduction of different saturated (linear, branched), unsaturated, cyclic, *etc.* alkyl halides (*e.g.*, see Refs 1, 3–7). In addition to the mentioned alkyl halides,[94, 127] the electrolysis of butyl bromide (DMF, 0.1 mol litre^{-1} Et_4NBr) at a Hg electrode at −(1.9–2.3) V in the presence of CO_2 produced dibutylmercury as one of the main products, whereas at a graphite electrode, butane, butene, octane, *etc.* formed.[213, 214] In the reduction products of 1-bromohexane in DMF, small amounts (up to 2%) of dihexylmercury were detected,[4, 6] whereas no dipentylmercury formed in the pentyl bromide–CO_2 system.[214] Electroreduction of 2-iodooctane afforded di(*sec*-octyl)mercury,[219] electroreduction of 2-bromooctane produced only a mixture of hydrocarbons, whereas in the electrocatalytic system 1-bromooctane–Ni^{II}(salen) with Me_4NBF_4 as the supporting electrolyte di(n-octyl)mercury was detected under certain conditions (excess of substrate).[238] This fact was associated with the catalytic generation of octyl radicals at a mercury electrode. In the electroreduction of 1-bromo- and 1-iododecane, OMC were identified and isolated;[125, 239–241] moreover, depending on the conditions [potential,[239] concentrations of a substrate and proton-donating additive (H_2O)[241]], the 100% yield of di(n-decyl)mercury was attained.

A parameter of fundamental importance that affected the OMC formation in the RHal electroreduction was the duration of the process. For instance, in the controlled-potential electrolysis of 1-iododecane, the number of transferred electrons in the first wave plateau was close to unity throughout the studied potential range.[240] However, the results of chronocoulometric method (pulse duration 50 ms) and the results of polarographic and CV measurements indicated the transfer of two electrons. The shape of polarograms depended on the dropping period while the shape of cyclic voltammograms was determined by the scan rate v. At low v (0.1 V s^{-1}), a peak was observed that corresponded to the C–I bond cleavage and had the 'reverse' peak in the anodic branch. For low $v \geqslant 0.5$ V s^{-1} (or for the dropping period $\leqslant 0.5$ s), two irreversible one-electron steps were observed. Taking them into account, the authors of the above study[240] concluded that in the controlled-potential electrolysis, the number of transferred electrons equal to unity implies that 1-iododecane was mainly consumed in a chemical step competitive with the electrochemical cleavage of the carbon–halogen bond. However, at the shorter contact times of the depolarizer with the electrode, the contribution of the chemical reaction was small. This is in agreement with conclusions[4, 70] on the formation of di(β-cyanoethyl)mercury as a main electrolysis product of 3-iodopropionitrile by the following mechanism:

$$ICH_2CH_2CN + Hg + e \longrightarrow NCCH_2CH_2Hg^{\bullet} + I^-, \quad (33)$$

$$2\,NCCH_2CH_2Hg^{\bullet} \longrightarrow (NCCH_2CH_2)_2Hg + Hg. \quad (34)$$

However, under polarographic conditions, the electroreduction of 3-iodopropionitrile proceeded without preliminary step (33) of pre-conversion to β-cyanoethylmercuric iodide.[70] For the ER of 3-iodopropionitrile and ethylene iodohydrin, voltammograms demonstrated two separate peaks at close potentials, although the polarographic behaviour of these compounds was different in principle.[70] In this aspect, the results presented in Ref. 242 on the controlled-potential electrolysis are of interest. In the first step of electroreduction of 3-chlorocycloalk-2-enones performed under conditions used in another study[240] and in water–ethanol solutions in the presence of acids, the corresponding

symmetrical OMC were isolated. However, in contrast to polarography, the voltammetric measurements on a stationary electrode in the form of a hanging mercury drop failed to detect these compounds. Presumably,[242] the primarily formed radicals could react with the electrode material to form a polylayer that either was reduced or could block the OMC formation.

The preparative ER of allyl dimethyl sulfonium salts was also complicated by the subsequent slow chemical reactions resulting in organomercury intermediates that could not be detected under polarographic conditions.[193]

Besides the duration of the studied process, the state of the mercury electrode surface often proved to be of fundamental importance for the OMC formation. For example, voltammograms of iodo- and bromobenzenes,[128] lysozyme,[243] glutathione,[244] thiadiazoline derivative of spiroadamantane[245,246] and several other compounds, recorded on fresh mercury surface, on the one hand, and during repeated scans, on the other hand, dramatically differed from one another, the latter demonstrating new cathodic and anodic peaks. This fact was associated with the electrode reactions of OMC formed on the surface. Apparently, this was one of the major reasons for the wide disagreement in the data on the electroreduction of RX, for example, benzyl halides, published in the 1969s–1970s.[211]

Sterically hindered cyclic monohaloalkanes formed OMC more slowly. For example, in the electrolysis of 1-iodo- and 1-bromonorbornanes the yield of R_2Hg did not exceed 3%–5%,[247] and, for bridged iodides of adamantane, cubane, bicyclo[2.2.2]octane, *etc.*,[5,6,247] the mass spectrometric method revealed only traces of OMC. Only for the corresponding dihaloalkanes (1,4-diiodo- and 1,4-dibromonorbornanes), especially, at low temperatures (−34 °C), the yield of R_2Hg approached 70%.[248]

Alkenyl and alkynyl halides, especially, bromides and iodides, formed organomercury derivatives[235–237,249,250] much more easily than alkyl halides. Probably, this is why the corresponding allyl and vinyl derivatives were among the model compounds used in elucidating the main relationships of electrode reactions of RHgX (*e.g.*, see Refs 236 and 237). Particularly, even the short-term contact of cinnamyl bromide, 1,1-diphenyl-1-bromo-3-prop-2-ene and several other 1,3-dihalides[236,237] (water–organic medium or anhydrous DMF) with the mercury electrode could result in the formation of a RHgX salt, whereas the corresponding chlorides did not react.[236] 6-Iodo-1-phenylhex-1-yne, 5-iodo-1-phenylpent-1-yne[239] and 1-iododec-5-yne[249] in the DMF–Bu_4NClO_4 (or Me_4NClO_4) system formed, depending on the electrolysis potential, di(5-phenyl-5-pent-1-ynyl)mercury and di(6-phenyl-5-hex-1-ynyl)mercury (the yield of the latter reached 65%),[239] and bis(dec-5-ynyl)mercury (yield up to 89%).[249] For the ER of bromides, the OMC yield was considerably lower. Alicyclic R_2Hg compounds were also isolated in low yields.[171]

Bard and Merz[235] using low scan rates ($v \leqslant 0.5$ V s^{-1}) observed two cathodic peaks in voltammograms of allylic bromides and allyl iodide in DMF at a mercury electrode; the second peak potential was close to the ER potential of diallylmercury (−2.15 V).[67] With the substitution of a glassy carbon and platinum for the mercury electrode, a peak of two-electron ER of allylic halides was observed. Similar differences were typical of the ER of 1-bromobut-2-ene at Hg and Au electrodes, although no individual peak was observed in the CV of di(but-2-enyl)mercury[129] (presumably, due to the low stability of this compound). Note that for (*E*)-5-bromo-2,2,6,6-tetramethylhept-3-ene, which did not react with mercury due to steric hindrances, the voltammograms were approximately the same at Hg, Pt and GC electrodes.[235]

Phenylethynyl iodide and bromide as well as diiodoacetylene easily formed OMC being brought in contact with a mercury electrode.[250] This is why it was proposed[250] to revise the polarographic data[70] for these compounds.

The electrochemical transformations of allylic derivatives of sulfur, nitrogen, phosphorus and other elements often afforded OMC.[2,192–197,251–257] Thus a considerable difference in the electrochemical behaviour of *trans*-2-allyl-6-phenyl-1,2,3,6-tetrahydropyridine in anhydrous and aqueous DMF was revealed.[194] For the water content $\geqslant$40%, the electroreduction proceeded at the more positive (by ~0.5 V) potential and was accompanied by the hydrogen evolution, which was attributed to the reduction of the amine–water associate to afford radical species that reacted with the electrode. This led to intermediates such as 'organic amalgam', which either decomposed with hydrogen evolution or attacked the original molecule to form oligomeric products.

Thiols RSH form OMC in both the anodic processes[252–255] in reactions such as

$$2\,RSH + Hg \longrightarrow (RS)_2Hg + 2\,H^+ + 2\,e^-$$

and their adsorption or ER at a mercury electrode (*e.g.*, see Refs 100 and 102). Compounds containing sulfur and nitrogen atoms, for instance, 1-benzyltetrazole-5-thiol,[254] 6-propyl-2-thiouracil,[255] 2,2′-dithiodipyridine (Aldrithiol),[257] also form organomercury intermediates. Studying the electrochemical behaviour of allyl 2-pyridyl sulfones in solutions in DMF revealed[195] the effect of H_2O addition on the selectivity of their reduction. It is known that the radical anion formed in the ER of methyl 2-pyridyl sulfone in DMF decomposed to the sulfonate anion and the pyridine radical.[195] The latter either reacted with the electrode material to afford 'organic amalgam' $[Py\cdots Hg_x]^{\bullet}_{ads}$, or reacted in the bulk of the solution with the starting compound to form a polymer.

$$PySO_2Me \xrightarrow{e} [AP]^{-\bullet} \xrightarrow{Hg} [Py\cdots Hg_x]^{\bullet}_{ads} + MeSO_2^- , \qquad (35)$$

$$[Py\cdots Hg_x]^{\bullet}_{ads} \rightleftharpoons [Py\cdots Hg]^{\bullet}_{ads} \begin{cases} \xrightarrow{n\,PySO_2Me} \text{polymer} \\ \xrightarrow{[PyHg]^{\bullet}_{ads}} Py_2Hg_2 \xrightarrow[-Hg]{} Py_2Hg. \end{cases}$$

Pyridine could be isolated in the yield of 65% using 70% DMF–H_2O + 0.1 mol litre^{-1} LiCl as a supporting electrolyte observed.[195] In water–ethanol solutions, its yield was virtually quantitative, which allowed electrolysis to be recommended as a convenient method for the removal of a sulfonyl protecting group from position 2 of the pyridine ring.

It was established[192,193] that preparative two-step ER of allyl methyl sulfonium perchlorates at a mercury cathode in DMF was accompanied by the OMC formation and subsequent slow chemical transformations. Based on the proposed mechanism, the methods of preparation of α-isoprenoids were proposed. It was assumed that in contrast to the Pt electrode, the ER at a mercury electrode produced compounds of the R_2Hg kind (highly dispersed mercury was present in the solution after the electrolysis)

that could not be reduced under the experimental conditions used. Such inactive OMC were formed, for example, in the ER of alkyl *p*-toluenesulfonates.[2]

The reduction mechanism of OMC produced *in situ* upon addition of Hg(II) salts to alkenes in water–alcohol media in the electrochemical cell[35–37,61,62] (Nesmeyanov called these OMC 'quasicomplex compounds'), is very complicated. According to experimental data,[2,37] it depended on pH, solution composition and other factors (*e.g.*, see Ref. 62 and Section II); hence, the interpretation of experimental curves was difficult. Thus polarograms of the $ViOAc-Hg(OAc)_2$ mixture in water–alcohol (MeOH, EtOH, Pr^nOH, Pr^iOH) media[37] and of $AllCl-HgX_2$ ($H_2O-EtOH$) contained from two to three waves depending on the nature of the alcohol, its concentration and the supporting electrolyte.[37] It was shown that the first reversible wave was of the diffusion nature, the second kinetic and the third adsorption waves were considered[37] as irreversible. According to the general scheme of RHgX electroreduction, it was proposed that these waves corresponded to the following processes: reduction of the Hg–X bond (first wave), reduction of 'organic calomel' (second wave) and reduction of the solvated compound R_2Hg (third wave).

In turn, studying[258] the ER of ethyl α-bromophenylacetate at mercury (DMF, 0.1 mol litre^{-1} Et_4NClO_4) revealed several waves that were assigned to the sequential reduction of RHgX, $RHg^{\bullet}$ and R_2Hg_2 (more probably, the last two waves corresponded to the reduction of R_2Hg_2 or R_2Hg). However, at Pt and GC electrodes, the same authors observed only the wave of RX electroreduction, as in other studies.[165,235] Detailed CV studies of the ER of ethylene iodo- and bromohydrins at mercury and GC in MeCN substantiated[259] the transient formation of organomercury intermediates. The analogous assumption is true for the electroreduction of 4-iodoanisole; thus it was noted[260,261] that the yield of bis(4-anisyl)mercury in the electrolysis at controlled potential reached 30%–45% depending on the initial potential.

Organomercury compounds were often produced in the reduction of oxygen-containing compounds (esters, acids, alcohols, aldehydes, ketones, *etc.*) in aqueous and non-aqueous media, especially, in acidic media.[2] This was typical of, for example, aliphatic, cycloaliphatic and alkyl aryl ketones,[1,2] acetaldehyde,[262] benzaldehyde[263] and *p*-methylbenzaldehyde[133] and also of chalcones.[2] Particularly, this is the reason for severe complications in the photoemission studies in acidic solutions (at pH < 4–4.5) of carbonyl compounds, namely, acetophenone[229] and acetone.[224,233] Protonated but-3-en-2-one at pH < 6.3 was reduced in a single one-electron step to afford a radical, the subsequent reactions of the latter led to $Hg[CH_2CH_2C(O)Me]_2$.[264]

In acidic media, ketones MeC(O)R underwent tautomeric keto-enol transformations

$$Me-\overset{\overset{O}{\|}}{C}-R \overset{H^+}{\rightleftharpoons} \overset{\overset{OH}{|}}{H_2C}=CHR',$$

followed by the reaction with Hg(II) ions to form electrochemically active complexes[265] (probably, resembling the aforementioned 'quasicomplex compounds'):

$$Hg^{2+} + \overset{\overset{OH}{|}}{H_2C}=CHR' \longrightarrow \overset{\overset{O}{\|}}{MeCCH(R')Hg^+} + H^+.$$

The presence of a nitrogen atom in a compound, especially, if the latter contained an aromatic fragment, usually facilitated the OMC formation. Thus the one-electron ER of aryldiazonium salts afforded only RHgX salts.[1,2] However, the directed synthesis (for example, the preparation of diaryl disulfides from aryldiazonium tetrafluoroborates at mercury in the presence of carbon disulfide[256]) can result in undesirable consequences; thus even although the process at mercury was faster than at graphite, it produced OMC rather than the target product.

The electroreduction of nitrogen-containing organic compounds could also produce OMC. It was found[196] that at a dropping mercury electrode, amalgamated copper and lead, the reduction of perfluoropyridine occurred in two one-electron steps (MeCN, Et_4NBr), whereas at silver, graphite and platinum, it was reduced in a single two-electron step. Moreover, the difference of half-wave potentials reached ~1 V. The cathode mass loss (amalgamated copper disk) was observed[196] in the preparative ER of the compound mentioned. In addition, the qualitative reaction of the cathodic deposit with NH_3 (the appearance of finely dispersed mercury) pointed to the presence of calomel Hg_xF_x in the catholyte. This altogether gave the grounds to assume[196] the formation of an organomercury intermediate.

No OMC were detected in the electroreduction products of perfluoropyridine in DMF; however, perchloropyridine and tetrachloropyridine formed bis(tetrachloro-4-pyridyl)-mercury in addition to other products.[266]

Bromoalkylnitriles $BrCR_2(CH_2)_nCN$ (R = H, Me, n = 1–3), like β-iodopropionitrile, also reacted with the electrode during their reduction at mercury (DMF, Et_4NClO_4).[267] The corresponding nitriles were the main ER products at both mercury and GC, but dimeric and polymeric products additionally formed at a mercury electrode. This was associated with the direct involvement of the electrode material in the reduction process.

A comparative polarographic and CV study of the electrochemical reactions of Δ^3-1,3,4-thiadiazolines[245] and spiro[Δ^3-1,3,4-thiadiazoline-2,2′-adamantane][246] at a dropping mercury and hanging mercury electrodes (MeCN; water–ethanol and water–acetonitrile solutions, pH 1.3–12) demonstrated their substantial differences. Thus the repeated potential scanning resulted in the appearance of new peaks in the CV curve, which corresponded to polarographic waves. They were associated with the redox reactions of OMC formed in the reaction of ER products of 2,5-dihydro-1,3,4-thiadiazoles with the electrode material. No new peaks were observed at Pt, Ag and GC electrodes. In alkaline solutions, an ER peak of RHgX salts appeared that corresponded to the products of the spiropyran ring-opening.[246] The electroreduction of 4-methyl-2-nitrophenylguanidine afforded mercury-containing oligomers.[268] The insecticide Imidacloprid, *N*-nitro-*N*-[1-(6-chloro-3-pyridylmethyl)imidazolidin-2-yl]amine, exhibited strong chemisorption at a hanging mercury drop electrode at temperatures <(0–10) °C.[269] The reduction of nitroso-, azoxy- and azobenzenes at a dropping mercury electrode in DMF, in addition to conventional peaks, produced peaks associated with redox transformations of a reaction product of the azobenzene dianion adsorbed on mercury and the electrode material.[197]

This kind of reactions, especially if mercury ions formed (or originally present) in the solution, could result in the formation of not only the covalent C–Hg bond but also

complexes of the depolarizer (adsorbate) with these ions. The question of differences in the electrochemical behaviour of such structures was comprehensively considered [105] by the example of Hg(II) complexes with electrochemically inactive polynucleotides Poly(U), on the one hand, and covalently bound Poly(U−Hg)X derivatives, on the other hand. It was found that the voltammogram of the Hg(II)−Poly(U)$_{ads}$ complex contained a single broad ER peak (in the vicinity of −0.7 V), and the Poly(U−Hg)X derivatives (particularly, 'weakly mercurated') obeyed the general mechanism of RHgX electroreduction at a mercury electrode (see Section II). The adsorption behaviour of all these compounds also differed in principle. The problem of better analytical detection of different mercury forms is important for practice because the method of anodic stripping voltammetry allows determination of only the overall mercury concentration.

Naturally, the electrochemical behaviour of mercury ions differed from that of their complexes with inorganic anions and (the more so) organic ligands, particularly, amino acids and their derivatives [270] and also with diethylenetriaminepentaacetic,[270, 271] picolinic and other organic acids. For example, the Hg^{2+} cation formed with glycine a series of complexes, ranging from labile to very stable, which included one or two ligand molecules and were reduced at substantially different potentials.[270] Such precoordination made it possible to diminish the limit of analytical determination of mercury.

Usually, the formation of mercury ion complexes with an organic depolarizer was observed at potentials higher than or equal to the zero charge potential and, most often, at the positive potentials and for substances that contain atoms of sulfur,[269, 272, 273] nitrogen [197, 274] or both these elements.[245, 246, 252, 253, 275] In the centre of this process, usually lied a redox reaction of the depolarizer (RH) (Refs 253, 273), its radical ($RH^{\bullet}$) (Ref 246) or ionic (R^-) (Refs 252, 272, 272), or dianionic (R^{2-}) (Ref. 197) forms with polarized mercury to afford derivatives containing either R−Hg(I) or R−Hg(II) bonds. For example, under these conditions the adsorption of thiocytosine,[275] xanthine, xanthosine,[273] dithiocarbamates [272] and many other compounds was assumed to involve the formation of R_2Hg and also of the RH−Hg(I) derivatives (RH is pentoxifylline [274]), associates (for example, $[AB^{2-}Hg^{2+}]$, where AB^{2-} is azobenzene dianion,[197] lysozyme [243]) or the mixtures of $(SR)_2Hg$ and $(SR)_2Hg_2$ in the case of cystine,[252] cysteine,[253] spiro[Δ^3-1,3,4-thiadiazoline-2,2′-adamantane].[246] As a rule, these derivatives exhibited sufficiently high electrochemical activity, which substantially complicated the interpretation of results. This problem is not considered in detail in this review, because the ER of organomercury derivatives $(SR)_2Hg$ and $(SR)_2Hg_2$ containing S−Hg bond is beyond its scope. However, summarizing the issues described above, it can be noted that the formation of OMC in anodic and cathodic processes can formally be described by the following scheme:

negatively polarized electrode

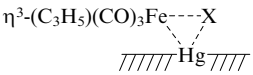
$$RX + Hg + e \longrightarrow RHgX \text{ (or } [RHg_{ads}]_n);$$

positively polarized electrode

$$2\,RX + Hg^{2+};\ Hg_2^{2+} \longrightarrow R_2Hg + 2e + 2X^-.$$

Organomercury intermediates often formed [1−3, 8, 9] during the ER of other organometallic compounds at a mercury electrode (transmetallation reaction). The formation of OMC was hypothesized (or directly observed) in the one-electron ER of $ArPbX_3$ salts (Ar = Ph,[188] *p*-MeC_6H_4, *p*-$MeOC_6H_4$; X = OAc, OH),[186] Ph_3Pb^+ (Refs 3, 8, 9), Ph_4Sb^+ (Ref. 9), η^5-$C_5H_5Fe(CO)_2X$ (X = Cl, Br, I, $SnCl_2$, $GeCl_3$),[182] R_nMX_{4-n} {M = Sn, Pb; R = Me, Bu,[276−280] Alk, Neophyl [$PhC(Me)_2CH_2$] (see Ref. 187)}. In the latter case, the $RHg^{\bullet}$ radical the stability of which substantially depended on the nature of R disproportionated to afford electroinactive compounds $(R_2Sn)_2Hg$. However, the $(R_3Sn)_2Hg$ (R = Me, Et, Pr) compounds formed by the analogous mechanism were immediately reduced through the addition of two electrons.[187] It is known [172] that the DMF adsorption prevents the formation of the Sn−Hg bond so that the aforementioned effects could be observed only in a protogenic medium, for example, in MeOH. In turn, the $Et_2Pb^{\bullet\bullet}$ biradical, the two-electron ER product of the $Et_2Pb^{2+}\cdot n\,H_2O$ cation, either underwent disproportionation to Et_4Pb or afforded Et_2Hg.[9]

Chemisorption of organometallic compounds (particularly, of iron [182, 183] and ruthenium [184] carbonyl complexes) on mercury in anhydrous THF could also produce OMC. A comparative analysis of the electrochemical behaviour of allyl iron carbonyl complexes such as (η^3-$C_3H_5Fe(CO)_3X$ (X = Cl, Br, I) at platinum and mercury electrodes pointed to the involvement of mercury in the first step of their reduction, which resulted in the acceleration of this step as compared with the Pt electrode.[183] Presumably,[183] the adsorption of such compounds on mercury resulted in insertion of mercury into the Fe−X bond



to afford a metastable heterometallic complex (η^3-$C_3H_5Fe(CO)_3HgX$), probably, *via* unstable 'organic calomel' RHgMX.[107] The final product in the reaction of the η^5-$C_5H_5Fe(CO)_2^{\bullet}$ crypto radical with the electrode material was the electrochemically inactive compound $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2Hg$.[182]

The oxidation of carbonyl complexes $Fe(CO)_4L$ (where L = PPh_3, $AsPh_3$, $SbPh_3$) in acetone, dichloromethane and MeCN at a mercury electrode involved a step of formation of 'mercury-stabilized' cations such as $[HgA]^+$ and $[A-Hg-Hg-A]^{2+}$ (where A is the organometallic residue).[185] The unusual behaviour of $NiX_2(RNC)_2$ complexes (X = I, Br, Cl; R = 2,6-$Me_2C_6H_3$, 4-Br-2,6-$Me_2C_6H_2$, 2,4-Bu^t_2-6-MeC_6H_2, 2,4,6-$Bu^t_3C_6H_2$) was noted.[281, 282] At a Pt electrode, the peaks of two-electron quasireversible reduction were observed in CV curves, whereas at a mercury electrode, the peaks of redox transformations of the $[Ni(RNC)_2HgX_2]$ intermediate appeared. A new peak in the presence of isocyanides was associated [282] with the ER of a new species, $[Ni(RNC)_4HgI_2]_2$.

Cations Me_3Pb^+ (Ref. 276), Ph_3Pb^+ (Ref. 8) and $Ph_2Pb(OAc)_2$ quickly reacted with the electrode material to form OMC [in the latter case, the rate constant for their reaction with mercury was 1.55×10^{-4} cm s^{-1} (Ref. 188)]. Such behaviour was typical of organic chalcogenides, namely, disulfides, diselenides and ditellurides.[1, 2, 97−101] For this reason, the reduction of disulfides proceeded quite easily at a mercury electrode and with great difficulty at platinum and graphite electrodes. Monoselenides reacted with mercury with greater difficulty; thus α-carbonylselenocyanates were decomposed in its presence but the corresponding thiocyanates did not react at all.[283] The Ph_6Sn_2

compound and the Ph_3Sn^+ cation also directly reacted with the Hg electrode (a black deposit was obtained).[284] The fast exchange of mercury atoms for gold atoms in organogold compounds,[189,190] for palladium in organopalladium compounds[2] and for thallium in organothallium compounds also proceeded even before the potential application.[180,181] Charging curves for ER of the Et_2Tl^+ cation with the structure isoelectronic with that of Et_2Hg, recorded at a mercury electrode demonstrated three delays.[181] The third delay at the potential of the Et_2Hg_2 electroreduction was attributed to the reduction of a mixture of Et_2Hg_2 and $EtHgTlEt^+$ cations. This was also the case for other R_2TlX derivatives (R = Alk, Ph) that dissociated in solutions to afford R_2Tl^+ cations. For R = Ph, this cation was reduced in the first delay together with Tl^+ by the following mechanism:[180]

$$Ph_2Tl^+ + Hg \overset{\text{rapid}}{\rightleftharpoons} PhHgTl^+Ph \overset{e}{\rightleftharpoons} \rightleftharpoons PhHgTl^{\bullet}Ph \overset{\text{rapid}}{\rightleftharpoons} Ph_2Hg + Tl. \quad (36)$$

As a result of such reactions, *N*,*N*-disubstituted gold dithiocarbamates $Au(Rdtc)_3$ (where R = Et_2, Pr^i_2, Bu^i_2, Bn_2) were reduced (propylene carbonate, 0.2 mol litre^{-1} $NaClO_4$) in two voltammetric steps at a mercury electrode and in one step at a platinum electrode.[190] In the same study, the quasireversible peaks at more positive potentials were associated with the electrode reactions of $Hg(Rdtc)_2$. In turn, the noticeable acceleration of the ER of di(β-cyanoethyl)mercury was observed[116] at an electrode of an In–Hg alloy as compared with the mercury electrode. It was proposed that the electrode reaction was preceded by the exchange of indium for mercury in the above-mentioned compound.

Interesting cases of OMC interaction with the mercury electrode were also observed during the EO. For instance, the electrooxidation of Alk_2Hg_{ads} at a mercury electrode produced intricate complexes $Hg_3L_4^{2+}$ (L is an organic ligand) and adducts such as $R_2Hg_3^{2+}X_2$; $[R_2Hg_5Cl_2]^{2+}X_2$ (R = Me),[176] or (for other organometallic compounds) $[R_nM_m-Hg-R_nM_m]$ (M = Pb, Sn, Cd, Bi).[176,177]

The data shown clearly demonstrate that chemical reactions of mercury-free organic and organometallic compounds with the Hg electrode were sufficiently complicated and diversified while the ER mechanism is often obscure for many compounds.

V. Acid-catalyzed degradation of the organomercury intermediates

A typical example of the special role of the interaction of mercury-free compounds with the Hg electrode in the electrode reactions is the involvement of OMC in the electrocatalytic evolution of hydrogen. Thus the electrosynthesis of OMC, particularly, R_2Hg from RHgX, can be accompanied by blocking of the electrode surface by poorly soluble ER products; to remove this, small amounts of an acid has to be added.[285] The acidic medium was often necessary for the electrochemical synthesis of OMC from mercury-free compounds, for example, in the synthesis of R_2Hg from ketones[2] or of RHgX from aldehydes.[262] However, such products could induce the electrochemically catalyzed hydrogen evolution at a mercury electrode,[99–102,143,160,174,178] which presumably[143] involved both the formation of mercury-containing intermediates and their proton donor-induced degradation.

It deserves mentioning that the mechanism of catalytic evolution of hydrogen from buffer solutions of nitrogen-containing compounds[155,160] was one of the most actively debated problems in the 1950s. In the early 1960s, a hypothesis was first put forward and later developed[155] that the catalyst (particularly, pyridine and its derivatives) can be recovered by a bimolecular reaction of pyridyl radicals formed in the ER of the protonated substrate (PyH^+),

$$2\,PyH^{\bullet} \longrightarrow 2\,Py + H_2. \quad (37)$$

According to this mechanism, both the Py protonation and its regeneration occurred in the bulk of the solution. At the same time, even the authors of this theory in their publications of 1980s[174] noted that in certain cases, for example, in solutions of acridine, the catalytic evolution of hydrogen was complicated by the OMC formation. To ascertain the role of such compounds, additional studies were carried out.[143] Based on the thorough analysis of polarographic data and *I vs. t* curves in Py solutions, it was concluded[143] that the catalyst represents the depolarizer reduction product adsorbed on a mercury electrode. Moreover, the unusual *I vs. t* curves, namely, concave towards the time axis in their initial segment, were observed in solutions of *N*-methyl(ethyl)pyridine, and also of quinine and keto-derivatives of adamantane. This pointed to the general character of the mechanism of hydrogen catalytic evolution that involves the formation of a catalytically active product adsorbed on the electrode. As to the chemical nature of catalysts, it was assumed that it is radicals and/or 'organic calomels'[142] existing in equilibrium with the radicals that represent the hydrogen evolution catalysts. Based on these data, it was concluded[143] that the catalytic evolution of hydrogen was the result of degradation of these organic amalgams by proton donors (as that of tetraalkylammonium amalgams[178]). For Py solutions, the mechanism of catalytic evolution of hydrogen was described by the following scheme:

$$Py \overset{BH^+}{\underset{-B}{\rightleftharpoons}} PyH^+ \overset{e}{\rightleftharpoons} PyH^{\bullet} \xrightarrow{n\,Hg} PyH/Hg_n \quad (38)$$

$$PyH/Hg_n \xrightarrow{BH^+} PyH^+ \quad \left(-\tfrac{1}{2}H_2,\ -n\,Hg\right)$$

Later, this mechanism was confirmed.[178] The question of the nature of the phenomenon under consideration was finally elucidated with the appearance of new data.[144] It was shown that in the case of *N*-dimethylbenzylanilinium chloride, *i.e.*, compound that cannot be protonated, the catalytic evolution of hydrogen induced by the decomposition of an organic amalgam under the action of water or a proton donor was observed, too. It should be stressed that hydrogen also evolved in the electrolysis of Et_4NBF_4 at a mercury electrode in neutral solutions, pH increased to 12 and a black deposit with the composition $Et_4N\cdot Hg_n$ ($n = 2.9 \pm 0.8$) formed.[179]

The next aspect of this problem, namely, the proton donor-induced degradation of mercury-containing intermediates was discussed.[121] It was found[122] that the addition of even small amounts of acids ($3 < pH < 6$) to solutions of C_6F_5HgBr resulted, in place of the expected blockage removal, in the disappearance (Fig. 11, curve *4*) of the

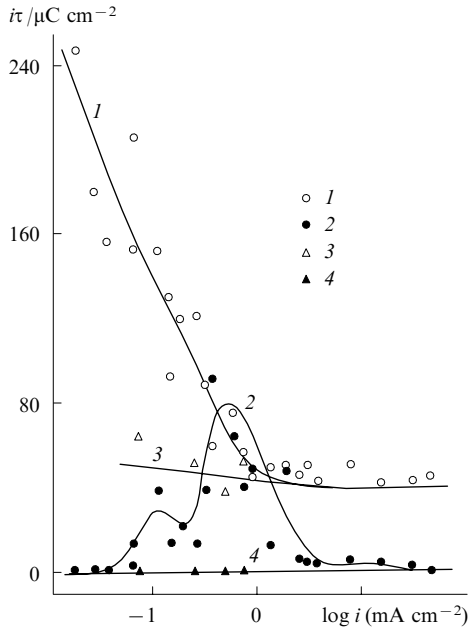


Figure 11. Lengths of the first (*1*, *3*) and the second (*2*, *4*) delays during the reduction of perfluorodiphenylmercury synthesized by microelectrolysis of 5×10^{-5} mol litre^{-1} pentafluorophenylmercuric bromide as a function of the current density in weakly alkaline (*1*, *3*) and weakly acidic (*2*, *4*) media.[121]
Solutions of NaOAc in aqueous ethanol (10 vol.% EtOH) served as supporting electrolytes. [NaOAc] /mol litre^{-1}: (*1*, *2*) 0.9; (*3*, *4*) 2.7.

delay corresponding to the ER of the near-electrode condensed perfluorodiphenylmercury phase, while the length of the delay of monolayer reduction no longer depended on either *i* (curve *3*) or the polarization time t_p (Fig. 12, curve *4*) and decreased to virtually monolayer values.

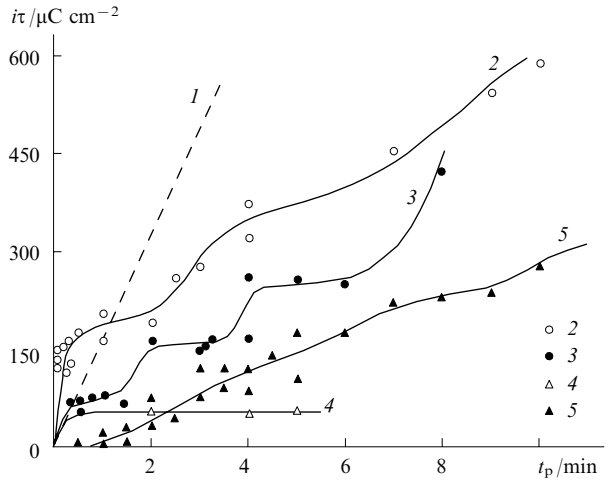


Figure 12. Curves $i\tau$ *vs.* t_p for electroreduction of perfluorodiphenylmercury in the first (*2*–*4*) and the second (*5*) delays synthesized by microelectrolysis of 5×10^{-5} mol litre^{-1} pentafluorophenylmercury bromide under potentiostatic conditions.[121]
(*1*) Calculations according to the equation for stationary diffusion of the depolarizer to the hanging mercury drop electrode.[160] $10^5\, c_0$ /mol litre^{-1}: 5 (*1*, *2*, *4*, *5*) and 4.4 (*3*); $i = 0.072$ (*2*), 0.115 (*3*), 0.752 (*4*) and 0.482 (*5*) mA cm^{-2}. Solutions of NaOAc, pH 8.6 (*2*, *3*, *5*) and NaOAc + HOAc, pH 4.2 (*4*) in aqueous ethanol (10 vol.% EtOH) served as supporting electrolytes.

A similar effect also complicated the electrochemical behaviour of bis(phenylethynyl)mercury. For low AcOH concentrations (0.9 mol litre^{-1} NaOAc, pH 4.4–5.5), the delay corresponding to the ER of this compound [see Eqn (7), Scheme 1], which was the only delay at high *i*, remained virtually unchanged,[121] whereas the delay corresponding to the ER with the preliminary formation of 'organic calomel' $[RHg_{ads}]_n$ (see Section III and Ref. 113) disappeared. Effects qualitatively resembling the action of acids[121] were observed[119] in C_6F_5HgBr solutions with 0.1–1 mol litre^{-1} KBr as the supporting electrolyte. The first delay corresponding to the ER of the near-electrode perfluorodiphenylmercury phase formed on the electrode from C_6F_5HgBr was constantly shortened during the experiment, while the second delay disappeared soon after its beginning. This was explained by the fact that halide ions (especially, Br^- and I^-) induced irreversible solvolytic degradation of R_2Hg in aqueous solutions (*e.g.*, see Ref. 26). It is known[132] that bromodemercuration often proceeded at high rates even at room temperature (probably, *via* unstable intermediates of the radical nature, as was observed in other publications[121, 143, 144, 178]).

Symmetrical OMC easily underwent acid-induced degradation,[26] aromatic derivatives more readily than aliphatic, whereas alkalis usually do not cleave the C—Hg bond. At the same time, both aliphatic and aromatic R_2Hg compounds with electronegative substituents (particularly, fluoro derivatives[159]) demonstrated the high stability of the C—Hg bond with respect to protolysis and impact of other electrophilic agents.[26] The reactions with nucleophiles were more characteristic of such compounds due to the high sensitivity of the mercury atom towards the nucleophilic attack.[26] Salts RHgX, on the other hand, underwent protolysis with higher difficulty. Thus PhHgBr in the presence of AcOH decomposed extremely slowly,[26] while the energy barrier to the protolysis of the Hg—C bond with hydrohalic acids became lower from 146 (MeHgCl) to 86.6 kJ mol^{-1} (Me_2Hg).[286] The Hg—Cl bond was virtually resistant against both nucleophilic and electrophilic attacks.[26] For example, storage of MeHgCl (5×10^{-4} mol litre^{-1}) in HCl solution with pH 1 for a week did not change its polarogram.[26, 121]

As a rule, protolysis of OMC is a lengthy procedure carried out under sufficiently drastic conditions (elevated temperatures, high acid concentrations).[26] For the described[121] systems, the protolytic effect was observed even in weakly acidic media ($pH \leqslant 4.8$–5.5) at room temperatures; after the solutions of pentafluorophenylmercuric bromide and bis(phenylethynyl)mercury were neutralized with an alkali in the electrochemical cell, the original state was completely recovered, which pointed to the absence of protolysis of these compounds.

Carboxylic acids did not as a rule react with RHgX, and the C—Hg bond cleaved more easily under the action of hydrohalic acids and was to a certain extent more resistant to oxoacids.[26] The effect was reversed[121] for the electrolysis of C_6F_5HgBr. [It should be noted that according to acquired data,[119–121] the pefluorodiphenylmercury complexes with halide ions are also somewhat more labile (see Section II) than, *e.g.*, with AcO^-]. Coordination strengthened the C—Hg polarization in OMC thus making easier its protolysis.[287] For Me_2Hg, hydrogen sulfide turned out to be a very active protonating agent; moreover, the $[HgMe_2SH^-]$ complex was formed by the virtually barrierless route.

The observed [121] effect of small portions of acid can hardly be associated with the protolysis of perfluorodiphenylmercury, because the length of the delay corresponding to the ER in solutions of this compound proved to be pH-independent in the same pH range (4.4–9.2). Hence, these effects were explained [121] by the acid-catalyzed protolysis of intermediates of OMC electroreduction. At a mercury electrode in weakly acidic buffer solutions, such a reaction was observed at the ER of *N*-methylpyridinium halides, adamantanones and some other compounds the reduction of which involved the transient formation of OMC (see above).[143]

Note that dibenzylmercury was detected among the products of the Co^{II}(salen)-catalyzed ER of benzyl chloride at mercury; however, the addition of diphenylphosphine (a proton donor) led to the disappearance of OMC from the reaction mixture.[209] The latter can also be explained by the acid-catalyzed degradation of organomercury intermediates. For solutions of 1-bromobut-2-ene, iodo-, bromo- and dibromobenzenes, the peaks in voltammograms corresponding to electrode reactions of organomercury intermediates disappeared even in the presence of a proton donor such as phenol.[128, 129] The proton donor-mediated (AcOH) degradation of organometallic intermediates [$AlkNi^{II}$(salen)] at the electrocatalytic reduction of dihalobutanes and halohydrins at Hg and GC electrodes was postulated.[259]

In weakly acidic solutions ($5 \leqslant pH \leqslant 7$), the electroreduction of 3,6-bis(dimethylamino)acridine and 3,6-diamino-10-methylacridinium chloride was accompanied by the fast degradation of intermediate OMC (presumably,[178] polymercurides) and the evolution of H_2. However, for unsubstituted acridine, the ER was slower. Thus, a chronammogram of this compound (for $c_0 \geqslant 2 \times 10^{-4}$ mol litre^{-1}) demonstrated two peaks:[174] the first peak was ascribed to the ER of OMC formed from the monolayer, whereas the second peak corresponded to the ER from the next layers. At pH 1.17, the height of the second peak was considerably lower than at pH 4, although did not disappear altogether. In other cases, for example, at the chemisorption of diphenyl selenides on a mercury electrode, pH (in the range of 4.6–9.1) had virtually no effect [97] on the formation of OME polylayers.

It is possible that the stabilization of $[RHg_{ads}]_n$ (the intermediate in the electroreduction of RHgX adsorbed on a monolayer) could inhibit acid-catalyzed degradation. Note that many scientists hypothesized the presence of such stabilization at a mercury electrode surface (*e.g.*, see Ref. 4). According to Willett and Peters,[60] in the course of desorption of the decylmercury radicals from the electrode surface, like other acyclic and alicyclic mercury-containing radicals,[171] they underwent very fast demercuration (in $\leqslant 10^{-8}$ s) [see step (5) in Scheme 1]. Note that for the case where quasiequilibrium was established between $[RHg_{ads}]_n$ and R_2Hg (R = Pr) in the monolayer [see steps (6a), (6b) in Scheme 1], such stabilization was substantiated at a quantitative level (see Section III and Ref. 124). Photodecomposition of organometallic (particularly, organolead) compounds also proceeded faster in the bulk of the solution as compared with the Pd electrode surface.[233]

It was shown [90] that the adsorption of perfluoro-n-hexyl iodide on a polarized mercury electrode ($DMF + LiClO_4$; Bu_4NClO_4) afforded n-$C_6F_{13}HgI$, its one-electron ER produced (n-$C_6F_{13})_2Hg$. In turn, with halides (LiCl, LiBr, LiI, Bu_4NI) as the supporting electrolytes, the reduction of n-$C_6F_{13}I$ to n-$C_6F_{13}H$ occurred. These results were explained [90] by the different effects of the adsorption of components of this system on the ER mechanism. For example, whereas the halide ions were adsorbed in the vicinity of the zero-charge potential and displaced organomercury intermediates from the dense part of the electric double layer, they could be decomposed in the bulk by the mechanism described above. Using the method of hidden limiting currents, it was shown [206] that the Li^+ cations also affected (albeit weaker) the ER of chloroform like H_3O^+.

The described reactions of acid-induced degradation of mercury-containing intermediates could undoubtedly complicate the procedure of preparative electrolysis. Particularly, acidification of solution is hardly a reliable method for intensifying the synthesis of R_2Hg compounds from RHgX. Moreover, the electrolyte composition should be selected more carefully, because the nature of the supporting electrolyte anion has a great effect on the process. In turn, the acid-catalyzed degradation of OMC under mild conditions can prove to be efficient even for chemically stable RHgX salts, especially where R is a substituted aryl. Such reactions of 'electrochemical protodemercuration' (or, taking into account the data from Ref. 259, 'protodemetallation') of intermediates played the important role in the chemistry of organometallic compounds.

VI. Adsorption and structural effects in electrode reactions of organomercury compounds

The electrochemical transformations of RHgX, RHgR′ (R = R′; R ≠ R′) were often accompanied by different adsorption effects associated with the high adsorption activity of many OMC (R_2Hg, RHgR′) and also with considerable differences in the adsorbability of RHgX and organomercury intermediates. First of all, this concerns the electrode surface blockage that results in hindering of the electrode reaction and also in its autoinhibition by the depolarizer (the intermediate or final product of its chemical reaction with the electrode) or by the unsoluble film formed by ER products.

The products of the first step of the polarographic reduction of PhHgX salts are known [52] to block the electrode surface. This was manifested by violation of the linear dependence of the limiting current on the depolarizer concentration,[52] the appearance of maxima, adsorption pre-waves (usually for $c_0 \geqslant 10^{-3}-10^{-4}$ mol litre^{-1}) (see Refs 36, 52, 54, 97–99) and the deformation of *I vs. t* curves (see Refs 55, 124, 174, Fig. 13). The electrode surface blockage could also manifest itself as oscillations in the second wave [52] or a 'reverse' peak in the CV anodic branch.[36, 84, 241, 251] The blockage often shifted the electroreduction potentials of R_2Hg_2 ($[RHg_{ads}]_n$) and R_2Hg to more negative values.[111, 192] 'Reverse' peaks in the CV method are the analogues of polarographic maxima [241] being associated with the adsorption of intermediates of the electrode process, which results in the mercury surface motion. Localization of such peaks in the potential range of the second step (Fig. 14) was associated with the adsorption of organomercury intermediates.[36, 84, 60] Such peaks were observed in solutions of organic halides that formed OMC at the ER of, *e.g.*, triphenylcyanopropylphosphonium bromide,[251] bromoalkanenitriles [267] or iododecane.[241] However, these peaks disappeared with the increase in the scan rate [241] or in the presence of a suppressor of peaks such as Triton X-100.[36] The adsorption of $[RHg_{ads}]_n$ intermediates

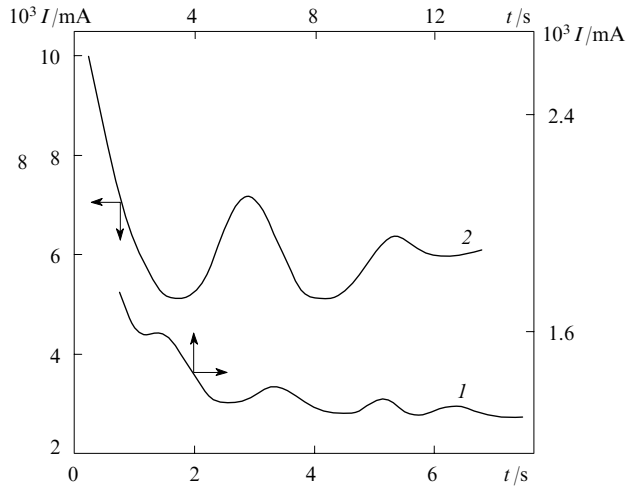


Figure 13. *I vs. t* curves recorded in the potential range corresponding to the plateau of the first electroreduction wave of 2.2×10^{-4} (*1*) and 7.3×10^{-4} mol litre^{-1} (*2*) PrHgOAc.[124]
A 0.9 mol litre^{-1}solution of NaOAc in aqueous ethanol (10 vol.% EtOH) served as a supporting electrolyte.

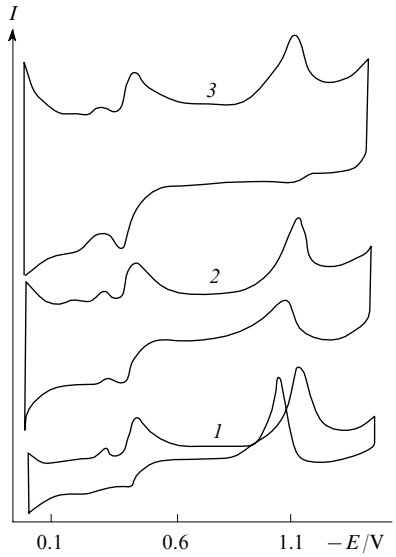


Figure 14. Cyclic voltammograms of the mercury electrode recorded in 2×10^{-4} mol litre^{-1} $MeHgNO_3$ solution containing 0.01 mol litre^{-1} $HClO_4$, pH 3.8,[84] with potential scan rates of 0.05 (*1*), 0.2 (*2*), 0.5 (*3*) V s^{-1} (http://electroanalytical.org/SEACcom/SEACcom-nov88.pdf).

could inhibit both the first and the second steps of RHgX electroreduction.[54]

In the electrosynthesis of bis(3,4,5-tribromo-2-thienyl)-mercury from tetrabromothiophene, the process was completely blocked upon the formation of a monolayer. The blockage was removed[285] with the addition of an acid (HBr). However, the monolayer coverage with the mercury-containing final or intermediate product sometimes did not prevent the electrosynthesis,[97, 98, 117, 118] although could result in its deceleration (for example, as in the anodic synthesis of mercury alkoxides[288]). The adsorbed monolayer affected neither the formation of [PhSeHg] and [PhTeHg] phases[97, 98] nor the electrode reactions of the $Ru(NH_3)_6^{3+/2+}$ redox pair.[97] In turn, the condensed [PhSeHg] phase inhibited the ER of components of this redox pair and completely blocked their oxidation.

The method of *I vs. t* curves makes it possible to elucidate whether the reaction occurs on the adsorbate blocked surface. The distortions in *I vs. t* curves at the foot of the second ER wave of pyridyl- and thienylmercuric acetate were explained as early as in 1968 by Degrand and Laviron[55] by the adsorption of R_2Hg, the final product of the first step of RHgX electroreduction. Similar results were obtained for PhHgX salts[52] and mercury derivatives of acridine.[174] It was demonstrated[143] that non-linearity of initial segments of *I vs. t* curves for *N*-methyl(ethyl)-pyridinium, quinine and keto derivatives of adamantane was also due to the chemisorption of a mercury-containing intermediate (see Section V). Curves *I vs. t* measured at the plateau potentials of the first ER wave of PrHgOAc (see Fig. 13)[124] pointed to the depolarizer diffusion complicated by tangential motions of the mercury drop.

The data obtained from experimentally measured electrocapillary[36, 54, 78, 79, 99] and *I vs. t* curves and differential capacitance[118] also pointed to the considerable surface activity of $[RHg_{ads}]_n$ intermediates. As to the adsorption of the RHgX depolarizer itself and its final electroreduction product RH, several scientists[54, 79] considered the adsorption contribution as insignificant at both the potentials before the first wave of RHgX reduction and the limiting current of the second wave. However, a considerable decrease in the surface tension of mercury or in its differential capacitance was observed in solutions of MeHgX,[78] EtHgX,[79] PrHgX and C_6F_5HgX (Ref. 118) just at the potentials preceding the first wave. For the majority of AlkHgX and ArHgX salts studied,[109, 110, 123] the electrode surface coverage (θ) was $\sim 0.1-0.3$. No considerable decrease in the mercury surface tension and differential capacitance was observed for potentials more negative than those of R_2Hg desorption and $[RHg_{ads}]_n$ reduction, which pointed to the low surface activity of these hydrocarbons (AlkH, ArH), the final electroreduction products of RHgX, Alk_2Hg and Ar_2Hg.[78]

If the one-electron ER of a depolarizer with the higher solubility c_1^* (including RHgX) afforded a product with the lower solubility c_2^* (*i.e.*, $c_1^* > c_2^*$), then the formation of a condensed near-electrode phase was possible. The latter often consisted[117–119] of the reduction products (R_2Hg), intermediates ($[RHg_{ads}]_n$) or their mixtures[109, 110, 124] (provided the lifetimes of these intermediates were sufficiently long).[174] The solubility of AlkHgX in aqueous salt media was usually $10^{-3}-10^{-4}$ mol litre^{-1} (Ref. 289), whereas for $[RHg_{ads}]_n$ this value was at least one order of magnitude smaller.[124] 'Organic calomels' such as XHgHg(X′HgHg)R (see Section III) proved to be virtually insoluble in all known solvents.[173] Diacridinedimercury[174] and substituted alkylaminoacridines[178] were also insoluble in EtOH, chloroform, hexane, DMF and diethyl ether. Only methylpyridinium salts MePyHgHgX dissolved in many organic solvents.[18]

Obviously, not only the products adsorbed in the first step but also the condensed phase should affect the kinetics of RHgX electroreduction. Chronopotentiometric studies have shown[110, 123, 124] that for PrHgOAc with $c_0 \geqslant 4 \times 10^{-4}$ mol litre^{-1}, the near-electrode layer was saturated with R_2Hg and $[RHg_{ads}]_n$. As a result, the signals (delays) corresponding to both ER of RHgX and EO of $[RHg_{ads}]_n$ were split,[110, 124] in analogy with the appearance

of a polarographic prewave. Such 'pre-delays' (or 'pre-peaks' in CV[84,128]) of the adsorption nature were observed fairly often in the RHgX electroreduction (see Fig. 14). They were also observed during the ER of mercury ions [*e.g.*, Hg^{2+} (Ref. 270)], where the first peak ($\sim$0.1 V) was of the adsorption nature and the second (at $E \leqslant 0.1$ V) corresponded to the ER of these ions diffusing from the bulk.[270] For RHgX, the analogous peak (and all the rest peaks) was also of the diffusion nature and corresponded to redox transformations of the depolarizer localized in the bulk of the solution.

Using the CV method and chronopotentiometry with current reversal, it was found[108] that for $c_0 \geqslant 10^{-4}$ mol litre^{-1} the ER signal of the $PhHg^+$ cation split into two signals, namely, of the adsorption (1*A*) and the diffusion (1*B*) nature (Fig. 15). The current reversal after (or in the middle) of any signal led to the appearance of an anodic delay, which, taking into account certain results,[109,110] could be attributed to the Ph_2Hg desorption. Note that the current density values[108] ($\leqslant$1 mA cm^{-2}) were too low to reveal the Ph_2Hg_2 oxidation on the electrode[110] because the 'organic calomel' lifetime was $\sim 10^{-4}$ s (see Table 1). It is most likely that $PhHg^{\bullet}$ radicals formed in delay 1*A* were lost faster to form electrochemically inactive Ph_2Hg, whereas in delay 1*B*, the rate of their loss was much lower (this assumption is equivalent to that of stabilization of the intermediate by the electrode surface,[60,232] see Section V).

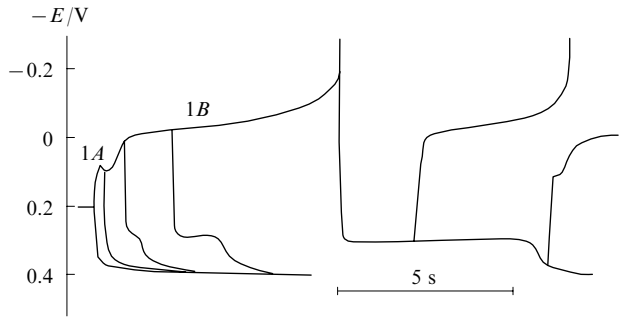


Figure 15. Chronopotentiograms of mercury electrode measured by a galvanostatic method with the current reversal in 8.9×10^{-4} M PhHgOH solution.[108]
i = 0.1 mA cm^{-2}, t_p = 1 min.

At sufficiently high currents or prolonged potentiostatic polarization ($t_p \geqslant 1-3$ min), a minimum $\sim$0.05 V deep appeared in delay 1*A* (see Fig. 15) and the charging curve changed its shape (as well as the VA curve); delays 1*A* and 1*B* merged together at potentials of delay 1*B*,[108] which, in our opinion, was due to the changes in the structure of the near-electrode condensed phase. This kind of structural changes that manifested themselves in the unusual shape of the second ER peak of RHgX (5-mercuriouridine di- and triphosphates) typical of two-dimensional nucleation were described.[104] As the example, the adsorption behaviour of double-decker sandwich organomercury heterocomplexes such as $C_4R_4CoC_5(HgX)_5$ (R = H, COOEt; X = SMe, SCOMe, *etc.*) can be mentioned.[290] Their ER in the positive potential range at a mercury electrode afforded a dense layer that had the compact structure and was stable due to the strong adhesion of HgX fragments to the surface and lateral interactions. The relatively slow formation of such a layer was accompanied by a phase transition; its destruction took place at the zero charge potential.

With the increase in t_p, the parallel growth of the VA peak height analogous to peak 1*B* in $10^{-3}-10^{-4}$ M solutions of PhHgX (X = NO_3, OAc)[128] and n-$C_{10}H_{21}HgI$; n-$C_{10}H_{21}Br$ was observed[60] as well as at the formation of multilayers of mercurated polyuridine derivatives poly(U−Hg)X.[105] The latter case is of special interest. For $t_p < 1-2$ s, the voltammograms of poly(U−Hg)X demonstrated a single peak of two-electron reduction of this compound. However, when the polarization time reached several minutes, the second peak appeared at potentials $\sim$0.4 V more positive and grew with the increase in t_p, whereas the second peak height ceased to change. Presumably,[105] the second peak was due to the reduction of multilayers formed by the depolarizer as the latter underwent slow structural changes induced by coordination interactions of polyuridine substituents within the layer. However, the reduction of the Hg(II)−Poly$(U)_{ads}$ complex corresponded to a single broad peak with the height (Q) several orders of magnitude larger as compared with the monolayer value.

Using the chronopotentiometric method, it was shown[117] that in the first step the electroreduction of 2-acetyl-5-thienylmercuric bromide [*i.e.*, for $E^{(1)}_{1/2} > E_{in} > E^{(2)}_{1/2}$] under potentiostatic conditions produced the condensed phase of poorly soluble bis(2-acetyl-5-thienyl)mercury. This phase was reduced together with the adsorbed monolayer in the only delay with the duration ($i\tau$). The latter increased at low i with the decrease in the current density and, with the increase in t_p, increased by a nonlinear law virtually with no limit. The condensed phase of perfluorodiphenylmercury formed in the electroreduction of C_6F_5HgBr (Ref. 118) under the same conditions and by the analogous mechanism [reaction (41a)][119–121]

$$C_6F_5HgBr + e \rightleftharpoons C_6F_5Hg^{\bullet} + Br^- \quad (E^{(1)}_{1/2} = -0.02 \text{ V}), \tag{39}$$

$$C_6F_5Hg^{\bullet} \xrightarrow{e,\ BH^+} C_6F_5H + Hg + B \quad (E^{(2)}_{1/2} = -0.31 \text{ V}) \tag{40}$$

$$C_6F_5Hg^{\bullet} \xrightarrow[(a)]{C_6H_5Hg^{\bullet}} Hg + (C_6F_5)_2Hg \xrightarrow[(b)]{2e,\ 2BH^+} \tag{41}$$

$$\longrightarrow 2\,C_6F_5H + Hg + 2\,B \quad (E_{1/2} = -1.1 \text{ V}),$$

could be reduced [in contrast to the condensed phase of bis(2-acetyl-5-thienyl)mercury[117]] in either single or two delays, with the monolayer being reduced at more positive potentials (see Section II). The fact that at $\theta \to 1$, in contrast to many analogous cases, no complete blockage of the ER of perfluorodiphenylmercury occurred pointed to the formation of a sufficiently loose monolayer (as in the ER of diphenyl diselenides[97]).

For low i (irrespective of the C_6F_5HgBr concentration) in all the cases, only delay *1* was observed[118,119] (see Fig. 4), which corresponded to co-reduction of the monolayer and the near-electrode condensed phase. This delay is shortened with the increase in i (curve *1*). At more negative E, delay *2* appeared (curve *2*), became wider with the increase in i, passed through a maximum and vanished. In this range of current, delay *1* is shortened approximately to values typical of the monolayer and then no longer depended on i. Such dependences by and large retained their qualitative similarity for the majority of inorganic salts as supporting electrolytes.[119,120]

At low i, the delay corresponding to the ER of the perfluorodiphenylmercury condensed phase also demonstrated the non-linear and virtually infinite increase with the increase in t_p (see Fig 12, curves *2*, *3*, *5*), the same as for the ER of bis(2-acetyl-5-thienyl)mercury.[214] However, in some cases, almost linear Q *vs.* t_p dependences were obtained by the CV method (mercury complexes with polyuridinic acids[105]).

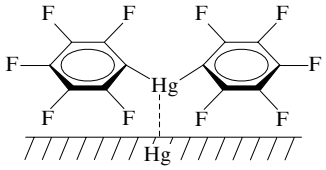
Mercury sulfides formed upon the adsorption of thiols RSH (RSH is 1-benzyltetrazole-5-thiol,[254] 6-propyl-2-thiouracil[255]) on the Hg electrode in the anodic region also produced a condensed phase, but the monolayer was reduced at more negative potentials.

In certain cases, a uniform phase was formed. Thus in the formation of organic amalgams such as Me_4P-Hg and $Me_2Py(Hg_5)$ at a mercury electrode, first their monolayer was formed ($i\tau = 43-46.5$ μC cm^{-2}) to be later transformed into a three-dimensional structure.[291]

In electrochemistry of organic (particularly, organometallic) compounds, the cases are known where poorly soluble or altogether insoluble ER/EO products formed. Hence, the differences in the solubility of the starting compounds and products were often exploited in industrial[1,9] or preparative[2,3] electrosyntheses of organometallic compounds. In addition to RHgX, the condensed phases were typical of mercury-containing polymers formed in the reduction of $RHal_2$ [R = Me,[136] cyclo-C_6H_{11} (Refs 134, 135)] and R_nMX_{m-n} salts (M = Sn, Tl, Si, Ge, Pb, *etc.*[1-3,8]). Complexes of Hg(II) alkoxides/glycolates with 1,10-phenanthroline and 2,2 -bipyridyl, which were synthesized at a sacrificial mercury anode[292] and possessed presumably the polymeric structure, turned out to be altogether insoluble in conventional organic solvents. In addition to the easy of isolation of final products, this synthetic method[288,292] also provided high yield of the target compounds.

The differences in the adsorbability of the first-step ER products were especially big for organotin compounds. For example, the adsorption of n-$C_{10}H_{21}HgBr$ in anhydrous DMF was $\Gamma_\infty \approx 4.1\times10^{-11}$ mol cm^{-2} and, for its reduction intermediate, ($[RHg_{ads}]_n$), $\Gamma_\infty \approx 8.3\times10^{-10}$ mol cm^{-2} (Ref. 60), whereas under the same conditions, the adsorption of $R_2Sn^{\bullet}$ radicals (or R_4Sn_2 dimer) was almost an order of magnitude higher as compared with R_2SnCl_2 and the electrode surface was blocked with the inactive dimer formed (particularly, Ph_6Sn_2, see Ref. 3) up to the potentials of the supporting electrolyte discharge.

For symmetrical OMC, in the general case, the high surface activity was characteristic not only at a mercury electrode but also on amalgams, for example, the same as for di(β-cyanoethyl)mercury on indium(55 mass %)–gallium alloys.[116] In addition to the mentioned compounds, mercury dimethyldithiocarbamate complexes deserve mention.[272] The adsorbability was quantitatively characterized by the Damaskin–Stenina–Fedorovich criterion,[293,294] namely, the sum ($\ln B + a$), where B is the adsorption equilibrium constant and a is a constant that Frumkin referred to as an 'attraction constant'. This criterion[293] is widely used in assessing the adsorbability of miscellaneous substances.[121,294] Considering the adsorption characteristics of OMC by the example of two representative compounds containing strongly polar groups, *i.e.*, perfluorodiphenylmercury[115,120,121] and di(β-cyanoethyl)-mercury,[116,126] mention should be made of the high attraction constant (1.82) for perfluorodiphenylmercury (E = 0 V) (Ref. 120) and 0.92 for di(β-cyanoethyl)mercury ($E = -0.6$ V).[126] These compounds are adsorbed flatly on the electrode and can contact one another only with either fluorine atoms (perfluorodiphenylmercury[118]) or still more electronegative cyanoethyl groups [di(β-cyanoethyl)mercury],[126] which should result in repulsion of adsorbed molecules rather than in their attraction. In such orientation, mercury atoms could interact with the electrode material rather than with one another, *i.e.*, through the molecule–electrode interactions or the 'classical' pair coupling between adsorbate molecules but transferred through the electrode metal.



Insofar as due to the presence of the coordinatively unsaturated mercury atom,[11,14,154] R_2Hg molecules could form complexes with different ligands (see Section II), it can be expected for the complex to disintegrate upon the adsorption and for the Hg atom to form a bond of the coordination type with the electrode material.

It is probable that for more negative substituents in the organometallic molecule and more positive central metal atom the stronger interactions of such a kind could arise.[120,121] In this case, a can depend on the potential, *i.e.*, with its increase, the electrostatic component of the electrode metal–metal in the molecule interaction could increase (incongruence of the isotherm with respect to potential), as observed[126] for di(β-cyanoethyl)mercury, where a varied from 0.92 to 1.77 in the potential range of $-(0.6-1.3)$ V. These factors in aggregate (including the low solubility of perfluorodiphenylmercury[115,118]) were arguably attributed[121] to the anomalously high value (14.33) of the Damaskin–Stenina–Fedorovich criterion for this compound. It is noteworthy that for much better soluble di(β-cyanoethyl)mercury, this criterion was also large, *i.e.*, 11.64 in the vicinity of the zero charge potential.[126]

Thus, the range of weak interactions in the adsorption layer was probably wider[121] than assumed earlier and a could depend on some other factors besides the pair interactions.

The adsorption characteristics of symmetrical OMC had a substantial effect on the kinetics of their electrode reactions. Thus for the ER of di(β-cyanoethyl)mercury at indium amalgams,[116] αn_a smoothly decreased from 0.55 to 0.30 as the indium content increased from 0 at.% to 67.8 at.%. The formation of an R_2Hg complex with the electrode material was also postulated;[116] the latter dependence was due to the proportional decrease in the coefficient of partial charge transfer at the adsorption, namely, the higher the coefficient the lower charge n_a transferred in the slow electrochemical step, because it is unlikely for α to depend on the electrode material.

From the dependences of the electron transfer rate on the adsorption (*i.e.*, on the electrode surface coverage) of perfluorodiphenylmercury, bis(phenylethynyl)mercury and di(β-cyanoethyl)mercury,[114,116,119] it follows that the ER reactions of these OMC were unimolecular with the effective reaction order close to zero (probably due to the strong intermolecular interactions in the adsorption layer). The electron transfer rate for $\theta \to 1$ usually decreased.

Thus, the ER of a considerable number of OMC is complicated by adsorption phenomena, including the formation of condensed phases on the electrode surface, which substantially affected the kinetics of electron transfer and the mechanisms and rates of near-electrode reactions.

VII. Determination of organic and inorganic mercury compounds using electrochemical methods

In the early stages of the development of OMC electrochemistry, the studies of the electrochemical behaviour of these compounds were associated with the demands for elaboration of electrochemical methods of their analysis, first, polarographic and, then, voltammetric techniques (*e.g.*, see Refs. 78, 79). However, by the 1950s, it became clear that the mechanisms of reactions of mercury-containing compounds are very complicated, especially, at a mercury electrode. This conclusion seems obvious, taking into account numerous decisive factors, particularly, adsorption, acid-catalyzed transformations of OMC and their intermediates and also the kinetics of inter-transitions 'organic calomel' – R_2Hg symmetrical compounds. This should be taken into account in developing state-of-the-art electrochemical methods for the analysis of OMC.

Often, the necessity arose of the determination (simultaneous or selective) of OMC and inorganic mercury (Hg_2^{2+}, Hg^{2+}) (see Introduction); hence, the problems of their analysis should apparently be considered jointly. Enormous number of publications were devoted to the determination of OMC and inorganic mercury derivatives using different methods (including electrochemical [78–88, 270, 271, 295–396]) and their number still continues to increase. Thus it was reported [295] that from 1967 to 1995 alone, ~10 000 studies were published and no less than 5000 publications appeared over the past 15 years (from 1995 to February, 2010) [information from ISI Web of Science (http://apps.isiknowledge.com)].

Now, the most efficient methods for the determination of such compounds are as follows (Table 3): atomic absorption, luminescence or X-ray fluorescence spectroscopy, mass spectrometry and inductively coupled plasma optical emission spectroscopy, neutron-activation analysis, different types of chromatography (the latter, as was noted,[326] proved to be not very convenient for the determination of total mercury, in contrast to neutron-activation analysis used for this very purpose [295]). However, these methods are very time-consuming, require expensive equipment and lengthy procedures of sample pre-treatment. At the same time, some of them are insufficiently selective, *e.g.*, spectroscopy [295] (especially for samples containing heavy metal ions). This is why the joint use of some of these methods is recommended. For example, gas chromatography together with cold vapour atomic absorption spectroscopy are highly efficient [295] in the co-determination of monomethylmercury, inorganic mercury and also of their overall content in biological objects [the detection limit was 6×10^{-10} and 13×10^{-10} g litre^{-1} for Hg(II) and monomethylmercury, respectively].

It is believed that the electroanalytical methods of OMC determination [78–88, 301, 323, 327–335] (Table 4), including those exploiting enzyme electrodes,[319, 322, 326–331] sensors [298, 331, 332, 376] or in combination with other methods (for instance, with chromatography,[295, 321–323, 326] capillary electrophoresis,[324, 325, 334, 335] atomic absorption spectroscopy,[295, 377] cold vapour atomic absorption spectrome-

Table 3. Potential of electrochemical and non-electrochemical methods of analytical determination of OMC and Hg(II).

Analyte	Determination method	Detection limit	Linearity range of concentration dependence	Ref.
Hg^{2+}	cyclic voltammetry	4 μg litre^{-1}	10 – 50 μg litre^{-1}	80
$MeHg^+$	the same	10 μg litre^{-1}	10^{-4} – 10^{-7} mol litre^{-1}	78
		2 μg litre^{-1}		80
		4.5×10^{-11} mol litre^{-1}	$(10 – 250) \times 10^{-9}$ mol litre^{-1}	82
MeHgCl	"	5.6×10^{-7} mol litre^{-1}	$(5 – 250) \times 10^{-6}$ mol litre^{-1}	83
Hg^{2+}	voltammetry	3.2 μg litre^{-1}	10 – 200 μg litre^{-1}	299
		0.1 μg litre^{-1}	0.5 – 4.5 μg litre^{-1}	300
EtHgCl	AC sinusoidal voltammetry	10^{-7} mol litre^{-1}	10^{-3} – 10^{-7} mol litre^{-1}	94
MeHgCl	stripping voltammetry	2×10^{-8} mol litre^{-1}	$(2 – 8) \times 10^{-7}$ mol litre^{-1}	301
		0.49 μg litre^{-1}		87
		0.2 μg litre^{-1}		88
Hg^{2+}	the same	3.4×10^{-10} mol litre^{-1}	10^{-8} – 10^{-9} mol litre^{-1}	302
		3×10^{-12} mol litre^{-1}	3×10^{-12} – 10^{-8} mol litre^{-1}	303
		0.40 μg litre^{-1}	1 – 5 μg litre^{-1}	304
		1.5×10^{-4} μg litre^{-1}	0.01 – 50 μg litre^{-1}	305
		0.12 μg litre^{-1}	1 – 8 μg litre^{-1}	306
		5×10^{-11} mol litre^{-1}	$(0.2 – 400) \times 10^{-9}$ mol litre^{-1}	307
		0.005 μg litre^{-1}	0 – 50 μg litre^{-1}	308
		0.06 μg litre^{-1}	0.1 – 250 μg litre^{-1}	309
		0.012 μg litre^{-1}	0.05 – 1 μg litre^{-1}	310
	differential pulse anodic stripping voltammetry	1 μg litre^{-1}	5 – 1000 μg litre^{-1}	311

Table 3 (continued).

Analyte	Determination method	Detection limit	Linearity range of concentration dependence	Ref.
Hg^{2+}	stripping chronopotentiometry	0.080 μg litre^{-1}	0.02 – 200 μg litre^{-1}	312
		0.005 μg litre^{-1}	38 – 154 μg litre^{-1}	313
		10^{-4} μg litre^{-1}	0.005 – 30 μg litre^{-1}	314
	stripping chronopotentiometry with coulometric detection	1 μg litre^{-1}	1 – 1000 μg litre^{-1}	315
Hg^{2+}, PhHgX	potentiometry	4×10^{-6} mol litre^{-1}	1 – 200 μg litre^{-1}	316
Hg^{2+}	"	5×10^{-6} mol litre^{-1}	$(2 – 500) \cdot 10^{-6}$ mol litre^{-1}	317
	potentiometry with sorption preconcentration	10^{-8} mol litre^{-1}		318
Hg^{2+}, $MeHg^{+}$, $EtHg^{+}$	amperometry at enzyme electrodes	2 μg litre^{-1}	2 – 10 μg litre^{-1}	319
Hg^{2+}	colorimetry	1 μg litre^{-1}	—	295
	enzymatic methods [a]	3×10^{-6} μg litre^{-1}	$0.6 – 5 \times 10^{4}$ μg litre^{-1}	297
$PhHg^{+}$, $MeHg^{+}$	cold vapour atomic absorption spectrometry	0.001 – 0.0001 μg litre^{-1}		295
Hg^{2+}	the same	0.08 – 0.11 μg litre^{-1}		303
		5×10^{-5} μg litre^{-1}	5 – 40 μg litre^{-1}	303
		0.01 μg litre^{-1}		303
		0.008 – 0.012 μg litre^{-1}		310
	cold vapour atomic absorption spectrometry with stripping voltammetric detection	6.23×10^{-11} mol litre^{-1}		320
	fluorescence spectroscopy	$(1 – 2) \times 10^{-6}$ μg litre^{-1}		295
		$(2 – 5) \times 10^{-5}$ μg litre^{-1}		310
		0.080 μg litre^{-1}	0.2 – 6.2 μg litre^{-1}	303
$MeHg^{+}$, Et_2Hg	atomic absorption spectroscopy with electrothermal atomization	5×10^{-5} μg litre^{-1}		295
Hg^{2+}	the same	0.2 μg litre^{-1}	25 – 200 μg litre^{-1}	303
		1.1×10^{-4} μg litre^{-1}		295
	inductively coupled plasma	1.39 μg litre^{-1}		303
	atomic emission spectroscopy	0.5 – 4 μg litre^{-1}	10 – 1000 μg litre^{-1}	295
		10 μg litre^{-1}		303
	inductively mass spectrometry	3 μg litre^{-1}	5 – 20 μg litre^{-1}	303
	coupled plasma	0.008 μg litre^{-1}		295
	neutron activation analysis	1 μg litre^{-1}		303
MeHgCl, EtHgCl, PhHgCl	high-performance liquid chromatography	0.070 – 0.095 μg litre^{-1}		295
Hg^{2+}	the same	0.0035 μg litre^{-1}		295
Me, $PhHg^{+}$	"	0.0019 – 0.0025 μg litre^{-1}		295
MeHgCl, EtHgCl, PhHgCl	high-performance liquid chromatography with voltammetric detection	4×10^{-5} μg litre^{-1}		295
Hg^{2+}; MeHgCl, EtHgCl, PhHgCl	the same	$(8 – 19) \times 10^{-7}$ μg litre^{-1}		295
Hg^{2+}, MeHgCl, $EtHg^{+}$	"	1.2 – 1.8 μg litre^{-1}	2 – 1000 μg litre^{-1}	321
MeHgCl	"	5×10^{-8} mol litre^{-1}	10 – 120 μg litre^{-1}	322
Hg^{2+}; MeHgCl, EtHgCl, $PhHg^{+}$	"	8 – 10 μg litre^{-1}	20 – 1000 μg litre^{-1}	323
MeHgCl, EtHgCl, PhHgCl	gas chromatography	1 μg litre^{-1}		295
$MeHg^{+}$	gas chromatography with atomic absorption spectrometry	10^{-4} μg litre^{-1}		295
		5×10^{-5} μg litre^{-1}		295
	capillary electrophoresis with amperometric detection	3 μg litre^{-1}		324
		0.4 μg litre^{-1}	0.5 – 50 μg litre^{-1}	325
Hg^{2+}	the same	0.1 μg litre^{-1}	0.2 – 100 μg litre^{-1}	324
		0.005 μg litre^{-1}	0.01 – 1 μg litre^{-1}	325

[a] Horseradish peroxidase was used as the enzyme.

Table 4. Results of electrochemical analysis of organic and inorganic compounds of mono- and bivalent mercury.

Analyte	Determination method	Solution composition; analysis optimal conditions and possibilities; interfering impurities	Electrode/modifying agent	Detection limit; accuracy	Linearity range of concentration dependence	Ref.
Monomethyl-mercury	DP-polarography, CV	0.1 mol litre^{-1} $HClO_4$	HMDE	10 μg litre^{-1} (5×10^{-8} mol litre^{-1})	10^{-4}–10^{-7} mol litre^{-1}	78
EtHgCl	polarograpy, sinusoidal ac VA	0.1 mol litre^{-1} HNO_3; the Britton–Robinson buffer; separate determination of EtHgCl and PhHgCl	DME, HMDE	10^{-7} mol litre^{-1}	10^{-3}–10^{-7} mol litre^{-1}	94
Hg^{2+}	VA	HNO_3; 1 mol litre^{-1} HCl	Au ultramicroelectrode	3.2 μg litre^{-1} (1.6×10^{-9} mol litre^{-1})	10–200 μg litre^{-1} (10^{-8}–10^{-6} mol litre^{-1})	299
		0.05 mol litre^{-1} H_2SO_4; KI; As^{3+}, Cd^{2+}, Pb^{2+} (2 : 1) do not interfere with determination	SPAgE	0.1 μg litre^{-1}	0.5–4.5 μg litre^{-1}	300
Hg^{2+}, $MeHg^+$	CV	0.01 mol litre^{-1} KNO_3, 1 and 0.1 mol litre^{-1} HCl; HNO_3, H_2SO_4; pH 2–8; Na^+, K^+, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+}, Cu^{2+} do not interfere with individual determination of components (Hg^{2+}, $MeHg^+$, $EtHg^+$, $PhHg^+$)	carbon paste/ thiol resin Duolite GT-73 (30%)	4 μg litre^{-1}; 6–10% (Hg^+) 2 μg litre^{-1} ($MeHg^+$)	10–50 μg litre^{-1} (Hg^+) –	80 80
Hg^{2+}	CV, amperometry	pH 2–9; Ag^+, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+} do not interfere with determination, while Cu^{2+} ions interfere in less than tenfold excess	Pt	1.4×10^{-8} mol litre^{-1}; 2.2%	2×10^{-8}–3×10^{-6} mol litre^{-1}	336
$MeHg^+$	CV (single- and multipulse), square-wave VA	0.01 mol litre^{-1} $HClO_4$ + 0.2% HCl + 5% acetate buffer	GC, carbon paste/ Nafion®	4.5×10^{-11} mol litre^{-1}	$(10–250) \times 10^{-9}$ mol litre^{-1}	82
Thiomersal	CV, RDE	acetate buffer (0.1 mol litre^{-1}), pH 4;	GC	9 μg litre^{-1}; 2%–5%	50–100 μg litre^{-1}	81
Hg^{2+}	VA, square-wave and DP VA	0.05 mol litre^{-1} $HClO_4$; 0.01 mol litre^{-1} HNO_3, pH 2; Zn^{2+}, Pb^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+}, Fe^{3+}, Cu^{2+}, EDTA ($< 10^{-6}$ mol litre^{-1}), Cl^- ($< 10^{-4}$ mol litre^{-1}) do not interfere with determination	Pt	$(1–1.2) \times 10^{-8}$ mol litre^{-1}; 6%–7%	5×10^{-7}–4×10^{-8} mol litre^{-1}	337
	CV, square-wave VA	0.2 mol litre^{-1} NaCl (KCl, $LiClO_4$, NaOAc); Britton–Robinson buffer, pH 2 (2–8); Zn^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+} in tenfold excess do not interfere with determination	carbon paste/ cryptofix, bentonite, C18	0.12 μg litre^{-1}; 1.7%	0.16–0.4 μg litre^{-1}	338
MeHgCl	fast scan CV	1 mol litre^{-1} HCl; tenfold Hg^{2+} excess do not interfere with determination	thin Hg layer on Pt	5.6×10^{-7} mol litre^{-1}; 3%–10%	$(5–250) \times 10^{-6}$ mol litre^{-1}	83
	the same	0.1 mol litre^{-1} HCl	thin Hg layer on carbon fibre		75–300 μg litre^{-1}	85
	fast scan CV, RDE	0.1 mol litre^{-1} HCl or NaCNS; Cd^{2+}, Hg^{2+} and Cl^- (< 0.5 mol litre^{-1}) do not interfere with determination, Pb^{2+} partially inhibits ER of $MeHg^+$	thin Hg layer on GC, carbon fibre or Pt	$< 10^{-9}$ mol litre^{-1}; 3–10%	$(1–100) \times 10^{-9}$ mol litre^{-1}	86

Table 4 (continued).

Analyte	Determination method	Solution composition; analysis optimal conditions and possibilities; interfering impurities	Electrode/modifying agent	Detection limit; accuracy	Linearity range of concentration dependence	Ref.
MeHgCl	DP ASVA	0.1 mol litre^{-1} HNO_3, 0.1 mol litre^{-1} $NaNO_3$; pH 1–11; Hg^{2+} excess does not interfere with determination	~2 Au monolayers on GC support	2×10^{-8} mol litre^{-1}	$(2-8)\times10^{-7}$ mol litre^{-1}	301
Hg^{2+}	the same	0.1 mol litre^{-1} HNO_3, 0.1 mol litre^{-1} $NaNO_3$; pH 1–11; K^+, NH_4^+, Ag^+, Zn^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Sn^{2+}, Ni^{2+}, Cu^{2+} Bi^{3+}, Fe^{3+}, Cr^{3+} do not interfere with determination	carbon paste	5×10^{-9} mol litre^{-1}	$2\times10^{-6}-8\times10^{-9}$ mol litre^{-1}	298, 327
		0.1 mol litre^{-1} HNO_3, 0.02 mol litre^{-1} KCl; $AuCl_3$; Au deposition *in situ*	Au film on carbon paste	0.05 μg litre^{-1} (2.5×10^{-10} mol litre^{-1})	0.2–50 μg litre^{-1} ($10^{-9}-2.5\times10^{-7}$ mol litre^{-1})	339
		0.1 mol litre^{-1} HCl + 0.02 mol litre^{-1} KI	multi-walled carbon nanotubes on GC	2×10^{-10} mol litre^{-1}; 6%	$8\times10^{-10}-5\times10^{-7}$ mol litre^{-1}	340
		0.1 mol litre^{-1} $HClO_4$ + 3×10^{-3} mol litre^{-1} HCl; Cu^{2+} and Pb^{2+} (< 30 μg litre^{-1}) do not interfere with determination	Au film	0.12 μg litre^{-1}; < 5%	1–8 μg litre^{-1}	306
		0.1 mol litre^{-1} H_2SO_4 + 0.01 mol litre^{-1} HCl	GC/calixarene	0.04 μg litre^{-1} (~2×10^{-10} mol litre^{-1})	0.07–40 μg litre^{-1}	341
		0.1 mol litre^{-1} NaH_2PO_4, Na_2HPO_4, NaCl, Na_3PO_4, $NaNO_3$, NaI, HOAc, citric and tartaric acids; pH 1–6; Hg^{2+}, Me and Et_2Hg do not interfere with determination	carbon paste/ SWy-2 [a]	10^{-10} mol litre^{-1}; 2.6%	$10^{-9}-5\times10^{-7}$ mol litre^{-1}	342
		0.01 mol litre^{-1} KCl + 0.02 mol litre^{-1} H_2SO_4; pH < 5	SPCE/pcPVP [b]	0.003 μg litre^{-1}	0.025–0.15 μg litre^{-1}	343
Hg_2^{2+}	DP ASVA, VA, CV	0.1 mol litre^{-1} acetate buffer, pH 5; Zn^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+}, Co^{2+}, Ba^{2+}, Al^{3+}, Mg^{2+}, Ti^{2+}, Mn^{2+}, Cr^{3+} do not interfere with determination	GC/TP [c]	2×10^{-6} mol litre^{-1} (VA), 8×10^{-8} mol litre^{-1} (DP ASVA)	$10^{-6}-2\times10^{-7}$ mol litre^{-1}	344
Hg^{2+}	the same	0.5 mol litre^{-1} NaCl + 0.1 mol litre^{-1} acetate buffer, pH 4.5; 1000-fold excess of Cu^{2+} does not interefere with determination	SPCE/resin Sumichelate Q10R	1.2×10^{-11} mol litre^{-1}	$(1-10)\times10^{-9}$ mol litre^{-1}	345
		(0.01–1) mol litre^{-1} NaCNS; pH 3.4–3.8	GC	5×10^{-14} mol litre^{-1}	$5\times10^{-14}-3\times10^{-13}$ μg litre^{-1}	346
		0.1 mol litre^{-1} HCl	Au ultramicroelectrode on Ir	0.5 μg litre^{-1}	10–180 μg litre^{-1}	347
		0.1 mol litre^{-1} $HClO_4$ + 0.0025 mol litre^{-1} HCl	Au	0.05 μg litre^{-1}	1–20 μg litre^{-1}	348
		0.1 mol litre^{-1} $HClO_4$ + $(2.5-5.0)\times10^{-3}$ mol litre^{-1} HCl + $(2-5)\times10^{-7}$ mol litre^{-1} $HAuCl_4$	carbon fibre UMV-30	5×10^{-10} mol litre^{-1}	$10^{-10}-10^{-7}$ mol litre^{-1}	349
		$NaClO_4$, Ag^+, Pb^{2+}, Fe^{3+} do not interfere with determination	Pt/PVF^+ (see [d])	5×10^{-10} mol litre^{-1}; 6%	–	350
		0.1 mol litre^{-1} $HClO_4$ + 0.03 mol litre^{-1} HCl; Ag^+ in 10-fold, Cu^{2+}, Zn^{2+}, Pd^{2+}, Pb^{2+}, Au^{3+}, Pt^{4+} in 1000-fold excess do not interfere with determination	Au Film on GC, graphite	0.46 μg litre^{-1}; 6%	0.8–32 μg litre^{-1} ($10^{-9}-4\times10^{-8}$ mol litre^{-1})	351

Table 4 (continued).

Analyte	Determination method	Solution composition; analysis optimal conditions and possibilities; interfering impurities	Electrode/modifying agent	Detection limit; accuracy	Linearity range of concentration dependence	Ref.
Hg^{2+}	DP ASVA, VA, CV	0.1 mol litre^{-1} H_2SO_4 + 0.004 mol litre^{-1} HCl; pH 1; Tl^{+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Al^{3+}, Bi^{3+}, Cr^{3+}, Sn^{4+}, V^{5+}, Mo^{6+} in 1000-fold excess do not interfere with determination	carbon paste/ Au(III) – L [e]	0.005 μg litre^{-1}	0 – 50 μg litre^{-1}	308
		1 mol litre^{-1} KCl, KNO_3; pH 1	diamond film doped with boron	5×10^{-11} mol litre^{-1}	5 – 5000 μg litre^{-1}	352
	DP ASVA, CV, impedance	NaCl, KCl, $LiClO_4$, NaOAc; Britton – Robinson buffer, pH 2 (2 – 10); Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+} in 10-fold excess do not interfere determination	carbon paste/C18, pyrrole, 3-methyl-thiophene [f]	10 μg litre^{-1}	0.07 – 0.42 μg litre^{-1}	353
		1 mol litre^{-1} $NaClO_4$; pH 7.2; Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+} in 200-fold excess do not interfere with determination	Au/oligonucleotides [g]	6×10^{-11} mol litre^{-1}; 5.3%	$(0.2 - 1) \times 10^{-9}$ mol litre^{-1}	354
	DP ASVA, CV, RDE	0.5 mol litre^{-1} NaCl + 0.01 mol litre^{-1} HCl	GC/ionomer Tosflex® (see [h])	1.7×10^{-11} mol litre^{-1}	$10^{-11} - 10^{-8}$ mol litre^{-1}	355
	SVA, CV	0.2 mol litre^{-1} NaOAc; pH 7 – 7.5; 0.12 mol litre^{-1} HNO_3	carbon paste/ Cadion A [i]	2 μg litre^{-1}; 2.68%	0.1 – 20 μg litre^{-1}	356
	SVA	high selectivity of determination is reached even in the presence of large excess of other metals	carbon paste, SPCE/polymer [j]	5×10^{-10} mol litre^{-1}	–	357
		1 mol litre^{-1} HCl	SPCE/co-polymer [k]	–	$10^{-9} - 10^{-6}$ mol litre^{-1}	358
	SVA in dc and ac modes	1 mol litre^{-1} $HClO_4$ + 0.1 mol litre^{-1} HCl	Au- and Au-graphite film RDE	–	$10^{-8} - 1.5 \times 10^{-7}$ mol litre^{-1}	359
	SVA, square-wave ac VA	0.1 mol litre^{-1} $HClO_4$ + 2.5×10^{-3} mol litre^{-1} HCl; 200-fold excess of Cu^{2+} do not interfere with determination, whereas Cl^{-}, Br^{-}, I^{-}, CNS^{-}, $CS(NH_2)_2$, EDTA	Au-RDE		5 – 50 μg litre^{-1}	360
	SVA with sinusoidal potential scan	0.1 mol litre^{-1} $HClO_4$	Au-RDE	2×10^{-9} mol litre^{-1}	0.02 – 0.12 μg litre^{-1}	361
MeHgCl	SVA	acetate (pH 4.6 and 6.1) and ammonium (pH 8.5) buffers; 0.1 mol litre^{-1} $HClO_4$ + 0.003 mol litre^{-1} HCl	Au-film	0.49 μg litre^{-1} (2.3×10^{-9} mol litre^{-1})	$2.3 \times 10^{-9} - 10^{-7}$ mol litre^{-1}	87
		0.005 mol litre^{-1} NaCl pH 1; Au deposition on GC *in situ*	Au nanoparticles on GC	0.2 μg litre^{-1}	0.6 – 10 μg litre^{-1}	88

Table 4 (continued).

Analyte	Determination method	Solution composition; analysis optimal conditions and possibilities; interfering impurities	Electrode/modifying agent	Detection limit; accuracy	Linearity range of concentration dependence	Ref.
Hg^{2+}	SVA	0.035 mol litre^{-1} H_2SO_4 + 0.002 mol litre^{-1} KCl; interfering ions: Fe^{3+} and I^-; Cu^{2+} (>100-fold excess), Cl^-, Br^- (>0.02 mol litre^{-1})	carbon, Au	0.02 μg litre^{-1}	0.1–4.5 μg litre^{-1}	362
		0.1 mol litre^{-1} $HClO_4$; 0.1 mol litre^{-1} H_2SO_4	GC, carbon nanotubes/ Au nanoparticles	0.06 μg litre^{-1} (3×10^{-10} mol litre^{-1}); 1.84%	5×10^{-10}–1.25×10^{-6} mol litre^{-1}	309
		sea water + 0.01 mol litre^{-1} HCl; $B(OH)_4$, I^-, SO_4^{2-}, F^-, HCO_3^-, especially, Br^-, Cl^-, should be removed by pretreatment	Au microwire	6×10^{-12} mol litre^{-1}	–	363
		0.01 mol litre^{-1} HNO_3 + 0.01 mol litre^{-1} NaCl; Cu^{2+}, Pb^{2+}, Bi^{3+} do not interfere with determination; SO_4^{2-}, F^-, Cl^-, NO_3^-, ClO_4^- (>0.05 mol litre^{-1}) suppress the signal	Au-RDE	5×10^{-11} mol litre^{-1}	$(0.2–400)\times10^{-9}$ mol litre^{-1}	307
		0.2 mol litre^{-1} KNO_3	carbon paste/ silica gel [l]	8×10^{-9} mol litre^{-1}; 3%–5%	$(20–400)\times10^{-9}$ mol litre^{-1}	364
		0.15–0.8 mol litre^{-1} NaCl, $NaClO_4$; pH 3–12; Cd^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+} in 100-fold excess do not interfere with determination; Cu^{2+} ions interfere	GC/polymer film/ polyamines [m]	2×10^{-11} mol litre^{-1}	$(0.1–1)\times10^{-9}$ mol litre^{-1}	365
		1 mol litre^{-1} KCl, pH 2	GC/silica film [n]	4.3×10^{-9} mol litre^{-1}	$(1–10)\times10^{-8}$ mol litre^{-1}	366
		pH 3; co-determination of Hg^{2+}, Pb^{2+}, Cu^{2+}	carbon paste/ SBA-15 [o]	4×10^{-7} mol litre^{-1}	$(2–10)\times10^{-6}$ mol litre^{-1}	367
		0.03 mol litre^{-1} KCl + 0.04 mol litre^{-1} HNO_3, pH 1.5; Ni^{2+} and Cd^{2+} do not interfere with determination	Pt/P3HT film [p]	5 μg litre^{-1}; 1.3%	–	368
		1 mol litre^{-1} $HClO_4$ + 0.35 mol litre^{-1} HCl	Au film	3×10^{-12} mol litre^{-1}	3×10^{-12}–10^{-8} mol litre^{-1}	303
		Au deposition on GC *in situ*	Au nanoparticles on GC	1.5×10^{-4} μg litre^{-1}	0.01–50 μg litre^{-1}	305
		0.1 mol litre^{-1} HCl pH 1	graphite/antipyrine [q]	0.012 μg litre^{-1}	0.05–1 μg litre^{-1}	310
		0.05–0.1 mol litre^{-1} KNO_3, 0.1 mol litre^{-1} KCl; pH 2–3	GC, graphite, carbon paste/polymers [r]	$(0.85–1.1)\times10^{-6}$ mol litre^{-1}; 10%	10^{-6}–10^{-5} mol litre^{-1}	369
		Britton–Robinson buffer, pH 2.56	Au, GC/polymer [s]	4.4×10^{-11} mol litre^{-1}	$1.1\times(10^{-10}–10^{-7})$ mol litre^{-1}	370
Hg_2^{2+}	cathodic SVA with amperometric detection	deposition of iridium oxide film from saturated alkaline Ir(III) solutions	diamond doped with boron/iridium oxide	3.2×10^{-9} mol litre^{-1}	$5\times(10^{-9}–10^{-6})$ mol litre^{-1}	371

Table 4 (continued).

Analyte	Determination method	Solution composition; analysis optimal conditions and possibilities; interfering impurities	Electrode/modifying agent	Detection limit; accuracy	Linearity range of concentration dependence	Ref.
Hg^{2+}	cathodic SVA with amperometric detection, DP and square wave anodic SVA	0.06 mol litre^{-1} HCl, 0.05 mol litre^{-1} $HClO_4$, 0.07 mol litre^{-1} HNO_3; mixture $HClO_4-NaCl$	Au	0.40 μg litre^{-1}	1 – 5 μg litre^{-1}	304
Hg^{2+}, monomethylmercury	stripping chronopotentiometry	0.05 mol litre^{-1} HCl; 0.05 mol litre^{-1} HCl + 0.05 mol litre^{-1} HNO_3; natural water	Au on GC support	0.080 μg litre^{-1}; 1.4%	0.02 – 200 μg litre^{-1}	312
		HNO_3	Au	5 μg litre^{-1}	–	372
Hg^{2+}	"	0.05 mol litre^{-1} HCl; Zn^{2+}, Pb^{2+}, Fe^{2+}, Mn^{2+} below 25-fold excess do not interfere with determination, whereas Cu^{2+} — below 5-fold excess	Au film/self-organized monolayers [t]	0.3 μg litre^{-1}; 2%	5 – 100 μg litre^{-1}	373
		sea water; 30% HCl; pH 2	Au-RDE	0.005 μg litre^{-1}; 6.6%	38 – 154 μg litre^{-1}	313
	SVA with surface plasmon resonance and magnetohydrodynamic convection	–	Au	10^{-15} mol litre^{-1}	10^{-15} – 10^{-10} μg litre^{-1}	374
	electrochemiluminescence	tap water; 0.04 mol litre^{-1} HNO_3	Al	0.005 μg litre^{-1}	0.01 – 1000 μg litre^{-1}	375

Notes. The following designations were taken for determination methods and electrodes: DP-polarography is differential pulse polarography, CV is cyclic voltammetry, VA is voltammetry, RDE is a rotating disk electrode, SVA is stripping voltammetry, DP ASVA is differential pulse anodic stripping voltammetry; DME is a dropping mercury electrode, HMDE is a hanging mercury drop electrode, SPCE is an electrode prepared by screen printing. [a] Zeolite-modified electrode, SWy-2 is a sodium montmorillonite cation-exchanger; [b] pcPVP is poly(4-vinylpyridine) partially (7%) cross-linked with 1,5-dibromopentane; [c] TP is 2,2′: 6′:2″-terpyridyl; [d] PVF^+ is an anion-exchange polymer matrix of polyvinylferrocene (PVF^+)Cl^-; [e] Au(III) – L are complexes of Au(III) with pyrrolidine dithiocarbamate; [f] carbon electrode modified with 3-methylthiophene, pyrrole, poly(3-methylthiophene), polypyrrole and octadecane (C_{18}); [g] thiolated poly(thymine) oligodeoxynucleotide; [h] polycationic ionomer Tosflex® IE-SA 48; [i] Cadion A, 1-(4-nitrophenyl)-3-(4-phenylazophenyl)triazene; [j] coordinating polymer coating the electrodes was synthesized by oxidative electrochemical polymerization of ethylenediaminetetra-*N*-(3-pyrrol-1-yl)propylacetamide; [k] co-polymer of aniline, 2,2′-dithiodianiline and aniline derivatives containing S – S bonds; [l] nanoporous silica gel functionalized with bipyridyl; [m] acrylic resin Paraloid B72, co-polymers of ethyl methacrylate (70%) and methyl acrylate (30%) were used in preparation of the polymeric film electrode, while macrocyclic polyamine receptors, namely, 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane and 1,4,7,10,13,16,19,22,25,28,31-undecaazacyclotritriacontane, were used for its modification; [n] mesoporous silica gel film functionalized with thiol and containing 10% of mercaptopropyl groups; [o] nanostructured silica gel SBA-15 functionalized with benzothiazol-2-thiol; [p] P3HT is poly(3-hexylthiophene) synthesized by electrochemical polymerization of 0.1 mol litre^{-1} 3-hexylthiophene; [q] antipyrine or sulfosalicylic acid; [r] water-soluble coordinating polymers: poly(ethylene imine), poly(1-vinyl-2-pyrrolidone), their thiourea-containing derivatives, namely, poly(ethylene imine)methylthiourea and poly(1-vinyl-2-pyrrolidone)methylthiourea; [s] GC coated with a film of electrochemically polymerized Methyl Red with the thickness of 1.2×10^{-6} m; [t] self-organized monolayers, modified solid electrodes.

try,[320] inductively coupled plasma mass spectrometry[295, 302]) are still very important. The classical analytical methods such as colourimetry (especially in combination with chromatography)[295] or potentiometry[316–318] have not lost their importance. They give no way in determination of mercury [Hg(II) and Hg(I);[317] Hg(II) and phenylmercuric acetate[316]] in concentrations below 10^{-6} mol litre^{-1} (without its preconcentrating by sorption[318]) but are characterized by simplicity and good reproducibility of results. The same merits were typical of enzymatic methods the more so that different enzymes are characterized by different sensitivity with respect to organic and inorganic mercury compounds,[297] thus providing the possibility of selective determination.

Combinations of different electrochemical methods, for instance, electrolysis at a controlled potential and stripping voltammetry are considered as efficient.[378] Everything mentioned above pertains to the determination of mercury as such (in vapour, solutions and other media).[323–396]

Considering electrochemical methods as such, the most popular methods are different kinds of voltammetry (first of all, cathodic and anodic stripping voltammetry,[340, 349, 360, 361, 379] cyclic voltammetry,[78–86, 301] rotating disk electrode[81, 320]), reverse chronopotentiometry or coulometry with preconcentration.[314, 315] In recent years, in addition to the mentioned methods, the methods of electrochemiluminescence,[375] electrochemical impedance[353, 354, 376] and also of stripping voltammetry coupled with surface plasmon resonance and with magnetohydrodynamic convection[374] were used. According to certain data,[295] the method of cold vapour atomic absorption spectroscopy may prove to be more convenient than voltammetry in the analysis of biological objects, because it requires no time-consuming pre-treatment of samples before the analysis. At the same time, the voltammetric determination is much cheaper; this method is highly competitive with spectrometry (especially, the atomic absorption version) as regards the sensitivity and also allows the selective determination of ions of other heavy metals.[380] The data shown in Table 3 make it possible to compare the potentialities of the electrochemical analytical methods with other methods of analytical determination of OMC and Hg(II). This problem was comprehensively considered, for example, in several publications;[295, 303, 310, 345, 346, 380–382] the comparative analysis of purely electrochemical methods of analytical determination of compounds mentioned was also performed.[303, 313]

The main advantages of these methods include their relative simplicity, cheapness, quickness of determination, and, first of all, high sensitivity, selectivity and sufficiently low detection limit. In connection with this, it should be stressed that it is the low maximum permissible concentration (MPC) of mercury (for example, 5×10^{-5} mg litre^{-1} in drinking water, 0,1 μg litre^{-1} in natural water and 0.3 μg m^{-3} in residential area air, see Refs 297, 359, 379, respectively) that dictate the very high requirements to sensitivity of the determination methods. The modern voltammetric analytical methods[78–88, 326, 333] adequately meet the latter requirements (see Table 4); for instance, the detection limit of $MeHg^+$ on modified electrodes of carbon paste and GC was $\sim4.5\times10^{-11}$ mol litre^{-1} (Refs 80 and 82), which corresponds to the labile mercury concentration in the World ocean.[22] The detection limit of inorganic mercury compounds on a Cryptofix 222-modified carbon paste electrode,[338, 353, 383] a poly(vinylferrocene)-modified Pt electrode[350] and a GC electrode covered with either multiwalled carbon nanotubes[340] or Langmuir–Blodgett calixarene films[341] varied from 2×10^{-10} to 10^{-12} mol litre^{-1}. The use of differential stripping voltammetry in place of common voltammetry allowed the decrease in the detection limit by *ca.* two orders of magnitude,[346] for example, in thiocyanate electrolytes the latter was $\sim10^{-14}$ mol litre^{-1} (Ref. 346). However, it was noted[337] that partial desorption of Hg^{2+} occurs in its determination by this method if the scan rate was insufficiently high, which can lower the sensitivity of the analysis. The interest in such studies survived in recent years,[270, 350, 357, 364, 376, 384, 385] and the number of publications on these issues considrably exceeds the number of papers devoted to the ER mechanism of mercury-containing compounds. The detailed analysis of these studies is beyond the scope of this review. More detailed information can be found elsewhere (see, *e.g.*, Refs 295, 296, 298, 384 and 386).

The voltammetric determination of inorganic mercury [Hg(I) and Hg(II)] is based on the well-known reaction

$$\mathrm{Hg(II)} \overset{e}{\rightleftharpoons} \mathrm{Hg(I)} \overset{e}{\rightleftharpoons} \mathrm{Hg(0)}. \qquad (42)$$

The Latimer diagram containing formal redox potentials of reactions (42) (*vs.* SCE) has the following form:

$$\mathrm{Hg^0} \xrightarrow[(0.58)]{0.58} \mathrm{Hg_2^{2+}} \xrightarrow[(0.31)]{0.70} \mathrm{Hg^{2+}}$$
$$\mathrm{Hg^0} \xrightarrow{\quad 0.63 \quad} \mathrm{Hg^{2+}}$$

(figure in parentheses are the E values of the corresponding chloride complexes).[387] The thermodynamics of all possible steps of this process was comprehensively considered.[387, 388] At solid electrodes, Hg(I) and Hg(II) are often reduced at the same potential,[346] whereas at the Hg-electrode surface, they immediately react with the latter by the following scheme:

$$2\,\mathrm{Hg^{2+}} + 2\,\mathrm{e} \longrightarrow \mathrm{Hg_2^{2+}}, \qquad (43)$$

so that in place of steps (42) and (43), the following reaction occurs:

$$\mathrm{Hg(II)} + 2\,\mathrm{e} \rightleftharpoons \mathrm{Hg(0)}. \qquad (44)$$

It is known[160] that the mercury ions (Hg^{2+}, Hg_2^{2+}) do not induce any individual polarographic waves under polarographic conditions provided they form no complexes with organic or inorganic ligands.[72, 87, 270, 271, 346]

Considering OMC, the conditions optimal for their analysis (solution composition, temperature and pH, see Section I) were specified as early as in the polarographic studies of the electroreduction of RHgX salts that follows the Benesch mechanism.[52] Particularly, it was shown[78] that the first ER wave is of greater value for the analysis, being located in a sufficiently convenient potential range, namely, from -0.1 to -0.5 V [for example, it was shown[78] that for the $MeHg^+/MeHg^{\bullet}$ redox pair, $E^0 = -0.14$ V in 0.1 M $HClO_4$ solution, $E_p \approx -(0.2-0.3)$ V depending on the scan rate]. The limiting current of this polarographic wave in the concentration range of the determined substances of 10^{-7}–10^{-4} mol litre^{-1} is linear and allows quantitation of OMC in different samples. For $MeHg^+$, the detection limit of 1 μg litre^{-1} (or 5×10^{-9} mol litre^{-1}) was achieved.[78] The second wave of RHgX on mercury corresponding to the set of reactions (2) in Scheme 1 was shown[78, 83–86] to be of little use for analytical determination. The main reason

for this probably lies in the fact that this wave is of the adsorption-diffusion nature and contains a kinetic component (the formation of 'organic calomel', see Section VI). Even the use of high-potential scan rates in voltammetry (or high-density currents in chronopotentiometry) gives no way of avoiding the effect of kinetics of the formation and decomposition of this intermediate (see Section III) on the response. These complications affected to the lesser extent the monomethylmercury determination where the ER peak of 'organic calomel' observed at platinum (about -0.45 V) (Ref. 83) or carbon (about -0.35 V) (Ref. 86) microelectrodes coated with a mercury layer was used as the analytical signal.

However, in the general case, voltammetric methods proved to be less effective in the determination of R_2Hg and R′HgR compounds, first of all, due to the substantial inhibition of the ER of many OMC, especially alkyl derivatives (see Section II).

The earlier studies usually employed the mercury electrode in the electroanalytical determination of mercury-containing compounds;[78,79] at present, in addition to this electrode,[333,383] non-toxic solid electrodes, first of all, gold,[87,299,304–306,315,347,348,360,372,373,381] due to its high affinity to mercury, are used. Gold was shown to be the electrode material of choice for the determination of mercury by the method of stripping voltammery.[361] Its drawback is the difficulty of removal of mercury fom the electrode after the measurements.[387] For this purpose, when using the electrode containing gold nanoparticles deposited on GC,[88] it was recommended to bind mercury into complexes with ethylenediaminetetraacetic acid, in the similar manner as in bioelectrochemical studies of oligodeoxynucleotides in the presence of Hg(II).[389]

Moreover, in the electroanalytical practice, platinum[86,320,336,337,350] and different forms of carbon, namely, carbon paste,[310,311,327,342,356,364,365,390] fibres,[85,86,349] porous carbon,[391] GC,[81,86,314,340,344,370] graphite,[351] doped diamond[352,371,392] are widely used. Carbon materials of such a kind including also pyrolytic graphite and carbon nanotubes were considered[339,383] as the most convenient supports for mercury film electrodes. Note that the boron-doped diamond electrode proved to be more efficient in the determination of Hg(I) (Ref. 371) and Hg(II),[352,371,383] as compared with GC, because the background current on the former electrode was substantially lower. The presence of the nitrate and chloride ions made it possible to increase the sensitivity of detection; the lowest detection limit was 5 ng litre^{-1} (Refs 351, 371 and 383). At the same time, the data on the ER of RHgX (particularly, monomethylmercury[86]) at carbon electrodes were often irreproducible; the severe complications were also associated with surface cleaning, especially, the surface of carbon fibres. In the OMC determination, solid electrodes were used coated (preliminarily or *in situ*) with mercury[83–88] to enhance the analytical resolution (see Section III).

The mentioned complications can be eliminated if combined (also referred to as modified or sensor[298]) electrodes are used [for example, gold–graphite prepared *in situ*[359,393,394] or gold nanoparticles with carbon nanotubes with the detection limit of 3×10^{-10} mol litre^{-1} (Ref. 309)], which were prepared by deposition of the active metal on the backing (for instance, deposition of gold on carbon paste,[339] GC (Refs 88, 305) and iridium;[347] deposition of mercury on carbon,[85,86] GC,[86] Pt,[83] gold[386]), and also electrodes modified with various organic and inorganic additives.[298,338,345,346,353,383,395] Thus the electrode modification with polymers, resins and other reagents allowed extraction of the chloride ions thus preventing the adverse formation of calomel, which made easier the surface regeneration.[82,86,345] This procedure was especially efficient for electrodes prepared by screen printing[300,343,345,357,358] (particularly, carbon[343,345,357,358] as well as silver[300]), which ensured high sensitivity and selectivity of detection. The modification of a thick film graphite electrode with gold(III)/pyrrolidine dicarbamate complex resulted in enhancement of reproducibility.[308] A sensor based on single-walled carbon nanotubes of high sorbability was proposed.[382] The combined and simultaneously modified electrodes were recommended, for example, 3,3′,5,5′-tetramethylbenzidine-based nanofibers doped with Pt(II) followed by Au nanoparticles.[396] With this sensor, the detection limit of 0.008 μg litre^{-1} could be reached; however, what is more important, the presence of a tenfold excess of Zn^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Cr^{3+} ions did not prevent the determination of Hg(II). However, the determination of inorganic mercury at the subnanomolar level with such electrodes is sometimes impossible (*cf.* a review[298]). A substantial drawback of many such methods is that the electrode preparation is difficult; their reproducible operation required recovery of the sensor surface, sometimes before each analysis.[362,382] However, the 'classical' electrodes for mercury determination (impregnated graphite, carbon paste, GC, platinum, gold) sometimes required complex pre-treatment, while their sensitivity and the reproducibility of results were insufficient in some cases for serial analyses.[308]

The data for electrodes of other materials could somewhat differ from those obtained on the 'pure' dropping mercury electrode or the hanging mercury drop electrode. Thus, in the voltammogram of the $MeHg^+$ cation measured on a Pt microelectrode 25 μm in diameter coated with a thin mercury layer, the first ER step corresponded to a broadened peak ($E_p \approx -0.6$ V).[83] Insofar as the peak of 'organic calomel' oxidation (near -0.45 V) turned out to be more pronounced, especially, for $v = 50-100$ V s^{-1}, it was chosen[83] for the VA determination of monomethylmercury (with the detection limit no less than 7.5×10^{-10} mol litre^{-1}).

At mercury, $MeHg^+$ was reduced much easier[78] than at GC modified with Nafion® (Ref. 82), where E_p was -0.56 V (*i.e.*, with respect to the Hg electrode, the difference $\Delta E \geqslant 0.2-0.3$ V). This was explained[82] by the higher energy barrier to Hg^{2+} electroreduction at glassy carbon electrodes. However, at the electrode of gold nanoparticles deposited *in situ* on GC, the complete reduction of monomethylmercury occurred even at ~0 V; presumably,[88] this was due to the structural effects and the lower ER barrier on microparticles.

Simultaneous electroanalytical determination of inorganic and organic mercury derivatives seems also promising,[80,83,88] its alternative being time-consuming and expensive cold vapour atomic absorption spectroscopy. The latter proved to be more effective in combination with electrolysis at a Pt electrode where inorganic and organic mercury have been deposited separately at -0.1 and -0.2 V, respectively.[295] Monomethylmercury was easily determined by voltammetry in the presence of a tenfold excess of Hg^{2+}, because under recommended conditions (platinum[83] and carbon[85] microelectrodes), the difference of oxidation peaks (-0.45 and $+0.35$ V, respectively) was ~0.8 V. At

a carbon paste electrode, the anodic CV branch contained a sharp Hg(II) electrooxidation peak at 0.15 V, whereas a wide signal at *ca.* −0.7 V corresponded to the ER.[311] For these purposes, capillary electrophoresis with electrochemical detection, amperometric or voltammetric,[324, 325, 334, 335] was often used, which allowed, for example, separate quantitation[324] of $MeHg^+$, $EtHg^+$ and Hg^{2+} (and also of $PhHg^+$, Ref. 334) in a sample.

Different anions[353] and cations (for example, see Refs 86, 307, 311, 353, 361 and 384) usually exerted no substantial effect on the electroanalytical determination of mercury; however, their presence could affect (see Table 4) the analytical signal and the ER potential,[353] especially if such cation [for example, Au(III)] formed intermetallic compounds with mercury.[349] The exception were the anions well adsorbed on the Hg electrode in the working potential range [Cl^-, Br^-, and especially I^- (even in concentration $> 10^{-7}$ mol litre^{-1}),[362] CNS^- and several other[353, 360]], or coordinated with mercury. For example, the ER of the Hg^{2+} cations in neutral non-coordinating media produced two VA peaks, whereas in the presence of even a weak complex-forming reagent such as the acetate ion (at pH 4.5), only one peak was observed.[270] Only the ions with the oxidation peaks close to the corresponding Hg(II) signals, particularly, Ag^+, Tl^{3+}, Fe^{3+}, Cr^{6+}, or ions capable of interacting with Hg(II), such as I^-, V^{5+}, V^{4+}, could affect the accuracy of determination.[311, 362] In this case, binding the Hg^{2+} ions into complexes (for example, with diethylenetriaminepentaacetic acid)[87] that are not reduced at potentials of monomethylmercury ER (if the goal was to separately determine these components) or complexation of the ions that interfere with the Hg^{2+} determination (*e.g.*, Fe^{3+} with F^-) was efficacious. Due to the substantial difference in equilibrium constants of complexation, the coordination (for example with water-soluble polymers[369]) was successfully used in the selective determination of Hg^{2+} by the stripping VA in the presence of certain ions, namely, Ag^+, Cu^{2+}, Pb^{2+}, Cd^{2+}. To enhance the selectivity of determination, the analysis can be carried out in a solution containing the tetraphenylborate anion, which reacts with Hg^{2+} to form diphenylmercury; as a result, a linear dependence of the decrease in the oxidation peak height of this anion was observed on increasing the mercury(II) concentration.[327] Preliminary treatment of the analyte with $SnCl_2$, which reacts only with inorganic mercury, proved to be still more efficacious. This method was successfully used[88] in the separate quantitation of monomethylmercury and inorganic mercury in acidified aqueous and water–methanol solutions by the anodic stripping VA at an electrode of gold nanoparticles deposited *in situ* on GC. Without such pre-treament, the voltammogram demonstrated the peak of common ER of monomethylmercury and Hg^{2+} ($\sim$0.56 V,[88] the detection limit of mercury itself at such nanostructured electrode was[305] 0.15 ng litre^{-1}), which agrees with the data of other studies (see Refs 80, 83, 86). Approximately at the same potential (E_p = 0.53 V), a mercury oxidation signal was observed on the electrochemically polished gold electrode.[361] At the same time, at an electrode of carbon paste modified with sodium montmorillonite, Hg^{2+} could be determined with high selectivity by differential stripping VA where Me_2Hg, Et_2Hg and Hg_2^{2+} produced no analytical responses under these conditions.[342]

A sufficiently convenient method of indirect Hg(II) determination was preliminary binding of the metal into inactive complexes with different amino acids, for instance, with L-tyrosine.[336] Insofar as these ligands are electrochemically active, the mercury was quantitated based on the decrease in the tyrosine oxidation peak height. However, this approach could not be applied to methylmercury, phenylmercury and other OMC,[336] because they should be transformed beforehand into the inorganic form by oxidation with permanganate, persulfate and other strong oxidants.

The effect of a large number of cations and anions (more than forty) on the voltammetric determination of mercury on the carbon paste electrode modified with a liquid anion-exchanger Amberlite LA2 was studied in detail.[311] Determination of mercury is markedly interfered with by cations (Ag^+, Tl^{3+}, Cr^{6+}) that are also adsorbed by this anion exchanger and are oxidized at approximately the same potentials as Hg^{2+} (*i.e.*, 0.15 V), cations (Bi^{3+}, Au^{3+}) able to block the exchanging groups of the anion exchanger, and platinum group metals (except for Os^{6+}, see[311]).

These facts should be borne in mind in the simultaneous determination of inorganic mercury and OMC. Thus Pb^{4+} can exert a certain effect on the monomethylmercury ER due to the competetive lead methylation reaction and the concomitant partial blockage of the electrode surface with the reaction product.[86] The EO peak height of this compound sharply increased in the presence of Hg^{2+}; however, the EO peak height corresponding to 'organic calomel' remained unchanged.[86]

The high sensitivity and selectivity was typical of sensors based on oligonucleotides.[376, 385] Thus when such biosensors were used in the determination of Hg^{2+} by the electrochemical impedance method, the detection limit varied from 10^{-10} (Ref. 376) to 6×10^{-11} mol litre^{-1} depending on the nature of modifying agent.[354] In connection with this, it should be noted that the indirect determination of methylmercury, ethylmercury and inorganic mercury that employed a glucose sensor (from the suppression, in their presence, of glucose formation from sucrose catalyzed by the enzyme invertase) allowed the limit of only 2–10 μg litre^{-1} (Refs 319 and 331) or somewhat lower to be reached using a copper-modified GC electrode.[328] The presence of the Ni^{2+}, Co^{2+}, Mg^{2+}, Zn^{2+}, $Ba^{2+}$and Cd^{2+} ions (and, according to certain data,[385] Mn^{2+}, Pb^{2+}, Fe^{2+}, Cu^{2+}, Ca^{2+}) had virtually no effect on the determination, which was explained[376] by specific coordination between the thymine bases (T) of DNA and mercury [T–Hg(II)–T]. Such complexes of Hg(II) with oligonucleotides proved to be sufficiently stable; they are reduced at potentials different from those of the mercury ions.[389] Binding with, *e.g.*, cysteine proved to be very efficient for the separate determination of $EtHg^+$, $PhHg^+$ and Hg^{2+} in a mixture by the capillary electrophoresis with electrochemical detection.[334] This allowed the detection limit of 0.05 to be achieved for Hg^{2+} and 0.4 μg litre^{-1} for $MeHg^+$ (*i.e.*, $\sim 2.5 \times 10^{-10}$ and 2×10^{-9} mol litre^{-1}, respectively).[325]

The determination was usually preceded by pre-treatment of samples, for example, by transferring mercury from its organic form to inorganic (particularly, its conversion to mercuric chloride)[311] by traditional chemical methods, *e.g.*, by acid hydrolysis of Merfen Orange (phenylmercuric borate) at elevated temperatures,[311] ultrasonication, ozonization[362] and also by the microwave or conventional heating.[348, 368] It was shown[88] that acid hydrolysis in a microwave oven in the presence of a mixture of HNO_3 and H_2O_2 is the most efficient method of sample pre-treatment. Sample pre-treatment methods such as chromatomem-

brane,[379] ion-exchange [82, 311] and sorption [318] preconcentration were described. Chemical reactions [80] of mercury or OMC with an electrode modifier such as Nafion® (Ref. 82) or different resins, for example, thiol resins,[80] particularly Sumichelate Q10R,[345] were often used as well as reduction of the mercury cations to Hg^0 with $SnCl_2$ (Refs 88, 351, 376 and 377) (the detection limit is 0.46 ng litre^{-1}) [351] or $NaBH_4$ or oxidation with bromine, $KMnO_4$, $K_2Cr_2O_7$, *etc*. In the case of reduction with $NaBH_4$, centrifugation of an electrochemical cell with a gold film electrode allowed the detection limit to be lowered to 3×10^{-12} mol litre^{-1} (Ref. 303).

Yet another important pre-treatment method was the preliminary conversion of inorganic mercury or OMC to different kinds of coordination compounds [345] reducible at potentials different from those of ER of non-coordinated forms.[87, 270, 271] It should be stressed that this approach is vital for such methods as colourimetry or high performance liquid chromatography with spectroscopic detection.[295] Naturally, in certain cases, inorganic ions interfering with the detection [for example, Cl^-, Br^-, I^-, CNS^- in concentrations above 10^{-2}–10^{-4} mol litre^{-1} (Ref. 360)] should be bound and the strongly adsorbed organic ligands, particularly, thiocarbamide, should be eliminated.[360] The use of anodic stripping VA on a gold electrode enhanced dramatically the sensitivity and selectivity of the determination of inorganic mercury by inductively coupled plasma mass spectrometry;[302] analogous advantages were also observed at the combined use of cold vapour atomic absorption spectroscopy and VA.[320]

The analysis, far from being comprehensive, of publications on the electrochemical methods of analytical determination of mercury provided the grounds to assert that these methods not only retained their importance but also require constant modernization. It is largely for this reason that the interest in studying the peculiarities of the electrochemical behaviour of OMC in different media was not lost.

VIII. Conclusion

In this review, an attempt was undertaken to generalize the literature data on the electrochemical transformations of OMC and also to outline the prospects of studies in this field. Insofar as no generalization of such a kind was published for more than 25 years, the authors were going to fill this gap.

As was mentioned in the Introduction, despite the fact that the present studies of the mechanisms of electroreduction of OMC at mercury and other electrodes were developed less actively as compared with the 1980–1990s, the studies on upgrading of analytical methods have acquired a new sense. This, first of all, was associated with the necessity of solving environmental problems such as, *e.g.*, utilization of wastes of mercury industries and conversion of mercury from the organic to less toxic inorganic forms. On the other hand, the electrosynthetic and electroanalytical studies were characterized by the active trend to abandon the mercury electrode due to its 'non-inertness' and toxicity (which was not always justified and feasible). Although the application region of the mercury and other liquid electrodes (particularly, amalgam) has somewhat narrowed down, while the environmental requirements constantly become more stringent, the need in such materials as the electrodes will probably hold at least in the years ahead. Particularly, the method of dropping mercury electrode lies in the basis of polarographic techniques, while the precision adsorption and capacitance (and, sometimes, voltammetric) measurements are impossible without using the atomically smooth stationary mercury electrode (*e.g.*, the hanging mercury drop). However, it is these methods that were used most often in the detailed studies of the mechanisms of electrode reactions of organic compounds (including mercury-free compounds) at a mercury cathode, which are accompanied by the OMC formation. It should be stressed that due to their high sensitivity and selectivity, the electrochemical methods proved to be convenient for studying the kinetic parameters of the coordination of miscellaneous depolarizers. Based on indirect data (variations in $E_{1/2}$, αn_a, Γ_∞, *etc*.), even very unstable complexes can be characterized, because the coordinated depolarizers and electrochemically inert surfactants differ from those uncoordinated in their electrochemical and adsorption properties.

The possibility of quick and easy renewal of the surface, which is absent for solid electrodes, provides great advantages in the preparative electrosynthesis, too. For example, a series of α,α-dicarbonyl selenides were successfully synthesized [283] at a mercury cathode although the starting (α-acyl)alkyl and (α-acyl)aryl halides actively reacted with mercury. At the same time, at GC and Pt electrodes passivation occurred, threfore they turned out to be altogether useless in this synthesis.

It should be particularly emphasized that the mechanisms of electrochemical reduction of OMC are very complicated and their numerous aspects cannot be considered as conclusively established. Additional difficulties of these studies are associated with the high adsorbability of many OMC and mercury-containing intermediates, which give rise to the appearance of various adsorption effects. The probability of formation of such intermediates depends not only on the nature of depolarizer but also on other conditions often unmanageable experimentally and, among the chief factors, on the process duration. In some cases, this explains the substantial deviations in the electrolysis products for the same depolarizer at electrodes of different nature. This is why studying the electrochemical behaviour of OMC and their intermediates should employ a wide variety of modern chemical and physicochemical methods including quantum chemical computations.

We believe that many aspects of OMC electrochemistry still await their explorers and hope that this review will be useful for chemists of different specialization.

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References

1. *Organic Electrochemistry: An Introduction and a Guide* (Eds H Lund, M M Baizer) (New York, Basel: Marcel Dekker, 1983)
2. A P Tomilov, I N Chernykh, Yu M Kargin *Elektrokhimiya Elementoorganicheskikh Soedinenii (Elementy I, II, III Grupp Periodicheskoi Sistemy i Perekhodnye Metally)* [Electrochemistry of Organoelement Compounds (Elements of Groups I, II, III of the Periodic System and Transition Metals)] (Moscow: Nauka, 1985)
3. A P Tomilov, Yu M Kargin, I N Chernykh *Elektrokhimiya Elementoorganicheskikh soedinenii (Elementy IV, V i VI Grupp Periodicheskoi Sistemy)* [Electrochemistry of Organoelement Compounds (Elements of Groups IV, V and VI of the Periodic System and Transition Metals)] (Moscow: Nauka, 1986)

4. M R Rifi, in *Organic Electrochemistry: An Introduction and a Guide* (Ed. M M Baizer) (New York, Basel: Marcel Dekker, 1976) p. 279
5. D G Peters, in *Organic Electrochemistry: an Introduction and a Guide* (Eds H Lund, M M Baizer) (New York, Basel: Marcel Dekker, 1991) p. 361
6. D G Peters, in *Organic Electrochemistry: an Introduction and a Guide* (Eds H Lund, M M Baizer) (New York, Basel: Marcel Dekker, 2000) p. 341
7. J Casanova, V P Reddy, in *The Chemistry of Halides, Pseudo-halides and Azides* (Eds S Patai, Z Rappoport) (New York: Wiley, 1995) p. 1003
8. N B Fouzder, B Fleet, in *Polarography of Molecules of Biological Significance* (Ed. W F Smyth) (London, New York, San Francisco: Academic Press, 1979) p. 261
9. M D Morris, G L Kock, in *Encyclopedia of Electrochemistry of the Elements. Organic Section* Vol. 13 (Eds A J Bard, H Lund) (New York, Basel: Marcel Dekker, 1979) p. 1
10. J Tafel *Berichte* **39** 3626 (1906)
11. T J Taylor, C N Burress, F P Gabbai *Organometallics* **26** 5252 (2007)
12. S D Davydova, Yu T Pimenov, E R Milaeva *Rtut', Olovo, Svinets i ikh Organicheskie Proizvodnye v Okruzhayushchei Srede* (Mercury, Tin, Lead and Their Organic Derivatives in the Environment) (Astrakhan: Astrakhan State Technological University, 2001)
13. E R Milaeva *J. Inorg. Biochem.* **100** 905 (2006)
14. I P Beletskaya, K P Butin, A N Ryabtsev, O A Reutov *J. Organomet. Chem.* **59** 1 (1973)
15. A A Stepanov *J. Fluorine Chem.* **114** 225 (2002)
16. G B Deacon, C M Forsyth, S Nickel *J. Organomet. Chem.* **647** 50 (2002)
17. A K Yadav, M Manju *Indian J. Chem., Sect. B* **45** 2770 (2006)
18. V I Boev, A I Moskalenko, A M Boev *Usp. Khim.* **66** 874 (1997) [*Russ. Chem. Rev.* **66** 789 (1997)]
19. O A Reutov, A L Kurts, K P Butin *Organicheskaya Khimiya (v 4-kh Chastyakh)* [Organic Chemistry (in 4 Parts)] (Moscow: BINOM, 2004–2005)
20. V V Boev, A S Kamrukov, N P Kozlov, I S Lakoba, Yu S Protasov *Kvantovaya Elektron.* **18** 1441 (1991) [a]
21. G A Voskoboinik, L M Mazanova, Yu D Semchikov *Vestn. Nizhegorod. Univ., Ser. Khim.* (1) 113 (1998)
22. W F Fitzgerald, C H Lamborg, C R Hammerschmidt *Chem. Rev.* **107** 641 (2007)
23. R D Rakhimov, E R Milaeva, O V Polyakova, K P Butin *Izv. Akad. Nauk, Ser. Khim.* 309 (1994) [b]
24. A Renuka, K Shakuntala, P C Srinivasan *Indian J. Chem., Sect. A* **37** 596 (1998)
25. R C D M Micaroni, M I M S Bueno, W D Jardim *Quim. Nova* **23** 487 (2000)
26. O A Reutov, I P Beletskaya, V I Sokolov *Mekhanizmy Reaktsii Metalloorganicheskikh Soedinenii* (Mechanisms of Reactions of Organometallic Compounds) (Moscow: Khimiya, 1972)
27. V L Ivanov, G A Artamkina, A L Buchachenko *Vestn. Mosk. Univ., Ser. 2, Khim.* **49** 234 (2008) [c]
28. A L Buchachenko *Usp. Khim.* **78** 345 (2009) [*Russ. Chem. Rev.* **78** 307 (2009)]
29. C Miranda, J Yanez, D Contreras, R Garcia, W F Jardim, H D Mansilla *Appl. Catal. B: Environ.* **90** 115 (2009)
30. J A Navio, C Cerrillos, M Macias, M A Pradera *J. Adv. Oxidat. Technol.* **11** 411 (2008)
31. E M de la Fourniere, A G Leyva, E A Gautier, M I Litter *Chemosphere* **69** 682 (2007)
32. C Cerrillos, M A Pradera Adrian, J A Navio *J. Photochem. Photobiol. A* **84** 299 (1994)
33. L Abrankó, Z Jókai, P Fodor *Anal. Bioanal. Chem.* **383** 448 (2005)
34. G Henze *Polargaphie und Voltammetrie. Grundlagen und analytische Praxis* (Berlin, Heidelberg: Springer, 2001)
35. R Gmoch, J Pasciak *Chem. Anal.* **35** 407 (1990)
36. B Fleet, R D Jee *J. Electroanal. Chem.* **25** 397 (1970)
37. J Pasciak, R Gmoch *Wiad. Chem.* **39** 273 (1985)
38. K P Butin, V V Strelets, O A Reutov *Metalloorg. Khim.* **3** 814 (1990) [d]
39. K P Butin, R D Rakhimov, O A Reutov *Zh. Org. Khim.* **23** 905 (1987) [e]
40. O V Novikova, O V Kuznetsova, A N Egorochkin *Zh. Obshch. Khim.* **77** 1529 (2007) [f]
41. O V Novikova, O V Kuznetsova, A N Egorochkin *Zh. Org. Khim.* **43** 1277 (2007) [e]
42. V V Pinyaskin, A L Chistyakov, I V Stankevich, O B Tomilin, K P Butin, I V Novikova *Metalloorg. Khim.* **4** 440 (1991) [d]
43. P Schwerdtfeger, P D W Boyd, S Brienne, J S McFeaters, M Dolg, M-S Liao, W H E Schwarz *Inorg. Chim. Acta* **213** 233 (1993)
44. P Schwerdtfeger, J Li, P Pyykko *Theor. Chim. Acta* **87** 313 (1994)
45. P Pyykko, M Straka *Phys. Chem. Chem. Phys.* **2** 2489 (2000)
46. P Jiang, J Shi, H W Sun, M X Yuan, C M Lai *J. Mol. Struct. (THEOCHEM)* **528** 91 (2000)
47. T V Magdesieva, in *Elektrokhimiya Organicheskikh Soedinenii v Nachale XXI Veka* (Electrochemistry of Organic Compounds in Beginning of the 21st Century) (Eds V P Gul'tyai, A G Krivenko, A P Tomilov) (Moscow: Kompaniya Sputnik+, 2008) p. 250
48. E A Holley, A J McQuillan, D Craw, J P Kim, S G Sander *Chem. Geol.* **240** 313 (2007)
49. X B Feng, G L Qiu, X W Fu, T R He, P Li, S F Wang *Prog. Chem.* **21** 436 (2009)
50. J Kotnik, M Horvat, V Jereb *Environ. Model. Soft.* **17** 593 (2002)
51. B F Giannetti, W A Moreira, S H Bonilla, C M V B Almeida, T Raboczkay *Colloids Surf. A* **276** 213 (2006)
52. R Benesch, R E Benesch *J. Am. Chem. Soc.* **73** 3391 (1951)
53. J C G Monteagudo, J M L Fonseca *An. Quim.* **82** 345 (1986)
54. C Degrand, E Laviron *Bull. Soc. Chim. Fr.* 2228 (1968)
55. C Degrand, E Laviron *Bull. Soc. Chim. Fr.* 2236 (1968)
56. S S Katiyar, M Lalithambika, D Devaprabhakara *Electrochim. Acta* **17** 2077 (1972)
57. R E Dessy, W Kitching, T Psarras, R Salinger, A Chen, T Chivers *J. Am. Chem. Soc.* **88** 460 (1966)
58. J H Wagenknecht *J. Electrochem. Soc.* **119** 1494 (1972)
59. N T Berberova, A G Milyaev, O Yu Okhlobystin *Zh. Obshch. Khim.* **49** 621 (1979) [f]
60. B C Willett, D G Peters *J. Electroanal. Chem.* **123** 291 (1981)
61. A P Tomilov, O N Temkin, I A Esikova, R M Flid, S M Makarochkina, O A Kondakova, V A Dolinchuk *Elektrokhimiya* **5** 722 (1969) [g]
62. I A Esikova, O N Temkin, A P Tomilov, R M Flid, G P Pavlikova *Elektrokhimiya* **7** 139 (1971) [g]
63. V Ts Kampel', K P Butin, V I Bregadze, N N Godovikov *Izv. Akad. Nauk, Ser. Khim.* 1508 (1978) [b]
64. K Okamoto *J. Chem. Soc. Jpn., Pure Chem. Sect.* **817** (1) 125 (1960)
65. V R Polishchuk, M M Gol'din, L G Feoktistov, L S German *Izv. Akad. Nauk, Ser. Khim.* 322 (1972) [b]
66. M S Mbarak, D G Peters *J. Electroanal. Chem.* **152** 183 (1983)
67. K P Butin, I P Beletskaya, A N Kashin, O A Reutov *J. Organomet. Chem.* **10** 197 (1967)
68. L I Denisovich, S P Gubin *J. Organomet. Chem.* **57** 87 (1973)
69. L I Denisovich, S P Gubin *J. Organomet. Chem.* **57** 99 (1973)
70. L G Feoktistov, A P Tomilov, V A Smirnov, M M Gol'din *Elektrokhimiya* **1** 887 (1965) [g]
71. M von Stackelberg, W Stracke *Z. Elektrochem.* **53** 118 (1949)
72. L Newman, D N Hume *J. Am. Chem. Soc.* **83** 1795 (1961)
73. S Wawzonek, R C Duty, J H Wagenknecht *J. Electrochem. Soc.* **111** 74 (1964)
74. A N Ryabtsev, K P Butin, I P Beletskaya, O A Reutov *Zh. Org. Khim.* **4** 934 (1968) [e]
75. N T Berberova, D N Sadzhaya, O Yu Okhlobystin *Dokl. Akad. Nauk SSSR* **229** 92 (1976) [h]
76. N T Berberova, O Yu Okhlobystin *Zh. Obshch. Khim.* **47** 726 (1977) [f]
77. K P Butin, A N Kashin, I P Beletskaya, L S German, V R Polishchuk *J. Organomet. Chem.* **25** 11 (1970)

78. R C Heaton, H A Laitinen *Anal. Chem.* **46** 547 (1974)
79. I Tanase, I Ioneci, C Luca *Rev. Roum. Chim.* **30** 667 (1985)
80. R Agraz, M T Sevilla, L Hernández *J. Electroanal. Chem.* **390** 47 (1995)
81. M P DaSilva, J Rodriguez, L Hernández *Analyst* **119** 1971 (1994)
82. L M Moretto, P Ugo, R Lacasse, G Y Champagne, J Chevalet *J. Electroanal. Chem.* **467** 193 (1999)
83. R Lai, E L Huang, F M Zhou, D O Wipf *Electroanalysis* **10** 926 (1998)
84. D Durst *SEAC Commun.* **5** (4) 2 (1988)
85. F Afonso, F Ribeiro, L Proenca, M I S Lopes, M M Rocha, M M M Neto, I T E Fonseca *Electroanalysis* **17** 127 (2005)
86. F Ribeiro, M M M Neto, M M Rocha, I T E Fonseca *Anal. Chim. Acta* **579** 227 (2006)
87. M Korolczuk, I Rutyna *Electrochem. Commun.* **10** 1024 (2008)
88. O Abollino, A Giacomino, M Malandrino, S Marro, E Mentasti *J. Appl. Electrochem.* **39** 2209 (2009)
89. P Calas, P Moreau, A Commeyras *J. Electroanal. Chem.* **78** 271 (1977)
90. P Calas, A Commeyras *J. Electroanal. Chem.* **89** 363 (1978)
91. P Calas, P Moreau, A Commeyras *J. Electroanal. Chem.* **89** 373 (1978)
92. A Commeyras *Ann. Chim.* **9** 673 (1984)
93. O R Brown, H R Thirsk, B Thornton *Electrochim. Acta* **16** 495 (1971)
94. O R Brown, K Taylor *J. Electroanal. Chem.* **50** 211 (1974)
95. E Laviron, L Roullier *Electrochim. Acta* **18** 237 (1973)
96. J L Webb, C K Mann, H M Walborsky *J. Am. Chem. Soc.* **92** 2042 (1970)
97. J L Muñiz Álvarez, J A García Calzón, J M López Fonseca *Electrochim. Acta* **49** 1389 (2004)
98. J L Muñiz Álvarez, J A García Calzón, J M López Fonseca *J. Colloid Interface Sci.* **287** 592 (2005)
99. B Nygård, J Ludvik, S Wendsjö *Electrochim. Acta* **41** 1655 (1996)
100. J Ludvik, B Nygård *Electrochim. Acta* **41** 1661 (1996)
101. J Ludvik, B Nygård *J. Electroanal. Chem.* **423** 1 (1997)
102. J Ludvik *Phosphorus, Sulfur, Silicon Relat. Elem.* **136** 413 (1998)
103. G J Wagner, J Q Chambers *J. Electroanal. Chem.* **408** 243 (1996)
104. G J Wagner, J Q Chambers *Langmuir* **13** 3529 (1997)
105. R F Johnston, D M Lewis, J Q Chambers *J. Electroanal. Chem.* **466** 2 (1999)
106. A A Moiseeva, S V Stepanov, K P Butin, O B Zhidkova, O M Khitrova, V I Bregadze *Izv. Akad. Nauk, Ser. Khim.* 1877 (2003) [b]
107. K P Butin, R D Rakhimov, I V Novikova *Vestn. Mosk. Univ., Ser. 2, Khim.* **31** 574 (1990) [c]
108. R F Broman, R W Murray *Anal. Chem.* **37** 1408 (1965)
109. A B Ershler, V V Strelets, K P Butin, A N Kashin *J. Electroanal. Chem.* **54** 75 (1974)
110. A N Kashin, A B Ershler, V V Strelets, K P Butin, I P Beletskaya, O A Reutov *J. Organomet. Chem.* **39** 237 (1972)
111. K P Butin, A B Ershler, V V Strelets, A N Kashin, I P Beletskaya, O A Reutov, K Marcushova *J. Organomet. Chem.* **64** 171 (1974)
112. K P Butin, V V Strelets, A N Kashin, I P Beletskaya, O A Reutov *J. Organomet. Chem.* **64** 181 (1974)
113. V V Strelets, A N Kashin, K P Butin, A B Ershler *Elektrokhimiya* **12** 34 (1976) [g]
114. N N Ovsyannikov, V N Alekseev, A N Kashin, L L Knots, G A Tedoradze, A B Ershler *Elektrokhimiya* **8** 1543 (1972) [g]
115. A B Ershler, N N Ovsyannikov, V N Alekseev, A N Kashin, L L Knots, A P Mokrov, G A Tedoradze *Elektrokhimiya* **9** 952 (1973) [g]
116. A B Ershler, E A Nizhnikovskii, M M Gol'din *Elektrokhimiya* **17** 1771 (1981) [g]
117. A N Kashin, I M Levinson, K P Butin, A B Ershler *Elektrokhimiya* **7** 981 (1971) [g]
118. A B Ershler, A N Kashin, K P Butin, I P Beletskaya *Elektrokhimiya* **7** 953 (1971) [g]
119. A B Ershler, V A Kurmaz *Elektrokhimiya* **16** 960 (1980) [g]
120. V A Kurmaz, A B Ershler, in *Proceeding of International Conference 'Modern Trends in Organoelement And Polymer Chemistry', Moscow, 2004* p. P1
121. V A Kurmaz, A B Ershler *Mendeleev Commun.* 234 (2006)
122. V A Kurmaz, V Yu Filinovsky, A G Krivenko, in *Proceeding of IX International Meeting 'Fundamental Problems of Solid-State Ionics', Chernogolovka, 2008* p. 305
123. A B Ershler, V V Strelets, V A Kurmaz *Elektrokhimiya* **17** 695 (1981) [g]
124. A B Ershler, V A Kurmaz, V V Strelets *Elektrokhimiya* **17** 186 (1981) [g]
125. V A Kurmaz, V V Strelets, A B Ershler, in *Proceeding of the 6th International Frumkin Symposium, Moscow, 1995* p. 33
126. G P Girina, M Ya Kats, G A Tedoradze, L G Feoktistov, A G Gavlin *Elektrokhimiya* **13** 1527 (1977) [g]
127. R Bilewicz, J Osteryoung *J. Electroanal. Chem.* **226** 27 (1987)
128. J Casado, I Gallardo *Collect. Czech. Chem. Commun.* **54** 900 (1989)
129. J Casado, J R Cullere, M Julia, E Brillas *Collect. Czech. Chem. Commun.* **58** 2875 (1993)
130. K P Butin, M T Ismail, O A Reutov *J. Organomet. Chem.* **175** 157 (1979)
131. K P Butin, R D Rakhimov, O A Reutov *Zh. Obshch. Khim.* **55** 1309 (1985) [f]
132. K P Butin, R D Rakhimov, O A Reutov *Vestn. Mosk. Univ., Ser. 2, Khim.* **27** 60 (1986) [c]
133. M Atobe, K Sato, T Nonaka *Electrochemistry* **69** 10 (2001)
134. J Casanova, H R Rogers *J. Am. Chem. Soc.* **96** 1942 (1974)
135. L A Avaca, E R Gonzalez, N R Stradiotto *Electrochim. Acta* **22** 225 (1977)
136. G Feroci, M Mastragostino *J. Electroanal. Chem.* **85** 203 (1977)
137. J C Bart, D G Peters *J. Electroanal. Chem.* **280** 129 (1990)
138. A Ya Usiatinsky, V A Shreider, T M Shcherbina, V I Bregadze, N N Godovikov, L L Knunjants *J. Organomet. Chem.* **289** 17 (1985)
139. J Casanova, H R Rogers, J Murray, R Ahmed, O Rasmy, M Tarle *Croat. Chem. Acta* **63** 225 (1990)
140. M Tarle, O Rasmy, H R Rogers, J Casanova *Croat. Chem. Acta* **63** 239 (1990)
141. K P Butin, A A Ivkina, O A Reutov *Izv. Akad. Nauk, Ser. Khim.* 546 (1985) [b]
142. O A Reutov, K P Butin *J. Organomet. Chem.* **413** 1 (1991)
143. V N Leibzon, A P Churilina, A S Mendkovich, V P Gul'tyai *Elektrokhimiya* **27** 1174 (1991) [g]
144. V N Leibzon, in *Abstracts of the 96th Meeting of American Electrochemical Society, Los Angeles, CA, 1996* Vol. 96-1, p. 1260
145. *Handbook of Chemistry and Physics* (Ed. D R Lide) (New York, London, Tokyo: CRC Press, 1996–1997)
146. D W Smith *J. Organomet. Chem.* **585** 150 (1999)
147. V Barone, A Bencini, F Totti, M G Uytterhoeven *J. Phys. Chem.* **99** 12743 (1995)
148. E P F Lee, T G Wright *Chem. Phys. Lett.* **376** 418 (2003)
149. B B Damaskin, O A Petrii, G A Tsirlina *Elektrokhimiya* (Electrochemistry) (Moscow: Khimiya – KolosS, 2006)
150. J-M Savéant, in *Advances in Physical Organic Chemistry* Vol. 35 (London: Academic Press, 2000) p. 117
151. C P Andrieux, L Gelis, M Medebielle, J Pinson, J-M Savéant *J. Am. Chem. Soc.* **112** 3509 (1990)
152. A K Pikaev, G A Artamkina, I P Beletskaya *Dokl. Akad. Nauk SSSR* **232** 634 (1977) [h]
153. V Ts Kampel', K A Bilevich, V I Bregadze, O Yu Okhlobystin *Zh. Vsesoyuz. Khim. O-va im. D I Mendeleeva* **19** (1) 116 (1974) [i]
154. D P Graddon *Rev. Inorg. Chem.* **4** 211 (1982)
155. S G Mairanovskii *Kataliticheskie i Kineticheskie Volny v Polyarografii* (Catalytic and Kinetic Waves in Polarography) (Moscow: Nauka, 1966)
156. A G Kriivenko, V A Kurmaz, A S Kotkin, G V Simbirtseva *Elektrokhimiya* **38** 1146 (2002) [g]
157. R R Nazmutdinov, D V Glukhov, G A Tsirlina, O A Petrii *J. Electroanal. Chem.* **582** 118 (2005)
158. I Katsounaros, G Kyriacou *Electrochim. Acta* **52** 6412 (2007)

159. V B Shur, I A Tikhonova *Izv. Akad. Nauk, Ser. Khim.* 2401 (2003) [b]
160. J Heyrovský, J Kúta *Základy Polarografie* (Praha: Ceskoslovenské Akademie, 1962)
161. L N Saitkulova, E V Bakhmutova, E S Shubina, I A Tichonova, G G Furin, V I Bakhmutov, N P Gambaryan, A L Chistyakov, I V Stankevich, V B Shur, L M Epstein *J. Organomet. Chem.* **585** 201 (1999)
162. M Devaud, Y Le Moulec *J. Electroanal. Chem.* **68** 223 (1976)
163. D D Tanner, J A Plambeck, D W Reed, T W Mojelsky *J. Org. Chem.* **45** 5177 (1980)
164. M Devaud *J. Electroanal. Chem.* **220** C27 (1981)
165. R B Yamasaki, M Tarle, J Casanova *J. Org. Chem.* **44** 4519 (1979)
166. K Joshida, S Tsutsumi *J. Org. Chem.* **32** 468 (1967)
167. J Kraus *J. Am. Chem. Soc.* **35** 1732 (1913)
168. B Govenlock, J J Trotman *J. Chem. Soc.* (5) 2114 (1957)
169. B H M Billinge, B Govenlock *J. Chem. Soc.* (4) 1201 (1962)
170. R A G Marshall, D R Pollard *J. Organomet. Chem.* **27** 143 (1971)
171. B C Willett, W M Moore, A Salajegheh, D G Peters *J. Am. Chem. Soc.* **101** 1162 (1979)
172. Ch Feasson, M Devaud *C. R. Seances Acad. Sci.* **292** 1135 (1981)
173. E T Blues, D Bryce-Smith, H Karimpour *J. Chem. Soc., Chem. Commun.* 1043 (1979)
174. S N Slyusar', V D Bezuglyi, S G Mairanovskii *Elektrokhimiya* **22** 1122 (1986) [g]
175. J Snell, J Qian, M Johansson, K Smit, W Frech *Analyst* **123** 905 (1998)
176. A M Bond, N M McLachlan *Organometallics* **7** 619 (1988)
177. A M Bond, R T Gettar, N M McLachlan, G B Deacon *Inorg. Chim. Acta* **166** 279 (1989)
178. M Studničková *J. Electroanal. Chem.* **338** 133 (1992)
179. S Krasensky, M Studnickova *Collect. Czech. Chem. Commun.* **59** 2375 (1994)
180. K P Butin, V V Strelets, I F Gunkin, I P Beletskaya, O A Reutov *J. Organomet. Chem.* **85** 123 (1975)
181. K P Butin, V V Strelets, I P Beletskaya, O A Reutov *J. Organomet. Chem.* **64** 189 (1974)
182. D Micholova, A A Vlček *Inorg. Chim. Acta* **43** 43 (1980)
183. D Osella, M Ravera, S V Kukharenko, V V Strelets, C E Housecroft *J. Organomet. Chem.* **417** 421 (1991)
184. D Osella, L Milone, S V Kukharenko, V V Strelets, E Rosenberg, S Hajela *J. Organomet. Chem.* **451** 153 (1993)
185. S W Blanch, A M Bond, R Colton *Inorg. Chem.* **20** 755 (1981)
186. G Chobert, M Devaud *J. Chem. Microf.* 3024 (1980)
187. M Devaud, D Gula *Electrochim. Acta* **23** 565 (1978)
188. J-P Colliard, M Devaud *Bull. Soc. Chim. Fr.* 4068 (1972)
189. R D Rakhimov, K P Butin, K I Grandberg *J. Organomet. Chem.* **464** 253 (1994)
190. M Ahmed, R J Magee *Austr. J. Chem.* **34** 1861 (1981)
191. Ch Heitz *Bull. Soc. Chim. Fr.* 2442 (1967)
192. V P Gul'tyai, L M Korotaeva, L V Mikhal'chenko, M Yu Leonova *Elektrokhimiya* **27** 1635 (1991) [g]
193. L M Korotaeva, T Ya Rubinskaya, V P Gul'tyai *Izv. Akad. Nauk, Ser. Khim.* 1255 (1994) [b]
194. L M Korotaeva, T Ya Rubinskaya, E V Klimkina, V P Gul'tyai, Yu N Bubnov *Izv. Akad. Nauk, Ser. Khim.* 2072 (2000) [b]
195. L M Korotaeva, T Ya Rubinskaya, V P Rybakova, V P Gul'tyai *Elektrokhimiya* **43** 1228 (2007) [g]
196. M M Gol'din, E A Nizhnikovskii, V R Polishchuk, L G Feoktistov *Izv. Akad. Nauk, Ser. Khim.* 885 (1975) [b]
197. M Lipsztajn, T M Krygowski, Z Galus *J. Electroanal. Chem.* **81** 347 (1977)
198. V A Kurmaz, A G Krivenko, A P Tomilov, V V Turygin, A V Khudenko, N N Shalashova, A S Kotkin *Elektrokhimiya* **36** 344 (2000) [g]
199. T V Magdesieva, I I Kukhareva, G A Artamkina, I P Beletskaya, K P Butin *J. Organomet. Chem.* **487** 163 (1995)
200. T V Magdesieva, K P Butin *Usp. Khim.* **71** 255 (2002) [*Russ. Chem. Rev.* **71** 223 (2002)]
201. Z Samec, J Langmaier *J. Electroanal. Chem.* **434** 107 (1996)
202. C Bellomunno, D Bonanomi, L Falciola, M Longhi, P R Mussini, L M Doubova, G Di Silvestro *Electrochim. Acta* **50** 2331 (2005)
203. K P Butin, T V Magdesieva, I I Kukhareva, G A Artamkina, I P Beletskaya *Izv. Akad. Nauk, Ser. Khim.* 1436 (1996) [b]
204. T V Magdesieva, V N Shishkin, K P Butin *Zh. Obshch. Khim.* **61** 2403 (1991) [f]
205. M O F Goulart, M B S Lisboa, J C M Cavalcanti, J Tonholo, M Navarro, N A Soares, R L Longo *J. Electroanal. Chem.* **567** 67 (2004)
206. G P Girina, V A Petrosyan, V A Kokorekina, L G Feoktistov *Elektrokhimiya* **34** 453 (1998) [g]
207. V A Kokorekina, G P Girina, L G Feoktistov, V A Petrosyan *Elektrokhimiya* **28** 823 (1992) [g]
208. G P Girina, V A Kokorekina, L G Feoktistov, V A Petrosyan *Elektrokhimiya* **28** 517 (1992) [g]
209. A A Isse, A Gennaro, E Vianello *J. Electroanal. Chem.* **444** 241 (1998)
210. J Grimshaw, J S Ramsey *J. Chem. Soc. B* 60 (1968)
211. L B Rogers, A J Diefenderfer *J. Electrochem. Soc.* **114** 942 (1967)
212. Y Matsui, T Soga, Y Date *Bull. Chem. Soc. Jpn.* **44** 513 (1971)
213. J H Wagenknecht *J. Electroanal. Chem.* **52** 489 (1974)
214. M M Baizer, J L Chruma *J. Org. Chem.* **37** 1951 (1972)
215. M Wojciechowski, J Osteryoung *Anal. Chem.* **57** 927 (1985)
216. R Carabias-Martinez, J Hernandez-Mendez, M G Garcia-Jimenez, E Rodriguez-Gonzalo *J. Electroanal. Chem.* **456** 193 (1998)
217. T Matsue, S Kitahara, T Osa *Denki Kagaku* **50** 732 (1982)
218. S G Mairanovskii, in *Elektrosintez i Bioelektrokhimiya* (Electrosynthesis and Bioelectrochemistry) (Eds A N Frumkin, Ya P Stradyn', L G Feoktistov) (Moscow: Nauka, 1975) p. 199
219. M S Mbarak, D G Peters *J. Org. Chem.* **47** 3397 (1982)
220. F Barba, M D Velasco, N Moreno, A Aldaz *Electrochim. Acta* **32** 1507 (1987)
221. D C Coomber, D J Tucker, A M Bond *J. Electroanal. Chem.* **452** 5 (1998)
222. A G Krivenko, A S Kotkin, V A Kurmaz *Elektrokhimiya* **41** 142 (2005) [g]
223. A G Krivenko, A S Kotkin, V A Kurmaz *Elektrokhimiya* **41** 157 (2005) [g]
224. V A Benderskii, A G Krivenko *Usp. Khim.* **59** 3 (1990) [*Russ. Chem. Rev.* **59** 1 (1990)]
225. A G Krivenko, A S Kotkin, V A Kurmaz *Mendeleev Commun.* 11 (2002)
226. V A Benderskii, A G Krivenko, V A Kurmaz, G V Simbirtseva *Elektrokhimiya* **24** 158 (1988) [g]
227. V A Benderskii *Electrochim. Acta* **39** 1067 (1994)
228. A G Krivenko, V A Kurmaz, A S Kotkin, A V Krestinin, G I Zvereva *Elektrokhimiya* **39** 1207 (2003) [g]
229. A G Krivenko, V A Kurmaz, A S Kotkin, G V Simbirtseva, V P Gul'tyai *Elektrokhimiya* **44** 1482 (2008) [g]
230. Ph Hapiot, V V Konovalov, J-M Savgant *J. Am. Chem. Soc.* **117** 1428 (1995)
231. V V Eletskii, Yu V Pleskov *Elektrokhimiya* **14** 1323 (1978) [g]
232. N M Rufman, Z A Rotenberg *Elektrokhimiya* **16** 1548 (1980) [g]
233. N M Rufman, Z A Rotenberg *Elektrokhimiya* **15** 349 (1979) [g]
234. V V Konovalov, Yu D Tsvetkov, I I Bilkis, S S Laev, V D Shteingarts *Mendeleev Commun.* 51 (1993)
235. A J Bard, A Merz *J. Am. Chem. Soc.* **101** 2959 (1979)
236. J Simonet, P Martinet, H Doupeux, D Bretelle *Bull. Soc. Chim. Fr.* 808 (1970)
237. H Doupeux, P Martinet, J Simonet *Bull. Soc. Chim. Fr.* 2299 (1971)
238. A L Guyon, L J Klein, D M Goken, D G Peters *J. Electroanal. Chem.* **526** 134 (2002)
239. G M McNamee, B C Willett, D M La Perrire, D G Peters *J. Am. Chem. Soc.* **99** 1831 (1977)
240. D M La Perrire, B C Willett, W F Carroll Jr, E C Torp, D G Peters *J. Am. Chem. Soc.* **100** 6293 (1978)
241. D M La Perrire, W F Carroll Jr, B C Willett, E C Torp, D G Peters *J. Am. Chem. Soc.* **101** 7561 (1979)

242. H Matschiner, R Voigtlander, H Schick, H Lund *Acta Chem. Scand., Sect. B* **B34** 136 (1980)
243. W Jin, L Xiao *J. Electroanal. Chem.* **434** 37 (1997)
244. Wenrui Jin, Xin Zhao, Li Xiao *Electroanalysis* **12** 858 (2000)
245. M Turowska, G Mloston, J Romanski, J Raczak *Pol. J. Chem.* **77** 237 (2003)
246. M Turowska, G Mloston, J Raczak *Pol. J. Chem.* **67** 1105 (1993)
247. W F Carroll Jr, D G Peters *J. Org. Chem.* **43** 4633 (1978)
248. W F Carroll Jr, D G Peters *J. Am. Chem. Soc.* **102** 4127 (1980)
249. R Shao, J A Cleary, D M La Perrire, D G Peters *J. Org. Chem.* **48** 3289 (1983)
250. S M Peregudova, L I Denisovich, N A Ustynyuk, L I Leont'eva, V N Vinogradova, T V Filatova *Izv. Akad. Nauk, Ser. Khim.* 2055 (1995) [b]
251. D A Tyssee *J. Electroanal. Chem.* **30** App. 14 (1971)
252. M Heyrovsky, P Mader, V Veselá, M Fedurco *J. Electroanal. Chem.* **369** 53 (1994)
253. M Heyrovsky, P Mader, S Vavřička, V Veselá, M Fedurco *J. Electroanal. Chem.* **430** 103 (1997)
254. B Jordanoski, V Mirčeski, K Stojanova *Croat. Chem. Acta* **69** 37 (1996)
255. V Mirčeski, B Jordanoski, M Avramov-Ivic *J. Serb. Chem. Soc.* **63** 719 (1998)
256. F Barba, F Ranz, B Batanero *Tetrahedron Lett.* **50** 6798 (2009)
257. J M Antelo, F Arce, F Rey, M Sastre, J M L Fonseca *Electrochim. Acta* **30** 927 (1985)
258. L Rampazzo, A Inesi *J. Electrochem. Soc.* **127** 2388 (1980)
259. A L Butler, D G Peters *J. Electrochem. Soc.* **144** 4212 (1997)
260. M S Mubarak, L L Karras, N S Murcia, J C Bart, J Z Stemple, D G Peters *J. Org. Chem.* **55** 1065 (1990)
261. N S Murcia, D G Peters *J. Electroanal. Chem.* **326** 69 (1992)
262. I N Chernykh, A V Bukhtiarov, A P Tomilov *Elektrokhimiya* **18** 153 (1982) [g]
263. S Aoki, T Sekine *Denki Kagaku* **49** 281 (1981)
264. R M Bastida, E Brillas, J M Costa *J. Electrochem. Soc.* **138** 2296 (1991)
265. F N Ertas, H I Gökçel, H Tural *Turkish J. Chem.* **24** 261 (2000)
266. R D Chambers, W K R Musgrave, C R Sargent, F G Drakesmith *Tetrahedron* **37** 591 (1981)
267. A Curulli, I Carelli, A Inesi *J. Electroanal. Chem.* **235** 209 (1987)
268. P Pazdera, M Studničková, I Ráčková, O Fischer *J. Electroanal. Chem.* **207** 189 (1986)
269. E Giannakopoulos, P Stivaktakis, Y Deligiannakis *Langmuir* **24** 3955 (2008)
270. E Chekmeneva, J M Díaz-Cruz, C Ariño, M Esteban *J. Electroanal. Chem.* **629** 169 (2009)
271. E Chekmeneva, J M Díaz-Cruz, C Ariño, M Esteban *J. Electroanal. Chem.* **635** 58 (2009)
272. E Giannakopoulos, Y Deligiannakis *Langmuir* **23** 2453 (2007)
273. Y M Temerk, M M Kamal, G A-W Ahmed, H S M Ibrahim *Anal. Sci.* **19** 1115 (2003)
274. E Bicer, E Cinar Z *Phys. Chem.* **218** 1273 (2004)
275. Y M Temerk, M M Kamal, Z A Ahmed, M E Ahmed, M S Ibrahim *Fresenius J. Anal. Chem.* **342** 601 (1993)
276. A M Bond, J R Bradbury, G N Howell, H A Hudson, P J Hanna, S Stroter *J. Electroanal. Chem.* **154** 217 (1983)
277. A M Bond, J R Bradbury, P J Hanna, G N Howell, H A Hudson, S Stroter, M J O'Connor *Anal. Chem.* **56** 2392 (1984)
278. A M Bond, N J Turoczy, R J Carter *Anal. Chim. Acta* **310** 109 (1995)
279. N J Turoczy, R J Carter, A M Bond *Electroanalysis* **6** 844 (1994)
280. A M Bond, N J Turoczy, R J Carter *J. Electroanal. Chem.* **365** 125 (1994)
281. K Ehara, K Kumagaya, Y Yamamoto, K Takahashi, H Yamazaki *J. Organomet. Chem.* **410** C49 (1991)
282. Y Yamamoto, K Ehara, K Takahashi *Bull. Chem. Soc. Jpn.* **66** 778 (1993)
283. M D Otero, B Batanero, F Barba *Tetrahedron* **60** 4609 (2004)
284. D D Tanner, D J Harrison, J Chen, A Kharrat, D D M Wayner, D Griller, D J McPhee *J. Org. Chem.* **55** 3321 (1990)
285. R N Gedye, Y N Sadana, R Leger *Can. J. Chem.* **63** 2669 (1985)
286. V Barone, A Bencini, F Totti, M G Uytterhoeven *Organometallics* **15** 1465 (1996)
287. B Ni, J R Kramer, R A Bell, N H Werstiuk *J. Phys. Chem. A* **110** 9451 (2006)
288. J S Banait, S K Deol, Singh Baljit *Synth. React. Inorg. Metal-Org. Chem.* **20** 1331 (1990)
289. M H Abraham, J Gil-Lostes, W E Acree Jr, J E Cometto-Muniz, W S Cain *J. Environ. Monitoring* **10** 435 (2008)
290. L Pospišil, N Varaksa, T F Magnera, T Brotin, J Michl *Langmuir* **23** 930 (2007)
291. E Kariv-Miller, D M Loffredo, V Svetličič *Denki Kagaku* **62** 1276 (1994)
292. J S Banait, R Devi, B Singh *Bull. Chem. Soc. Jpn.* **64** 3669 (1991)
293. S L Dyatkina, B B Damaskin, E V Stenina, N V Fedorovich *Elektrokhimiya* **10** 313 (1974) [g]
294. E V Stenina, L N Sviridova, B B Damaskin, S I Nefedkin, N V Frolova *Elektrokhimiya* **43** 1297 (2007) [g]
295. M Morita, J Yoshinaga, J S Edmonds *Pure Appl. Chem.* **70** 1585 (1998)
296. W L Clevenger, B W Smith, J D Winefordner *Crit. Rev. Anal. Chem.* **27** 1 (1997)
297. T N Shekhovtsova, S V Muginova, I A Veselova, I F Dolmanova *Zh. Anal. Khim.* **57** 1308 (2002) [j]
298. K Kalcher, I Svancara, M Buzuk, K Vytras, A Walcarius *Monatsh. Chem.* **140** 861 (2009)
299. O Ordeig, C E Banks, J del Campo, F X Munoz, R G Compton *Electroanalysis* **18** 573 (2006)
300. M H Chiu, J M Zen, A S Kumar, D Vasu, Y Shih *Electroanalysis* **20** 2265 (2008)
301. J Ireland-Ripert, A Bermond, C Ducauze *Anal. Chim. Acta* **143** 249 (1982)
302. P Ugo, S Zampieri, L M Moretto, D Paolucci *Anal. Chim. Acta* **434** 291 (2001)
303. I ÜIrkmez, H I Gökçel, F N Ertas, H Tural *Microchim. Acta* **167** 225 (2009)
304. A Giacomino, O Abollino, M Malandrino, E Mentasti *Talanta* **75** 266 (2008)
305. O Abollino, A Giacomino, M Malandrino, G Piscionieri, E Mentasti *Electroanalysis* **20** 75 (2008)
306. F Okçu, F N Ertas, H I Gökçel, H Tural *Turkish J. Chem.* **29** 355 (2005)
307. Y Bonfil, M Brand, E Kirowa-Eisner *Anal. Chim. Acta* **424** 65 (2000)
308. C Faller, N Y Stojko, G Henze, K Z Brainina *Anal. Chim. Acta* **396** 195 (1999)
309. H Xu, L P Zeng, S J Xing, G Y Shi, Y Z Xian, L T Lin *Electrochem. Commun.* **10** 1839 (2008)
310. S V Temerev *Zh. Anal. Khim.* **63** 322 (2008) [j]
311. X Cai, K Kalcher, W Diewald, C Neuhold, R J Magee *Fresenius J. Anal. Chem.* **345** 25 (1993)
312. M A Augelli, R A A Munoz, E M Richter, A G Junior, L Angnes *Electroanalysis* **17** 755 (2005)
313. R D Riso, M Waeles, P Monbet, C J Chaumery *Anal. Chim. Acta* **410** 97 (2000)
314. J Svarc-Gajic, Z Suturovic, N Marjanovic, S Kravic *Electroanalysis* **18** 513 (2006)
315. E Beinrohr, J Dzurov, J Annus, J A C Broekaert *Fresenius J. Anal. Chem.* **362** 201 (1998)
316. M N Abbas, G A E Mostafa *Anal. Chim. Acta* **478** 329 (2003)
317. X G Li, Q Dou, M R Huang *Monatsh. Chem.* **139** 1157 (2008)
318. I A Gur'ev, N V Kuleshova *Zh. Anal. Khim.* **53** 20 (1998) [j]
319. A Amine, C Cremisini, G Palleschi *Mikrochim. Acta* **121** 183 (1995)
320. J Chylkova, R Selesovska-Fadrna, J Machalikova *Centr. Eur. J. Chem.* **5** 479 (2007)
321. T S Hsi, J S Tsai *J. Chin. Chem. Soc.* **41** 315 (1994)
322. N S Simon *Int. J. Environ. Anal. Chem.* **68** 313 (1997)
323. M P DaSilva, J R Procopio, L Hernández *J. Chromatogr. A* **761** 139 (1997)

324. E P C Lai, W Zhang, X Trier, A Georgi, S Kowalski, S Kennedy, T MdMuslim, E Dabek-Zlotorzynska *Anal. Chim. Acta* **364** 63 (1998)
325. L G Martin, L T Jongwana, A M Crouch *Electrochim. Acta* **55** 4303 (2010)
326. F Guo, T Gorecki, D Irish, J Pawliszyn *Anal. Commun.* **33** 361 (1996)
327. I Svancara, K Vytras, C Hua, M R Smyth *Talanta* **39** 391 (1992)
328. H Mohammadi, M El Rhazi, A Amine, A M O Brett, C M A Brett *Analyst* **127** 1088 (2002)
329. H Mohammadi, A Amine, S Cosnier, C Mousty *Anal. Chim. Acta* **543** 143 (2005)
330. H Mohammadi, A Amine, M El Rhazi, C M A Brett *Talanta* **62** 951 (2004)
331. H Mohammadi, A Amine, A Ouarzane, M El Rhazi *Microchim. Acta* **149** 251 (2005)
332. S Han, M Zhu, Z Yuan, X Li *Biosens. Bioelectron.* **16** 9 (2001)
333. P Gratteri, S Furlanetto, S Pinzauti, E Laporta, P Mura, G Santoni *J. Pharm. Biomed. Anal.* **12** 273 (1994)
334. P Kubá, P Houserová, Pav Kubá, P C Hauser, V Kubá *J. Separat. Sci.* **30** 1070 (2007)
335. P J Li, J Duan, B Hu *Electrophoresis* **29** 3081 (2008)
336. S Majid, M El Rhazi, A Amine, C M A Brett *Anal. Chim. Acta* **464** 123 (2002)
337. J M Pinilla, L Hernández, A J Conesa *Anal. Chim. Acta* **319** 25 (1996)
338. H Zejli, J L H H de Cisneros, J L Hidalgo-Hidalgo, I Naranjo-Rodriguez, H Elbouhouti, M Choukairi, D Bouchta, K R Temsamani *Anal. Lett.* **40** 2788 (2007)
339. I Svancara, M Matousek, E Sikora, K Schachl, K Kalcher, K Vytras *Electroanalysis* **9** 827 (1997)
340. H C Yi *Anal. Bioanal. Chem.* **377** 770 (2003)
341. H Dong, L Lin, H Zheng, G X Zhao, B X Ye *Electroanalysis* **18** 1202 (2006)
342. W S Huang, C H Yang, S H Zhang *Anal. Bioanal. Chem.* **374** 998 (2002)
343. Y Shih, A S Kumar, J M Zen, J C Hsu *Bull. Chem. Soc. Jpn.* **78** 2130 (2005)
344. Y T Kong, Y J Bae, Y B Shim *Bull. Korean Chem. Soc.* **23** 346 (2002)
345. P Ugo, L M Moretto, P Bertoncello, J Wang *Electroanalysis* **10** 1017 (1998)
346. S Meyer, F Scholz, R Trittler *Fresenius J. Anal. Chem.* **356** 247 (1996)
347. L Xiao, W Dietze, F Nyasulu, B A F Mibeck *Anal. Chem.* **78** 5172 (2006)
348. J Gorecki, J Golas *Electroanalysis* **13** 719 (2001)
349. G G Muntyanu *Zh. Anal. Khim.* **56** 614 (2001)[j]
350. M S Celebi, H Ozyoruk, A Yildiz, S Abaci *Talanta* **78** 405 (2009)
351. M Korolczuk *Fresenius J. Anal. Chem.* **357** 389 (1997)
352. M S Seehra, S Ranganathan, A Manivannan *Anal. Lett.* **41** 2162 (2008)
353. H Zejli, J L H H de Cisneros, I Naranjo-Rodriguez, K Temsamani *Anal. Lett.* **39** 1053 (2006)
354. J Wu, L Li, B Shen, G Cheng, P He, Y Fang *Electroanalysis* **22** 479 (2010)
355. P Ugo, L M Moretto, G A Mazzocchin *Anal. Chim. Acta* **305** 74 (1995)
356. M C Rizea, A F Danet, S Kalinowski *Rev. Chim.* **58** 266 (2007)
357. G O Buica, C Bucher, J C Moutet, G Royal, E Saint-Aman, E M Ungureanu *Electroanalysis* **21** 77 (2009)
358. V Somerset, J Leaner, R Mason, E Iwuoha, A Morrin *Electrochim. Acta* **55** 4240 (2010)
359. Yu V Tsapko, S S Ermakov, L N Moskvin *Zh. Anal. Khim.* **63** 1067 (2008)[j]
360. Yu I D'yachenko, V V Kondrat'ev *Zh. Anal. Khim.* **53** 401 (1998)[j]
361. S S Ermakov, A V Borzhitskaya, L N Moskvin *Zh. Anal. Khim.* **56** 610 (2001)[j]
362. L A Khustenko, L N Larina, B F Nazarov *Zh. Anal. Khim.* **58** 297 (2003)[j]
363. P Salauen, C M G van den Berg *Anal. Chem.* **78** 5052 (2006)
364. M Javanbakht, H Khoshsafar, M R Ganjali, A Badiei, P Norouzi, A Hasheminasab *Curr. Anal. Chem.* **5** 35 (2009)
365. A Domenech, M T Domenech-Carbo, E Garcia-Espana, M D Soriano *Analyst* **124** 1661 (1999)
366. I Cesarino, E T G Cavalheiro *Electroanalysis* **20** 2301 (2008)
367. I Cesarino, G Marino, J D Matos, E T G Cavalheiro *Talanta* **75** 15 (2008)
368. U Tamer, T Oymak, N Ertas *Electroanalysis* **19** 2565 (2007)
369. E A Osipova, V E Sladkov, A I Kamenev, V M Shkinev, K E Geckeler *Anal. Chim. Acta* **404** 231 (2000)
370. N J Yang, Q J Wan, J H Yu *Sens. Actuators B: Chem.* **110** 246 (2005)
371. A Salimi, V Alizadeh, R Hallaj *Talanta* **68** 1610 (2006)
372. M A Augelli, R A A Munoz, E M Richter, M I Cantagallo, L Angnes *Food Chem.* **101** 579 (2007)
373. M C Radulescu, A F Danet *Sensors* **8** 7157 (2008)
374. Y M Panta, J Liu, M A Cheney, S W Joo, S Z Qian *J. Colloid Interface Sci.* **333** 485 (2009)
375. B V Yagov, A S Korotkov *Zh. Anal. Khim.* **61** 1090 (2006)[j]
376. R-G Cao, B Zhu, J Li, D Xu *Electrochem. Commun.* **11** 1815 (2009)
377. C Locatelli *Electroanalysis* **20** 1330 (2008)
378. A Sheremet, E Averyaskina, E Chekmeneva, S Ermakov *Electroanalysis* **19** 2222 (2007)
379. E O Averyaskina, S S Ermakov, L N Moskvin *Zh. Anal. Khim.* **61** 1192 (2006)[j]
380. C Locatelli, D Melucci *Int. J. Environ. Anal. Chem.* **90** 49 (2010)
381. R A A Munoz, F S Felix, M A Augelli, T Pavesi, L Angnes *Anal. Chim. Acta* **571** 93 (2006)
382. A Safavi, N Maleki, M M Doroodmand, M Mahdi *J. Hazardous Mater.* **173** 622 (2010)
383. I Turyan, T Erichsen, W Schuhmann, D Mandler *Electroanalysis* **13** 79 (2001)
384. Y Bonfil, M Brand, E Kirowa-Eisner *Rev. Anal. Chem.* **19** 201 (2000)
385. D Han, Y-R Kim, J-W Oh, T H Kim, R K Mahajan, J S Kim, H Kim *Analyst* **134** 1857 (2009)
386. A Economou, P R Fielden *Analyst* **128** 205 (2003)
387. C M Watson, D J Dwyer, J C Andle, A E Bruce, M R M Bruce *Anal. Chem.* **71** 3181 (1999)
388. M Lovrić, F Scholz *Electroanalysis* **9** 1189 (1997)
389. N A Whittemore, A N Mullenix, G B Inamati, M Manoharan, P Dan Cook, A A Tuinman, D C Baker, J Q Chambers *Biocon. Chem.* **10** 261 (1999)
390. N Y Stojko, K Z Brainina, C Faller, G Henze *Anal. Chim. Acta* **371** 145 (1998)
391. M Huang, M J Huang, P W Faguy, W-P Pan *Electroanalysis* **9** 1201 (2005)
392. A Manivannan, L Ramakrishnan, M S Seehra, E Granite, J E Butler, D A Tryk, A Fujishima *J. Electroanal. Chem.* **577** 287 (2005)
393. E A Zakharova, V M Pichugina, T P Tolmacheva *Zh. Anal. Khim.* **51** 918 (1996)[j]
394. V N Batalova, E A Zakharova, G B Slepchenko, M V Malygina *Zh. Anal. Khim.* **59** 528 (2004)[j]
395. I Turyan, D Mandler *Electroanalysis* **6** 838 (1994)
396. J M Gong, T Zhou, D D Song, L Z Zhang, X L Hu *Anal. Chem.* **82** 567 (2010)

[a] — *Quantum Electron. (Engl. Transl.)*
[b] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[c] — *Moscow Univ. Chem. Bull. (Engl. Transl.)*
[d] — *Russ. J. Organomet. Chem. (Engl. Transl.)*
[e] — *Russ. J. Org. Chem. (Engl. Transl.)*
[f] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[g] — *Russ. J. Electrochem. Chem. (Engl. Transl.)*
[h] — *Dokl. Chem. (Engl. Transl.)*
[i] — *Mendeleev J. (Engl. Transl.)*
[j] — *J. Anal. Chem. (Engl. Transl.)*