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Acid-catalysed degradation of the organomercury intermediates of pentafluorophenylmercury bromide reduction near a mercury electrode

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The acid-catalysed protolysis of intermediates, formed either during one-electron reduction of substituted arylmercury salt (C_6F_5HgBr) or by the adsorption of bis(arylalkynyl)mercury compound [$(PhC{\equiv}C)_2Hg$] on a Hg electrode has been found in low-acidic media ($3 < pH < 6$), whereas it was not observed in alkylmercury salt (PrⁿHgOAc).

Organomercury compounds are much more toxic than inorganic mercury because of their higher solubility in lipids and the ability to interact directly with tissues.[1] The protolysis,[2] solvolysis[2] and electrochemical reduction/oxidation[3] of organomercury compounds should be attributed to effective demercuration methods under mild conditions.

However, electrosynthesis[3,4] of organomercury compounds is complicated by surface blocking with sparingly soluble electrochemical reduction products,[4] and small amounts of an acid are added to prevent it.[4(b)] Acid media are necessary for the electrosynthesis of organomercury compounds from non-mercurated depolarisers, *e.g.*, to produce R_2Hg from ketones[3(a),(b)] or RHgX from aldehydes,[4(a)] and the electrochemical reduction of some nitrogen- or oxygen-containing compounds is possible in a protonated form only.[3(a)] Intermediate species of the process may evoke electrocatalytic hydrogen evolution on a mercury electrode.[4(c),(d),5,6] It includes presumably organomercury intermediate formation, as well as their degradation with a proton donor.[5] This process was not studied practically for the electrochemical reduction of organomercury compounds although it could complicate their electrosynthesis. Therefore, we studied the electrochemical behaviour of organomercury compounds at pH ~3–10 to specify their electroreduction mechanism in low-acidic media.

A version of chronopotentiometry, namely, a current reversal pulse galvanostatic method,[‡,7(a),(b)] and conventional linear sweep voltammetry and chronovoltammetry[7(c)] were used.[8] Pentafluorophenylmercury bromide (PFMB) C_6F_5HgBr, perfluorodiphenylmercury (PFDM) $(C_6F_5)_2Hg$, bis(phenylacetylenyl)mercury (BPAM) $(PhC{\equiv}C)_2Hg$, and *n*-propylmercury acetate (PMA) PrⁿHgOAc were prepared by known methods.[2(a),§]

According to Benesh,[9(a)] the electrochemical reduction of RHgX salts occurs on a Hg electrode *via* two one-electron stages (1a)–(1e), and (2a), (2b) or (4a), (4b) (Scheme 1). R_2Hg derivatives[3,9,10] are main and sometimes the only[4(f),10(c),(d)] electrolysis end products at the controlled potentials E_i on the plateau of the first reduction wave of RHgX, *i.e.*, at $E^{(1)}_{1/2} > E_i > E^{(2)}_{1/2}$, stages (1a)–(1e), (3), (6a) in Scheme 1. Such a way of symmetric organomercury compounds synthesis is well known,[3] being a suitable electrochemical alternative to the chemical synthesis from RHgX salts under the action of reducing agents (amalgams, metal hydrides or salts[2(a)]), a version of recombination mechanism of hydrogen electrochemical reduction.[7(c)] This method is widely used in preparative and industrial electrosynthesis of organometallic compounds,[2(a),3] and in some cases it is most efficient and selective, *e.g.*, in the symmetrisation of C- and B-carboranylmercury salts.[10(c)]

Extremely unstable intermediates, organomercury radicals $RHg^{\cdot}$, were considered earlier[9(a)] as products of one-electron RHgX reduction [stages (1a)–(1e), Scheme 1]. They can be stabilised on a Hg electrode *via* either adsorption to yield ($RHg^{\cdot}_{ads}$)[3] or dimerisation into metastable ‘organic calomels’ R_2Hg_2 (RHgHgR, RHgHgR′ or RHgHgX).[11,12] A formation of similar intermediates was found during dialkylmercury[11(a),(b)] and BPAM[11(c)] adsorption. Other structures were also postulated, *e.g.*, ‘organometal’,[3] polymercurides[9(b),(c)] and organic amalgams,[5] R_mHg_n ($m = 2, 3, ...$; $n = 3, 4, ...$), and we use here the term ‘organic calomel’ for $[RHg_{ads}]_n$. These intermediates are reduced upon the second wave, stages (2) and (4) in Scheme 1, respectively. They were neither isolated nor characterised although sparingly soluble products with higher mercury contents were obtained.[4(c),(d),9(c)]

Products R_2Hg, formed at controlled potential electrolysis E_i upon the plateau of the first wave of RHgX reduction have often worse solubility than an initial salt and are hence accumulated near the electrode (*e.g.*, 2-acetyl-5-thienyl-mercury bromide,[10(b)] PrⁿHgOAc,[11(b),13(a),(b)] PhHgOH[10(e)] and C_6F_5HgBr.[8(b),10(a)]).

A condensed phase (suspension)[8(b)] of electrochemically active $(C_6F_5)_2Hg$ is formed near HMDE surface at one-electron reduction of C_6F_5HgBr. Its solubility does not exceed $(1.5–2)\times10^{-5}$ M[8,10(a)] in aqueous alcohol solutions (10 vol% EtOH or MeOH) of inorganic salts and buffers. A monolayer is fulfilled first,[10(a)] and monolayer and suspension are reduced together on the same faradaic delay [$E_1 \sim -1$ V; $(\alpha n_a)_1 \sim 0.8$] if current densities i are sufficiently small, but separately in an intermediate region ($0.02–0.4 \geq i \geq 30–70$ mA cm^{-2}) (Figure 1, curves *1*, *2*), whereas $\Delta(E_2 - E_1) \sim -(0.1–0.5)$ V. Only the PFDM monolayer is reduced at high current densities ($i \geq 1–4$ mA cm^{-2}). Here, $i\tau_1$ is ~(32–42)[8,10(a)] μQ cm^{-2}, and it does not depend on i. The lengths of 1 ($i\tau_1$) and 2 ($i\tau_2$) delays and their positions on the *i*–*E* curve depend on experimental conditions, particularly, on the nature and concentration of a supporting electrolyte (Figure 1, curves *1*, *2*). It was demonstrated earlier that a PFDM complex with an electrolyte anion or a solvent is reduced on a second delay.[8] The separated reduction of a monolayer and next layers was observed for other organometallic compounds, particularly, for chemisorption products of diphenylselenide and diphenyltelluride at a HMDE.[14]

Like other systems,[11(b),14] a filled monolayer does not prevent the formation of a near-electrode condensed phase even in spite of the high adsorbability of PFDM: the Stenina-Fedorovich criterion ln ($B + a$) is ~14.33[8(a)] (B is the adsorption equilibrium constant, and a is the attraction constant of the Frumkin isotherm). The electroreduction delay length $i\tau_1$ of a sparingly soluble product at stages (1a)–(1e) (Scheme 1) may increase with the time of potentiostatic accumulation t_p, *i.e.*, a full blockage of C_6F_5HgBr reduction does not occur at sufficiently small i. However, if a symbatic increase is observed for bis(2-acetyl-5-thienyl-5)-mercury,[10(b)] the $i\tau$–t_p relation has a more complicated character for PFDM. New faradaic delays may appear on charge curves if t_p are sufficiently long (≥ 3–4 min), and ‘old’ ones change their shape to exhibit minima and maxima like that observed in the one-electron reduction of phenylmercury salts.[10(e)] Apparently, a

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[†] Deceased.

[‡] Main characteristics of the method were as follows: the transition from potentiostatic into galvanostatic regime occurred within $(1–3)\times10^{-6}$ s, the range of current density i was 5–7 orders of magnitude, *i.e.*, up to $i \leq 10^2–10^3$ mA cm^{-2}. A three-electrode cell (0.05 dm^3) was used, the working electrode was a hanging mercury drop electrode (HMDE). We employed external reference electrodes, a counter electrode was Pt wire. All potentials were referred to a saturated calomel electrode.

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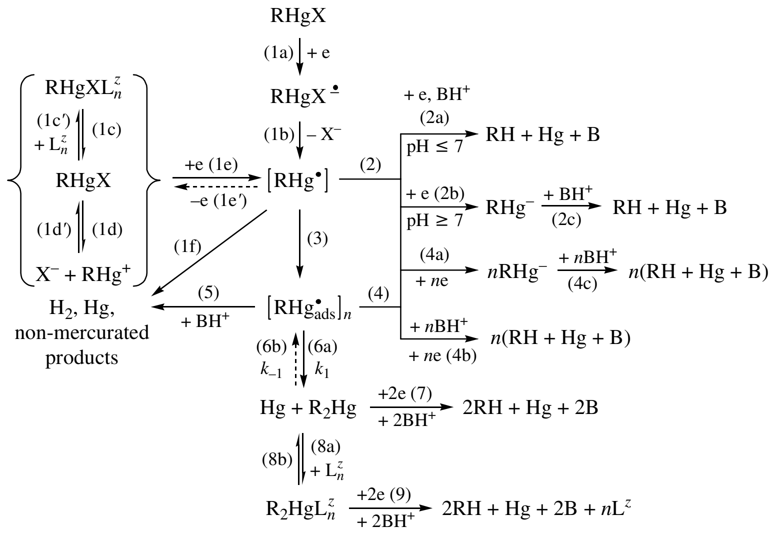

Scheme 1 Electrode reactions of organomercury salts RHgX and R_2Hg on a Hg cathode. BH^+ is a proton donor, L^z_n is a ligand with charge *z*.

change of the near-electrode phase structure occurred during PFDM electrosynthesis. The $i\tau_1$–t_p relation deviated from a linear one (Figure 2, curves *2*, *3*), and the amount of electrosynthesised depolariser is smaller than that calculated from the equation for diffusion to a stationary spherical electrode[3(*a*)] (see Figure 2, curve *1*):

$$I = nFc_0DS\left(\frac{1}{\sqrt{\pi Dt_p}} + \frac{1}{r}\right), \qquad (1)$$

for which electron number $n = 1$, *S* (the area of the electrode surface of radius *r*) is ~0.03 cm^2, the diffusion coefficient of a depolariser *D* (PFDM), obtained from *I*,*t*–, and, on Koryta equation[7(*c*)] – from $i\tau$–t_p curves is ~2×10^{-6} cm^2 s^{-1}, and *F* is the Faraday number.

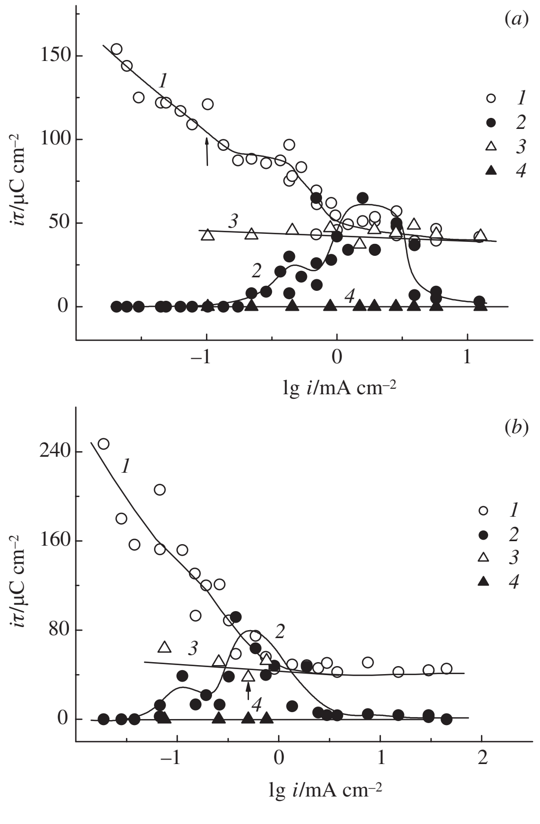

Figure 1 The dependence of delay lengths 1 ($i\tau_1$) and 2 ($i\tau_2$) on current density *i* in 5×10^{-5} M C_6F_5HgBr solutions. Supporting electrolyte: aqueous ethanol (10 vol% EtOH) NaOAc solutions or Walpole buffer; t_p = 2 min, 25±0.2 °C, E_i = –0.2 V. (*a*) curves *1*, *2*: 2.7 M NaOAc, pH 9.1; curves *3*, *4*: Walpole buffer (2.7 M NaOAc + 0.8 M HOAc, pH 5.5); (*b*) curves *1*, *2*: 0.9 M NaOAc, pH 8.6; curves *3*, *4*: Walpole buffer (0.9 M NaOAc + 0.8 M HOAc, pH 4.4). Arrows designate *i* values where curves *2* and *4* of Figure 2 were recorded.

It was revealed that even at small additions of acids (HOAc, HCl, H_2SO_4; 3 < pH < 6) into C_6F_5HgBr solutions the second delay of $(C_6F_5)_2Hg$ electrochemical reduction disappeared instead of blockage¶ removal[4(*b*)] (Figure 1, curves *4*). A length of delay 1 ceased to depend on *i* (Figure 1, curves *3*), as well as on t_p (Figure 2, curves *4*), and diminished practically until to that of monolayer values.

Additions of an acid render a similar influence on the electrochemical behaviour of BPAM, a compound that also contains an aromatic group. If applied current densities are not too high [≤ ~(0.1–1) mA cm^{-2}, see ref. 11(*c*)], one can observe two delays on a charging curve, at potentials near –1 and –0.3 V, respectively. They correspond to the electroreduction of R_2Hg [stage (7)] and $[RHg_{ads}]_n$ [stages (2) and (4)]. The 'organic calomel' is formed here apparently *via* stage (6b). The delay corresponding to the electroreduction of $[RHg_{ads}]_n$ disappears at small addition of acids [~(0.1–1) M, pH 4.4–5.5] but the second one is either without changes or slightly diminished. However, additions of the same AcOH amounts into (2–40)×10^{-4} M PMA solutions did not exert a remarkable influence on delay of

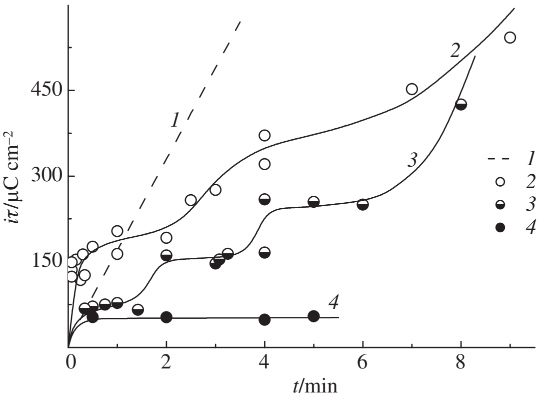

Figure 2 (*1*) Calculated and (*2*)–(*4*) experimental Γ–t_p curves of the electrochemical reduction of $(C_6F_5)_2Hg$ produced by controlled potential electrolysis on the plateau of the first reduction wave of C_6F_5HgBr within potentiostatic regime at E_i = –0.2 V. Curve *1*: calculation by equation (1); curves *1*, *2* and *4*: c_0 = 5×10^{-5} M; curve *3*: c_0 = 4.4×10^{-5} M; curve *2*: 25±0.2 °C; curves *3*, *4*: 20±0.2 °C. i = 0.072, 0.115 and 0.752 mA cm^{-2} (curves *2*, *3* and *4*, respectively). Supporting electrolyte: aqueous ethanol (10 vol% EtOH) 0.9 M NaOAc solutions, pH 8.6 (curves *2*, *3*) or Walpole buffer (0.9 M NaOAc + 1.4 M HOAc, pH 4.2, curve *4*).

¶ A temperature increase occurred to be more effective in these conditions to removal blockage, *e.g.*, the second delay of reduction disappears at 50 °C, and a length of delay 1 is increased remarkably.

$[RHg_{ads}]_n$ electrooxidation on the anodic branch of a chronopotentiogram.[††]

Therefore, the protolysis of the studied organomercury compounds should be considered. Symmetric organomercurials are known[2] to be protolysed, whereas aromatic R_2Hg compounds react more easily than aliphatic ones, and bases do not rupture, as a rule, the C–Hg bond. Meanwhile, both aliphatic and aromatic R_2Hg compounds with strong electronegative substituents (*e.g.*, if to introduce fluorine atoms into the benzyl ring instead of H[15(a)]) exhibit high C–Hg bond stability toward protons and other electrophilic reagents.[2] For example, PFDM was successfully crystallised from concentrated sulfuric acid.[15(b)] Organomercuric salts RHgX are, *vice versa*, protolysed much more difficultly; *e.g.*, phenylmercury bromide decayed extremely slowly in the presence of AcOH,[2(b)] and the polarographic currents of a 5×10^{-4} M MeHgCl solution did not change under keeping in an HCl solution at pH 1 over a week.[15(c)]

However, protolysis is performed for a long time at elevated temperatures, high acid concentrations and additions of strong nucleophilic agents like Br^- or I^- ions.[2] Here, the effect is observed even in slightly acidic solutions (pH $\leq$ 4.8–5.5) and at room temperatures. The behaviour of the systems before acid additions is entirely renewed after the neutralization of depolarizer solutions (C_6F_5HgBr and BPAM) with bases (KOH). This obviously evidenced the absence of any protolysis of initial compounds.

It is unlikely to attribute the observed phenomenon to PFDM protolysis, too. Moreover, its electroreduction delay length does not depend on pH within the same range (4.4–9.2), and the reduction potential of PFDM does not practically change: we observed only a small potential shift of 0.01–0.02 V at pH 4.6 with respect to pH 8.6.

It is very likely that acid-catalysed protolysis of reduction intermediates of organomercury compounds takes place in our case. It was postulated[5] that such a process accompanied, *e.g.*, the electroreduction of adamantanones, (methyl)halopyridines, methyl 2-hydroxy-4-hydroxyiminobutyrate *etc.*, on a mercury electrode in low-acidic media. Bibenzylmercury was detected among other products of electrocatalytic reduction of benzyl chloride [Co^{II}(salen) catalyst] on a mercury electrode. However, no organomercury compounds were found after such a proton and hydrogen atom donor as diphenylphosphine was added into a reaction mixture.[16(a)] This phenomenon was also explained[16(a)] by the acid-catalysed desctruction of organomercury intermediates. The proton donor (AcOH) promoted decomposition of organometallic intermediates [alkylnickel(II)salen] was also postulated to be at electrocatalytic reduction of dihalobutanes[16(b)] and halohydrines[16(c)] on Hg and GC electrodes.

The electroreduction of 3,6-di(dimethylamino)acridine and 3,6-diamino-10-methylacridinium chloride in low acid solutions (5 $\leq$ pH $\leq$ 7) is continued[4(d)] by a fast decomposition of formed organomercury compounds (polymercurides[4(d)]), and hydrogen bubbling. A similar process was found for unsubstituted acridine, although it occurred not so fast. It follows from reported data[14(a)] that pH practically does not affect the formation of organomercury compound polylayers during diphenylselenide chemisorption on a HMDE within the range 4.6–9.1.

Thus, influence of acids on the behaviour of intermediates of RHgX reduction depends on the nature of organic moiety R. $[RHg_{ads}]_n$ stability in a monolayer is changed within a broad range, whereas it is appreciably higher for alkylmercury rather than arylmercury.[11(b)] The lifetime τ of intermediates $[RHg_{ads}]_n$ is ~10^{-4} s for R = C_6F_5,[11(a)] and it is equal to 0.04 s for R = Pr^n,[13(b)] and rate constants k_2 of $[RHg_{ads}]_n$ formation from R_2Hg [stage (6b)] are $<< 7\times10^{-3}$, ~50, and 0.07–0.14 s^{-1} for R = C_6F_5,[13(a)] PhC≡C,[11(c)] and Pr^n,[13(b)] respectively.

Probably, the acid-catalysed intermediates destruction like $[RHg_{ads}]_n$ and/or their complexes with a proton donor might be retarded with stabilization by their adsorption interaction in a monolayer. Note that the time of a PFDM monolayer filling is almost constant and does not exceed several seconds independently on acid additions. However, it was proposed[10(d)] that fast intermediates decomposition occurred behind a monolayer, stage (5) in Scheme 1. Particularly, it was found quantitatively[13(a)] for R = Pr^n where a quasi-equilibrium in a monolayer was established between a metastable $[RHg_{ads}]_n$ and full R_2Hg compound [stages (6a), (6b), Scheme 1].

Let us to consider the possibility of metastable polar radical – proton donor complex formation on an electrode surface[17] if radical species participate in intermediates generation. Inasmuch as radicals polarity of the investigated compounds is altered in the next range: $C_6F_5Hg^{\cdot} >> PhC{\equiv}C^{\cdot} > Pr^nHg^{\cdot}$, the probability of $[C_6F_5Hg^{\cdot}{\cdot}H_3O^+]$ complex formation (and, hence, of an intermediates protolysis) will be sufficiently higher, and such complexes were not found for non-polar alkyl radicals.[17]

Thus, we experimentally found a depletion of surface-active intermediates formed either at electrochemical reduction or during adsorption on a Hg electrode some arylmercury compounds [C_6F_5HgBr, $(PhC{\equiv}C)_2Hg$] in low-acidic buffer solutions (3 < pH < 6). Such an approach could be efficient in a number of cases to decompose even highly chemically stable RHgX salts under mild conditions, especially if R is a substituted aryl. Apparently, such reactions of ‘electrochemical’ protodemercuration (or protodemetallation, if we take into account published data[16]) of intermediates can play an important role in the chemistry of organometallic compounds.

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