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Adsorption and Electrocatalytic Oxidation of Organomercury Salts

Yurii A. Borovsky, Kirill V. Nikitin,* Nonna P. Andryukhova and Grigorii A. Bogdanovsky

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation.
Fax: +7 095 939 2679

The adsorption of organomercury salts is found to proceed *via* dissociative chemisorption with irreversible poisoning of the platinum electrode with mercury; the principles of oxidation of organomercury salts on platinum and lead dioxides have been studied.

Over the last three decades, electrochemical methods, that give useful information concerning the redox characteristics and which simplify the identification and synthesis of reactive intermediates have been widely employed[1–8] for investigating the properties of organometallic compounds and for developing methods for the synthesis of organometallic compounds. However, the behaviour of organomercury compounds (OMCs) in electrocatalysis has scarcely been studied.

It is well known that even the adsorption of compounds whose structures are similar, such as methanol and ethanol, occurs according to different mechanisms. Therefore, one could expect that the adsorption behaviour of OMCs would differ from that of inorganic mercury compounds or organic compounds.

Since the industrial production and application of organomercury compounds is somewhat dangerous for the environment,[9] it seems promising to develop the bases of electrocatalytic destruction of organomercury compounds, a method which has been successfully applied to the treatment of waste water containing phenol,[10] dyes,[11] "biologically hard" detergents[12] and other dangerous compounds.

In this work we studied both simple organomercury compounds such as methylmercury(II) iodide, ethylmercury(II) bromide, phenylmercury(II) chloride, *n*-butylmercury(II) bromide and *sec*-butylmercury(II) bromide and rather complex compounds, such as sodium ethylmercuriothiosalicylate[13] and sodium *p*-chloromercuriobenzoate. We synthesised these compounds by known methods.[14]

In order to analyse the changes in the OMC concentration during the electrolysis, we elaborated a procedure based on the selective reaction of the C–Hg bond with iodine followed by back titration with sodium thiosulfate. Electrodes of platinised platinum and lead dioxide on a graphite support were used in the study. A 1 M solution of potassium hydroxide served as the supporting electrolyte. A silver chloride reference electrode was used and the potentials were recalculated to the hydrogen scale referring to the same electrolyte. A platinum wire sealed in glass was used as the auxiliary electrode. The potential sweep rate was 4 mV s^{-1} in all cases.

Both hydrogen and oxygen peaks on the potentiodynamic charging curves were observed to decrease as soon as 5 ml of a solution (100 mg dm^{-3}) of any of the OMC studied was added (Figs. 1 and 2). The non-stationary currents and the shifts of the potential were within the limits of experimental accuracy, which indicates either that slow adsorption occurs or that adsorption proceeds by a mechanism differing from the classical deoxygenation and dehydrogenation mechanisms.

The hydrogen and oxygen peaks increase after rinsing the electrodes but do not attain the initial values. This fact indicates that physical adsorption is accompanied by chemisorption. The charges consumed for the oxidation of adsorbed hydrogen or reduction of adsorbed oxygen were estimated from the potentiodynamic curves obtained. Further, assuming that monolayer adsorption of hydrogen on 1 cm^2 of neat platinum surface corresponds to 210 μC (for oxygen, 420 μC), we calculated the area of platinum capable of adsorption of hydrogen or oxygen. The degree of coverage was calculated as the ratio of the platinum surface, which has lost the ability to adsorb hydrogen or oxygen due to the adsorption of the substrate, to the original platinum surface. Thus, θ_R was calculated in the presence of adsorbate in solution and $\theta_{R'}$ after the electrode had been rinsed five times by the supporting electrolyte solution. The calculated overall degrees of coverage (θ_R) and the degrees of coverage with strongly chemisorbed species ($\theta_{R'}$) are presented in Table 1.

It is worth mentioning that the original shape of the charging curve was not attained after alternating cathodic and

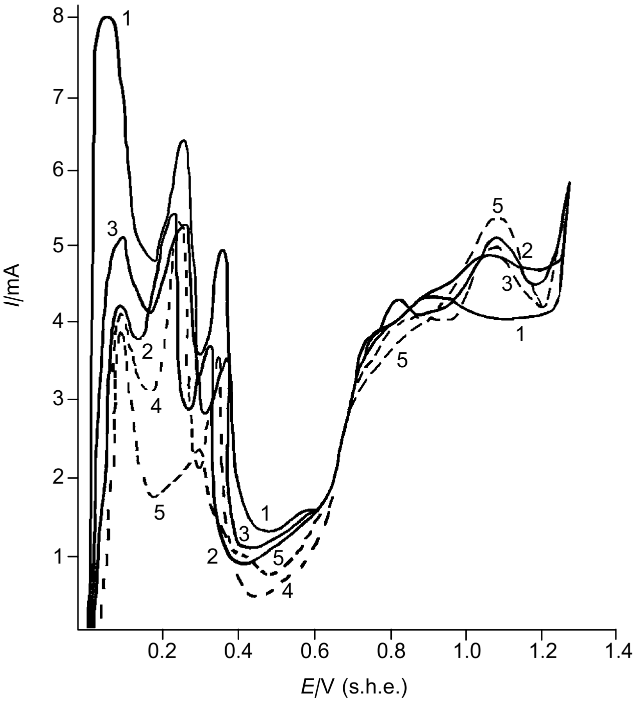

Fig. 1 Changes in the shape of the anodic branch of the potentiodynamic charging curve after the addition of 5 ml of an OMC solution (c = 0.1 g l^{-1}) to 1 M KOH as the supporting electrolyte: 1, original curve; 2, MeHgI; 3, EtHgBr; 4, Bu^{n}HgBr; 5, PhHgCl.

Table 1 Overall degree of coverage (θ_R), degree of coverage with a chemisorbed compound ($\theta_{R'}$) and extent of surface poisoning with mercury (θ_{Hg}) for platinised platinum.

Compound	θ_R^H (%)	θ_R^O (%)	$\theta_{R'}^H$ (%)	$\theta_{R'}^O$ (%)	θ_{Hg}^H (%)	θ_{Hg}^O (%)
MeHgI	43	5	9	6	7	0
EtHgBr	29	20	14	0	18	24
Bu^{n}HgBr	49	9	42	0	21	5
PhHgCl	43	0	30	0	20	12
Bu^{s}HgBr	60	30	20	15	10	10
p-NaOOCC$_6$H$_4$HgCl	40	10	10	0	10	0

anodic polarisation of the electrode (three times, $i = 100$ mA, 30 min each). We believe that this results from demercuration of the starting substance and poisoning of the platinum electrode with mercury. The changes in the shape of the potentiodynamic charging curves are most distinct in the case of ethylmercury(II) bromide (Figs. 3,4).

For all compounds studied, the anodic branches of the potentiodynamic charging curve have a peak at 1.10–1.15 V. This phenomenon is likely to result from oxidation of the products of dissociative chemisorption on the electrode surface. This explanation is supported by the charging curves recorded after rinsing the electrode by the supporting electrolyte (Fig. 3). The highest oxidation peak was observed at the first charging curve, while the peak height in the subsequent curves decreased to zero by the fifth cycle of charging in the range 0–1.6 V.

Since the organomercury compounds studied tend to undergo dissociative chemisorption, it was of interest to study their behaviour in the oxygen discharge overpotential region. The organomercury compounds were electrolysed under galvanostatic conditions ($I = 3$ mA, electrode surface S = 266 cm^2, duration t = 4 h) with isolated cathodic and anodic spaces. During the electrolysis, the potential was found to be almost constant and depended only on the electrode material: +1.7 V on a platinum anode and +1.85 V on PbO$_2$/C. The amounts of organomercury compounds in the electrolysis products were analysed by the above procedure. The results are given in Table 2.

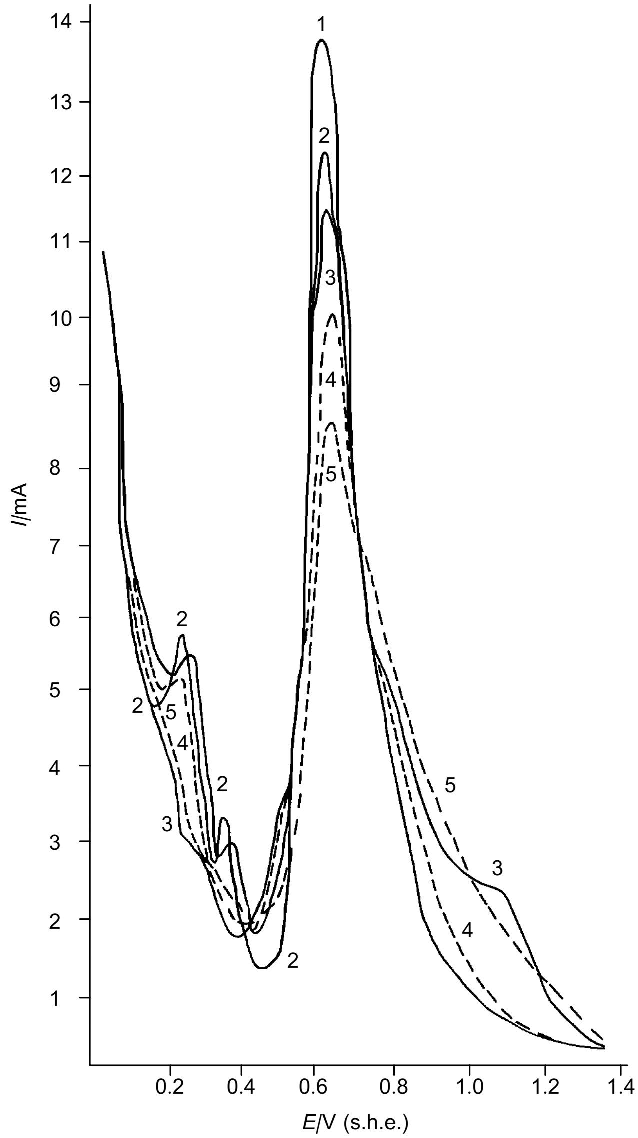

Fig. 2 Changes in the shape of the cathodic branch of the potentiodynamic charging curve after the addition of 5 ml of an OMC solution (c = 0.1 g l^{-1}) to 1 M KOH as the supporting electrolyte: 1, original curve; 2, MeHgI; 3, EtHgBr; 4, Bu^{n}HgBr; 5, PhHgCl.

Table 2 The degree of destruction (x), current yield for a bielectron process (y) and for complete oxidation (z) of organomercury compounds after electrolysis (I = 3 mA, 4 h, C_0 = 0.1 g l^{-3}, 1 M KOH).

Compound	Electrode type					
	Pt/Pt			PbO$_2$/C		
	x (%)	y (%)	z (%)	x (%)	y (%)	z (%)
MeHgI	53	4.8	19	2	0.2	0.7
EtHgBr	14	1.4	10	10	1.1	7.1
Bu^{n}HgBr	19	1.8	23	15	1.4	18
PhHgCl	15	1.5	22	38	3.8	57

The current yields for the bielectron process were calculated from the equation:

$$\mathrm{RHgX} - 2\mathrm{e}^- + 2\mathrm{OH}^- \longrightarrow \mathrm{ROH} + \mathrm{HgXOH}$$

The current yields for complete oxidation were calculated from the equation of reaction, *e.g.* for methylmercury(II) iodide:

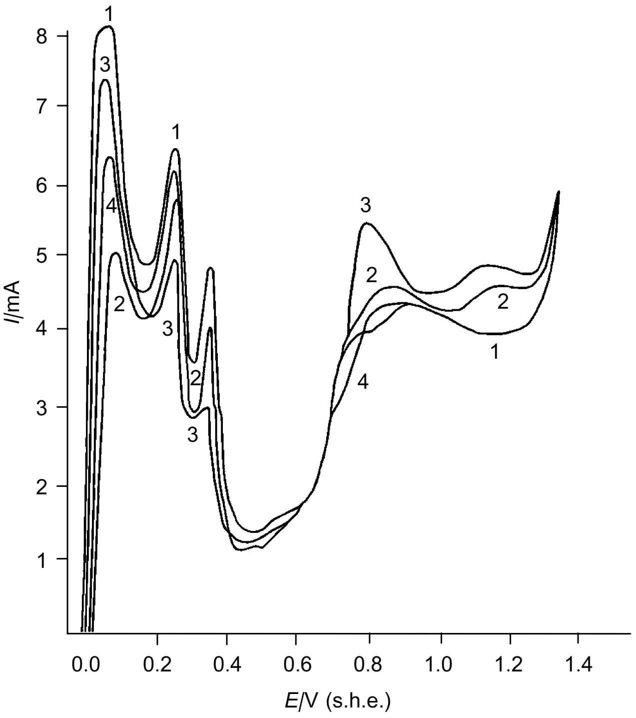

Fig. 3 Anodic branch of the potentiodynamic charging curve after the addition of 5 ml of an ethylmercury bromide solution ($c = 0.1$ g l^{-1}) to 1 M KOH as the supporting electrolyte: 1, original curve; 2, in the presence of EtHgBr; 3, after EtHgBr removal followed by rinsing the electrode with 1 M KOH; 4, after repeated anodic-cathodic polarisation of the electrode in the supporting electrolyte.

$$\mathrm{MeHgI} - 8e^- + 9\mathrm{OH}^- \longrightarrow \mathrm{CO}_3^{2-} + \mathrm{Hg}^{2+} + \mathrm{I}_2 + 6\mathrm{H}_2\mathrm{O}$$

The hypothesis of complete oxidation is based on the fact that organic products of bielectron oxidation are generally oxidised on platinised platinum into carbon dioxide and water.[16] It is also known[10,11] that even such barely oxidised compounds as phenol and dyes can be electrochemically oxidised into carbon dioxide and water in the presence of halide anions. One can see from Table 2 that Pt/Pt and $\mathrm{PbO_2/C}$ anodes possess different activity toward different compounds. The platinum anode is more efficient for compounds with smaller organic substituents while lead dioxide anodes are preferable in the case of compounds containing bulky aliphatic or aromatic groups.

Thus, the present study allows us to conclude that the behaviour of organomercury compounds in electrocatalytic systems is typical of usual organic compounds, *i.e.* they undergo dissociative chemisorption and oxidation at overpotentials of oxygen evolution. On the other hand, organomercury compounds possess properties typical of inorganic mercury salts, *i.e.* irreversible poisoning of platinum by mercury. The data obtained can form the basis for the development of a method for waste water purification from organomercury compounds present in low concentrations.

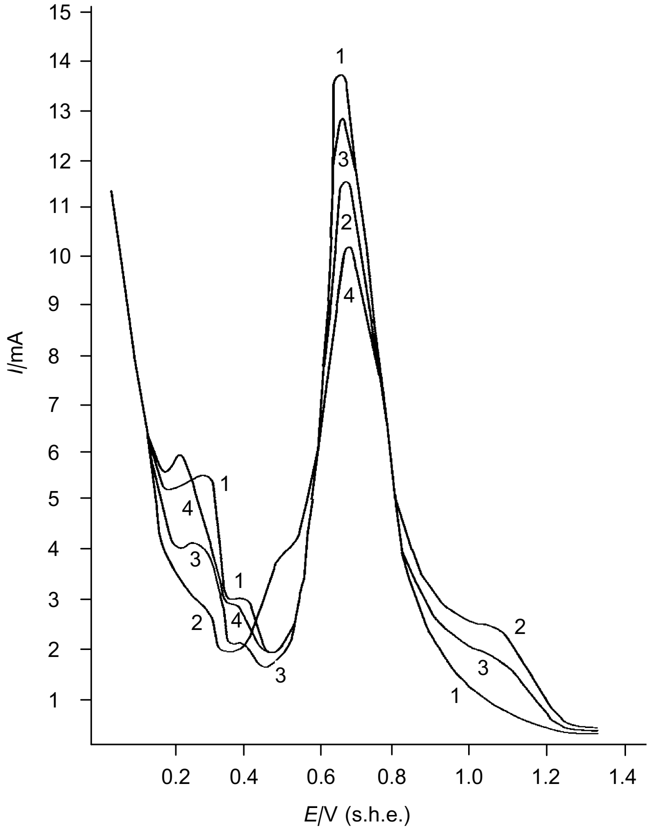

Fig. 4 Cathodic anodic branch of the potentiodynamic charging curve after the addition of 5 ml of an ethylmercury bromide solution ($c = 0.1$ g l^{-1}) to 1 M KOH as the supporting electrolyte: 1, original curve; 2, in the presence of EtHgBr; 3, after EtHgBr removal followed by rinsing the electrode with 1 M KOH; 4, after repeated anodic-cathodic polarisation of the electrode in the supporting electrolyte.

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