Recent developments in studies of organic calomels *

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Abstract

New experimental evidence for the existence of organic calomels of both symmetrical, R_2Hg_2, and non-symmetrical, RHg_2X, types, as well as theoretical calculations of corresponding electronic structures and molecular geometries are discussed.

Introduction

"Organic calomel" is a commonly used extrasystematic name for organodimercury compounds, like RHgHgR, RHgHgR′, or RHgHgX, where R and R′ are organic groups (alkyl, aryl, benzyl, etc.) and X is an inorganic residue, e.g. Cl, Br, etc. (see ref. 1 and the literature cited therein). This name emphasizes the relationship of such compounds to the "true" inorganic calomel, ClHgHgCl, in which covalent mercury–mercury bonding is the main structural feature of the molecule.
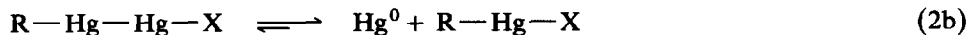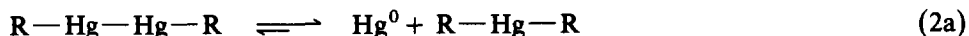
Thermodynamically, dimercury dichloride, Hg_2Cl_2, is a very stable molecule and that is why it has been known for a long time. There are inorganic calomels, e.g. halides (X = Cl, Br), nitrate, perchlorate, sulphate, acetate, chlorate, bromate and iodate, which are sufficiently stable in aqueous solutions at room temperatures [2]. There are others, however, e.g. Hg_2I_2, $Hg(SCN)_2$ and $Hg(CN)_2$ which are unstable and undergo disproportionation in aqueous solutions to give zero-valent mercury and mercury(II) salts:

$$Hg_2X_2 \xrightleftharpoons{\text{H}_2\text{O}} Hg^0 + Hg^{II}X_2 \tag{1}$$

The equilibrium 1 depends on the affinities of X^- anions for the Hg^{2+} dication: when the affinity is large enough, as in the case of X = I, SCN, CN etc., the equilibrium is shifted to the right, and Hg_2X_2 species are unstable. Nevertheless, the equilibrium 1 can be shifted more to the left when the reaction occurs at the interface between mercury metal and HgX_2 solutions. Since carbanions, especially

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those of alkyl type, have very high affinities for the Hg^{2+} ions, the equilibria 2a or 2b would be expected to be shifted far to the right:

$$R\!-\!Hg\!-\!Hg\!-\!R \quad \rightleftharpoons \quad Hg^0 + R\!-\!Hg\!-\!R \tag{2a}$$

$$R\!-\!Hg\!-\!Hg\!-\!X \quad \rightleftharpoons \quad Hg^0 + R\!-\!Hg\!-\!X \tag{2b}$$
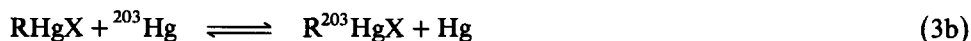
Indeed, organic calomels are very unstable species and they cannot be isolated as individual compounds at room temperatures. However, such compounds can arise in appreciable concentrations at the mercury metal surface when it comes in contact with solutions of R_2Hg or $RHgX$ [1].
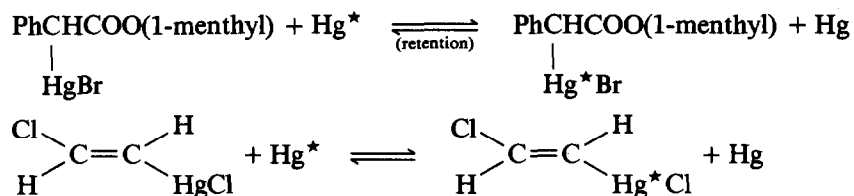
The present paper reports the results of our studies or organic calomels carried out since the publication of our short review [1] in 1975. Attention will be focussed on mercury isotopic exchange, organomercury electrochemistry and on theoretical studies of organic calomels.

Mercury isotopic exchange

The early suspicions about formation organic calomels as short lived intermediates came from the studies of mercury isotopic exchange between organomercury compounds and radioactive mercury metal, ^{203}Hg [3].

$$R_2Hg + {}^{203}Hg \quad \rightleftharpoons \quad R_2{}^{203}Hg + Hg \tag{3a}$$

$$RHgX + {}^{203}Hg \quad \rightleftharpoons \quad R^{203}HgX + Hg \tag{3b}$$

The reaction 3b has been shown to occur with the retention of stereochemical configuration at the carbon atom attached to mercury [3a,3d].

$$\underset{\overset{|}{HgBr}}{PhCHCOO(1\text{-menthyl})} + Hg^\star \quad \underset{(retention)}{\rightleftharpoons} \quad \underset{\overset{|}{Hg^\star Br}}{PhCHCOO(1\text{-menthyl})} + Hg$$
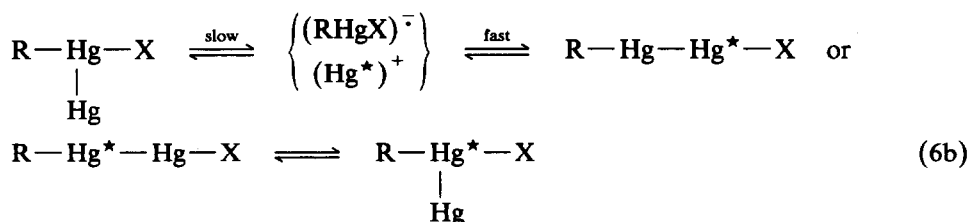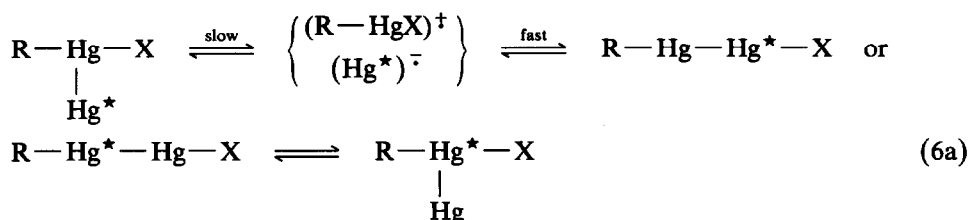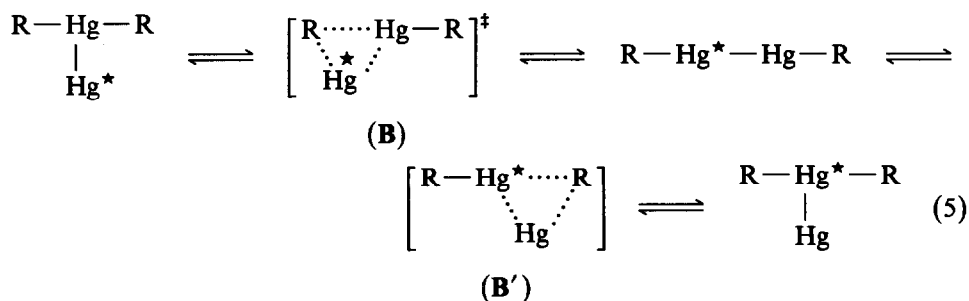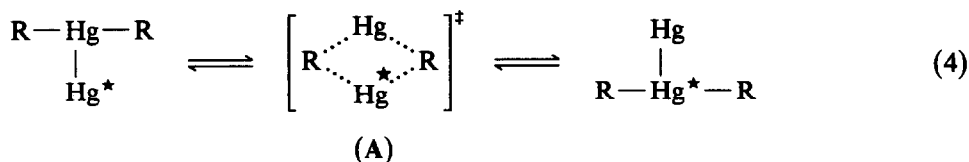

This means that organomercury compounds do not break into fragments (e.g. $R^\cdot$ and $XHg^\cdot$ radicals) during the reaction. Also, the exchange of $PhHgAr$ ($Ar = p$-tolyl or p-nitrophenyl) results in formation of $PhHg^\star Ar$ only, without any detectable quantities of Ph_2Hg and Ar_2Hg being formed [3b].

Three different mechanisms have been proposed for the reactions 3a and/or 3b: (1) a simultaneous "slipping" of the both groups from one mercury atom to another one via a four-centred transition state, **A**, (equation 4) [4], (2) a stepwise "slipping" via three-centered transition states, **B** and **B'**, (equation 5) [1], and (3) a SET-mechanism including cation-radical [5] (equation 6a) or anion-radical [1] (equation 6b) organometallic species.

The last two mechanisms involve organic calomels as intermediates.

Of the mechanisms quoted, the one described in equation 5 has been shown to be the most probable.

$$
\begin{array}{c}
\text{R}-\text{Hg}-\text{R} \\
| \\
\text{Hg}^\star
\end{array}
\rightleftharpoons
\left[
\begin{array}{c}
\text{Hg} \\
\text{R} \diagdown \quad \diagup \text{R} \\
\star \\
\text{Hg}
\end{array}
\right]^{\ddagger}
\rightleftharpoons
\begin{array}{c}
\text{Hg} \\
| \\
\text{R}-\text{Hg}^\star-\text{R}
\end{array}
\qquad (4)
$$

(A)

$$
\begin{array}{c}
\text{R}-\text{Hg}-\text{R} \\
| \\
\text{Hg}^\star
\end{array}
\rightleftharpoons
\left[
\begin{array}{c}
\text{R}\cdots\cdots\text{Hg}-\text{R} \\
\diagdown \quad \star \quad \diagup \\
\text{Hg}
\end{array}
\right]^{\ddagger}
\rightleftharpoons
\text{R}-\text{Hg}^\star-\text{Hg}-\text{R} \rightleftharpoons
$$

(B)

$$
\left[
\begin{array}{c}
\text{R}-\text{Hg}^\star\cdots\cdots\text{R} \\
\diagdown \quad \diagup \\
\text{Hg}
\end{array}
\right]
\rightleftharpoons
\begin{array}{c}
\text{R}-\text{Hg}^\star-\text{R} \\
| \\
\text{Hg}
\end{array}
\qquad (5)
$$

(B′)

$$
\begin{array}{c}
\text{R}-\text{Hg}-\text{X} \\
| \\
\text{Hg}^\star
\end{array}
\xrightarrow{\text{slow}}
\left\{
\begin{array}{c}
(\text{R}-\text{HgX})^{+} \\
(\text{Hg}^\star)^{-}
\end{array}
\right\}
\xrightarrow{\text{fast}}
\text{R}-\text{Hg}-\text{Hg}^\star-\text{X} \quad \text{or}
$$

$$
\text{R}-\text{Hg}^\star-\text{Hg}-\text{X} \rightleftharpoons
\begin{array}{c}
\text{R}-\text{Hg}^\star-\text{X} \\
| \\
\text{Hg}
\end{array}
\qquad (6a)
$$

$$
\begin{array}{c}
\text{R}-\text{Hg}-\text{X} \\
| \\
\text{Hg}
\end{array}
\xrightarrow{\text{slow}}
\left\{
\begin{array}{c}
(\text{RHgX})^{-} \\
(\text{Hg}^\star)^{+}
\end{array}
\right\}
\xrightarrow{\text{fast}}
\text{R}-\text{Hg}-\text{Hg}^\star-\text{X} \quad \text{or}
$$

$$
\text{R}-\text{Hg}^\star-\text{Hg}-\text{X} \rightleftharpoons
\begin{array}{c}
\text{R}-\text{Hg}^\star-\text{X} \\
| \\
\text{Hg}
\end{array}
\qquad (6b)
$$

It has been suggested [1,6,7] that the rate-determining step of reaction 3a is the chemical interaction of R_2Hg with metallic mercury on its surface resulting in organic calomel (but not adsorption, desorption or desolvation):

$$
R_2Hg + Hg \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2Hg_2 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} R_2Hg + Hg
\qquad (7)
$$
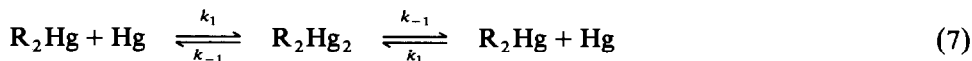
The kinetic equation for the reaction 7 may be written as: Reaction rate $= k_1\Gamma_{R_2Hg} - k_{-1}\Gamma_{R_2Hg_2}$, where Γ are the surface concentrations of R_2Hg and R_2Hg_2. Under steady-state conditions, when $d\Gamma_{R_2Hg_2}/dt = 0$: Reaction rate $= k_1\Gamma_{R_2Hg} = k_{-1}\Gamma_{R_2Hg_2}$, i.e. the rate of formation of organic calomel is equal to the rate of its demercurization. On a quiet surface of mercury, the steady-state conditions can be reached rather rapidly (within several seconds) and therefore the rate of both mercurization of R_2Hg and demercurization of R_2Hg_2 may be considered as a measure of reactivity in a series of organomercury compounds in the mercury exchange reaction [1,7].

The demercurization rates for various symmetrical organic calomels, R_2Hg_2, have been estimated using pulse electrochemical techniques [7,8]. The results obtained are in good agreement with Heitz's data [6] on the kinetics of exchange of organomercury compounds with mercury from a hanging drop of radioactive mercury:

R in R_2Hg	Ph	Et	Me	
Relative rate of exchange	112	1	0.7	Ref. 6
Relative rate of demercurization	100	1	0.7	Ref. 7

Electrochemical evidence for the formation of organic calomels at a mercury surface

In our previous work (see refs. 1 and 8 and the references cited therein), electrochemical evidence for the formation of symmetrical organic calomels, R_2Hg_2, at the surface of a mercury drop has been obtained (equation 3a). Using galvanostatic pulse techniques, we have shown that dialkylmercurials react with mercury metal to give R_2Hg_2. From the data of electrochemical experiments, we could estimate the influence of the nature of organic groups on relative stabilities in a series of symmetrical organic calomels at the mercury surface (Table 1).

In Table 1, the values of k_{-1} characterize the rates of extrusion of mercury atom from corresponding R_2Hg_2 molecules. These values can be taken as a measure of stability of the organic calomels quoted. In terms of extrusion rates, alkyl calomels appear to be significantly more stable than aryl ones, while dibenzyldimercury, $(PhCH_2)_2Hg_2$, is very unstable. The instability of benzylic calomel is most probably due to a relative weakness of the benzyl–mercury bond which can readily dissociate to give benzyl radicals adsorbed at the mercury surface.

Some evidence for the existence of a symmetrical organic calomels have been obtained in recent years. In an early work, R. Benesch and R.E. Benesch showed that organomercury salts RHgX are reduced at the mercury cathode in two one-electron steps (equation 8) [10]. Such a mechanism of reduction of organomercury salts was confirmed by numerous workers (see ref. 11 for a review) and now it is generally accepted. However, as we have shown recently, the two-step mechanism is realized only at a *mercury* cathode. If the electrochemical reductions

Table 1

Relative stabilities of organic calomels, R_2Hg_2, (in terms of k_{-1} in equation 7) [1]

R	k_{-1} (s^{-1})	R	k_{-1} (s^{-1})
PhCH$_2$	very fast	CH$_3$	55
Ph	8×10^3	CH$_3$	20 (Ref. 9) [a]
2-Naphtyl	5×10^3	C$_2$H$_5$	80
2,4,6-(CH)$_3$C$_6$H$_2$	3.5×10^3	n-C$_3$H$_7$	105
		i-C$_3$H$_7$	65

[a] In ref. 9, the value of k_{-1} for $(CH_3)_2Hg$ has been measured using pulse electrochemical radiolysis and laser photoelectronic emission.
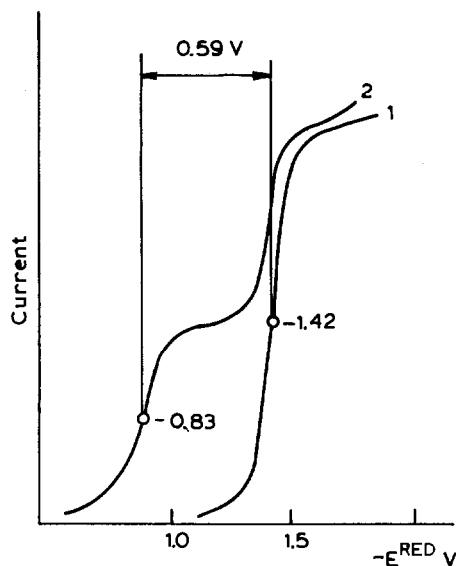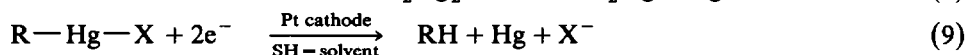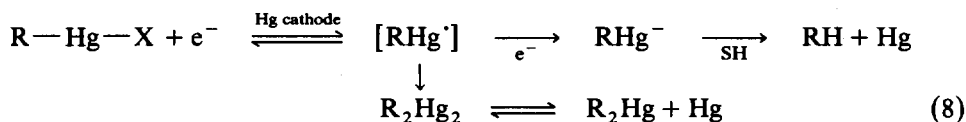
Fig. 1. Current–voltage graphs of CH$_3$HgCl registered using platinum cathode (curve 1) and mercury cathode (curve 2).

of RHgX are carried out at platinum, gold, glassy carbon or lead dioxide cathodes, they are one-step, two-electron processes [12–14] (equation 9).

$$R\!-\!Hg\!-\!X + e^- \underset{\text{Hg cathode}}{\rightleftharpoons} [RHg^{\cdot}] \xrightarrow[e^-]{} RHg^- \xrightarrow[SH]{} RH + Hg$$

$$\downarrow$$

$$R_2Hg_2 \rightleftharpoons R_2Hg + Hg \qquad (8)$$

$$R\!-\!Hg\!-\!X + 2e^- \xrightarrow[\text{SH – solvent}]{\text{Pt cathode}} RH + Hg + X^- \qquad (9)$$

Typical polarization curves are shown in Fig. 1.

The effect of electrode composition on reduction mechanism can be explained in two alternative ways: (1) mercury promotes the transfer of the first electron, or (2) platinum inhibits this process. The first alternative seems to be more acceptable because two-electron waves were observed at cathodes of very different natures: Pt, Au, GC, PbO$_2$ [14], while the two-step mechanism was realised at the mercury cathode only. We suppose [12–14] that the electrochemical reduction of organomercury salts occurs via a preliminary fast formation of asymmetrical organic
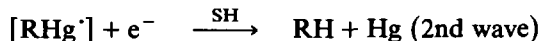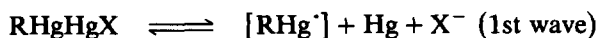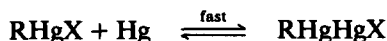
Table 2

Reduction potentials of RAuPPh$_3$ at platinum and mercury cathodes [15]

R	CH$_3$	Ph	Cl	Br	I
$-E_{1/2}^{\text{Red}}$ (Pt), V (SCE)	1.63	1.73	1.76	1.71	1.54
$-E_{1/2}^{\text{red}}$ (Hg), V (SCE)	a	2.48	0.12	0.16	0.22
$-E_{1/2}^{\text{red}}$ for R$_2$Hg	2.86 [16] b	2.48	0.12	0.16	0.22

a No wave was observed at platinum covered with mercury film. b At a mercury-dropping electrode.

calomels, RHgHgX, which are reduced at lower cathodic potentials than corresponding mercury(II) compounds, RHgX.

$$RHgX + Hg \xrightleftharpoons{fast} RHgHgX$$

$$RHgHgX \rightleftharpoons [RHg^{\cdot}] + Hg + X^{-} \ (\text{1st wave})$$

$$[RHg^{\cdot}] + e^{-} \xrightarrow{SH} RH + Hg \ (\text{2nd wave})$$

It should be pointed out that fast interaction with mercury metal is not only a property of organomercury compounds but of some other organometallics, also. For example, organogold(I) compounds, $RAuPPh_3$, are reduced at the mercury cathode at the same potentials as corresponding R_2Hg species [15]. At platinum, however, the values of reduction potentials are quite different from those at mercury (Table 2). We suppose that there is a fast reaction of organogold compounds at the surface of mercury cathode giving unstable bimetallic intermediates which decompose rapidly with elimination of zero valent gold.

$$RAuPPh_3 + Hg \rightleftharpoons RHgAuPPh_3 \xrightarrow{fast} \tfrac{1}{2}R_2Hg + \tfrac{1}{2}Hg + Au + PPh_3$$
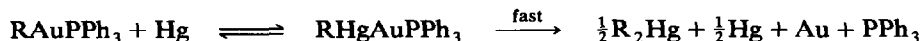
Theoretical studies of organic calomels

In our interpretations of electrochemical data on reduction of organomercury compounds, we suggested that organic calomels should be reduced at lower cathodic potentials compared to the corresponding compounds of bivalent mercury. unfortunately, this suggestion is difficult to confirm experimentally. The extreme instability of organic calomels rules out the possibility of their synthesis at room temperatures for direct electrochemical measurements.

In this situation, theoretical studies provide valuable quantitative information about the structure and energetics of unstable compounds like organic calomels. Electronic structures of several dimercury compounds, namely Hg_2Cl_2, CH_3Hg_2Cl and $(CH_3)_2Hg_2$, have recently been studied [16] using Dewar's MNDO method [17]. Each of these molecules has linear optimal geometry, with Hg–Hg distances of 255 to 258 pm and C–Hg bond lengths of 200 pm. The results of the calculations are given in Table 3.

Table 3

Calculated heats of formation (ΔH_f), ionization potentials (IP), electron affinities (ϵ(LUMO)) and experimental electrochemical potentials ($E_{1/2}^{Red}$) for organic calomels and corresponding compounds of bivalent mercury

Molecule	ΔH_f (kcal/mol)	IP (eV)	$-\epsilon$(LUMO) (eV)	$-E_{1/2}^{Red}$ (V)
ClHgCl	−37.2	12.6	2.54	0.23 [a]
ClHgHgCl	−26.4	11.78	2.86	0.00
CH_3HgCl	−18.1	11.69	0.81	1.42 [a]
$CH_3HgHgCl$	1.0	10.4	1.65	0.83 [b]
CH_3HgCH_3	10.1	10.2	−0.97	2.86 [18]
$CH_3HgHgCH_3$	33.1	9.17	0.48	1.84 [c]

[a] Reduction potential at Pt cathode [13]. [b] Reduction potential at Hg cathode [13]. [c] Reduction potential of Et_2Hg_2 [8].

From the data presented in Table 3, one can see that electron affinities of dimercury compounds are markedly higher than those of corresponding mono-mercury compounds. The experimental values of $E_{1/2}^{Red}$ follow these changes, becoming less negative with increasing electron affinity. The differences in LUMO energies $(\Delta\epsilon)$ and in electrochemical reduction potentials $(\Delta E_{1/2}^{Red})$ for related pairs of compounds are given below.

Pairs	$-\Delta\epsilon(LUMO)$ (eV)	$\Delta E_{1/2}^{Red}$ (V)
$HgCl_2/Hg_2Cl_2$	0.32	0.23
CH_3HgCl/CH_3Hg_2Cl	0.84	0.59
$(CH_3)_2Hg/(CH_3)_2Hg_2$	1.45	1.02

It should be noted that the electrochemical reduction of organomercury compounds is an irreversible process and therefore the values of $E_{1/2}^{Red}$ quoted in Table 3 cannot be considered as standard reduction potentials of the systems studied. So, one could hardly expect excellent agreement between $\epsilon(LUMO)$ and $E_{1/2}^{Red}$ values. Nevertheless, these values are of the same order of magnitude and they change in the same way as one goes from one pair of compounds to another. A quite good linear correlation described by the equation:

$$\epsilon(LUMO) = -1.31 E_{1/2}^{Red} - 2.86$$

is obtained when $\epsilon(LUMO)$ is plotted against $E_{1/2}$ (Fig. 2). In Fig. 2. $E_{1/2}^{Red}(HgCl_2)$ and $E_{1/2}^{Red}(CH_3HgCl)$ are the reduction potentials of corresponding compounds
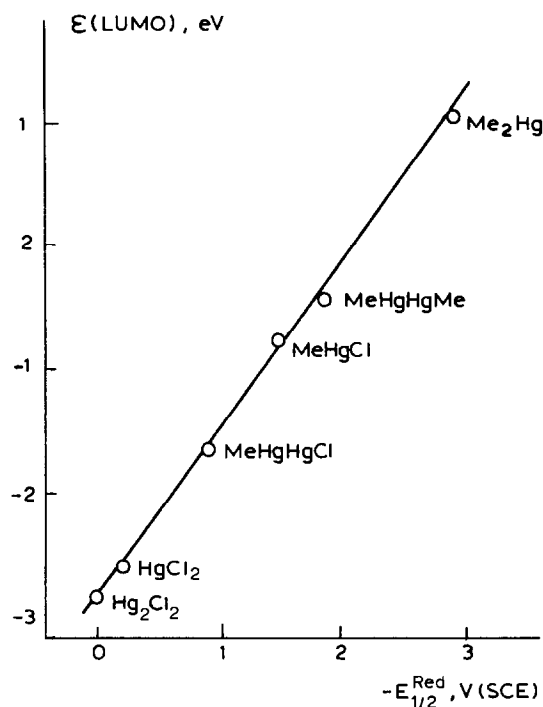
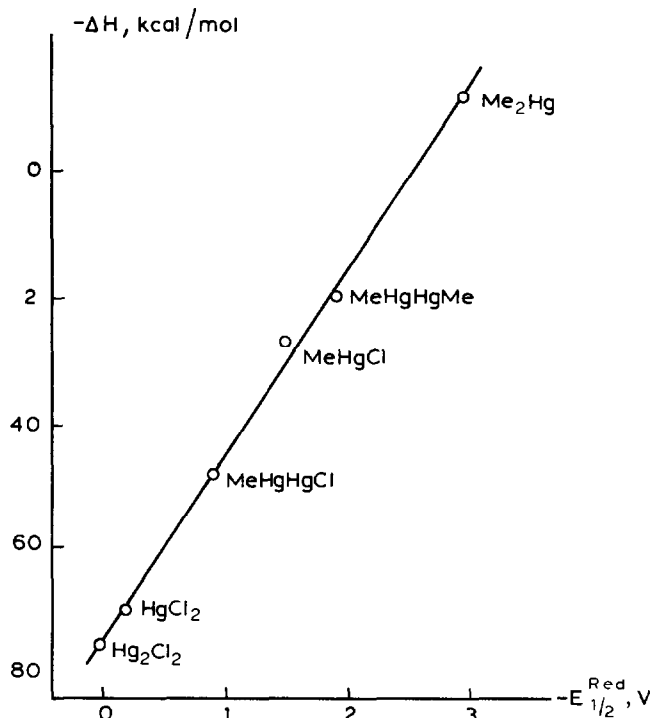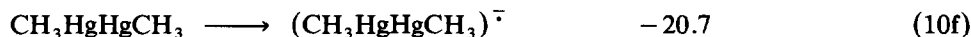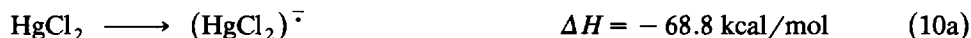Fig. 2. Correlation between calculated (LUMO) and experimental $E_{1/2}^{Red}$ values.

Fig. 3. Correlation between calculated enthalpies of reactions 10a–10f and experimental $E_{1/2}^{Red}$ values.

measured *at the Pt cathode*, while the reduction potentials of the same compounds *at the Hg cathode* are plotted as $E_{1/2}^{Red}(Hg_2Cl_2)$ and $E_{1/2}^{Red}(CH_3HgHgCl)$, respectively. The data for $(CH_3)_2Hg$ were taken from ref. [18]. Since the values of $E_{1/2}^{Red}$ for $CH_3HgHgCH_3$ are not known, we used $E_{1/2}^{Red}$ for EtHgHgEt from ref. [8].

MDNO(UHF) calculations of the molecules listed in Table 3 and of corresponding anion radicals permitted evaluation of the enthalpies of transfer "neutral molecule → anion-radical" (ΔH) (given below) which correlate quite well with experimental values of $E_{1/2}^{Red}$ for the molecules studied (Fig. 3).

$$HgCl_2 \longrightarrow (HgCl_2)^{\cdot -} \qquad \Delta H = -68.8 \text{ kcal/mol} \qquad (10a)$$

$$Hg_2Cl_2 \longrightarrow (Hg_2Cl_2)^{\cdot -} \qquad -76.4 \qquad (10b)$$

$$CH_3HgCl \longrightarrow (CH_3HgCl)^{\cdot -} \qquad -27.4 \qquad (10c)$$

$$CH_3HgHgCl \longrightarrow (CH_3HgHgCl)^{\cdot -} \qquad -48.3 \qquad (10d)$$

$$(CH_3)_2Hg \longrightarrow (CH_3)_2Hg^{\cdot -} \qquad +12.9 \qquad (10e)$$

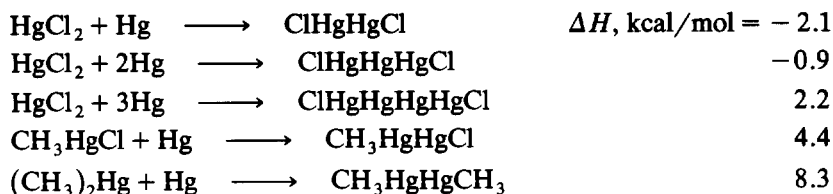$$CH_3HgHgCH_3 \longrightarrow (CH_3HgHgCH_3)^{\cdot -} \qquad -20.7 \qquad (10f)$$

The linear plots in Figs. 2 and 3 provide further evidence that the electrochemical reduction of organomercury salts occurs via a preceding fast chemical reaction with mercury of the electrode resulting in formation of organic calomels.

In principle, the existence of polymercury chains of the type R_2Hg_n, RHg_nX or X_2Hg_n where $n > 2$ cannot be ruled out *a priori*. The formation of such species,

though not detected experimentally, has often been suggested in discussions of various electrochemical data. We have calculated enthalpy changes accompanying the formation of polymercury compounds from mercury dichloride, methylmercury chloride and dimethylmercury. The results are given below:

$HgCl_2 + Hg \longrightarrow ClHgHgCl$ $\qquad \Delta H$, kcal/mol $= -2.1$

$HgCl_2 + 2Hg \longrightarrow ClHgHgHgCl$ $\qquad\qquad\qquad\qquad -0.9$

$HgCl_2 + 3Hg \longrightarrow ClHgHgHgHgCl$ $\qquad\qquad\qquad\quad\; 2.2$

$CH_3HgCl + Hg \longrightarrow CH_3HgHgCl$ $\qquad\qquad\qquad\quad\; 4.4$

$(CH_3)_2Hg + Hg \longrightarrow CH_3HgHgCH_3$ $\qquad\qquad\qquad\; 8.3$

Although the absolute values of ΔH are rather small, one can seen that the reactions resulting in Hg_2Cl_2 and Hg_3Cl_2 are exothermic, but the formation of Hg_4Cl_2 becomes an endothermic process. At the same time, the reactions leading to CH_3Hg_nCl or to $(CH_3)_2Hg_n$ are already endothermic for $n = 2$. The tendency to form organic calomels $(n = 2)$ increases with increasing value of the sum of electronegativities of terminal groups attached to the mercury chain:

$(CH_3, CH_3) < (CH_3, Cl) < (Cl, Cl)$

This statement is confirmed by the results obtained in the studies of mercury isotopic exchange [3].

As it should be expected, the increase of n leads to the increase in "softness" of polymercury molecules that is expressed in narrowing of the energy gap between HOMO and LUMO. Thus, for Hg_nCl_2 molecules, the calculations gave the following results:

n	1	2	3	4
$-\epsilon$(HOMO), eV	12.6	11.8	10.8	9.98
$-\epsilon$(LUMO), eV	2.54	2.86	3.05	3.34
Energy gap, eV	10.1	8.9	7.8	6.7

Varying the geometry of linear dimercury compounds, two further minima of the total energy have been detected. One of them corresponds to a triangular structure, **C**, the other one to a rhombic structure, **D**, as it is shown below for $CH_3HgHgCl$.

(**C**) $\Delta H_f = 4.5$ kcal/mol $\qquad$ (**D**) $\Delta H_f = 17.3$ kcal/mol
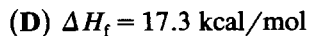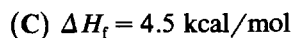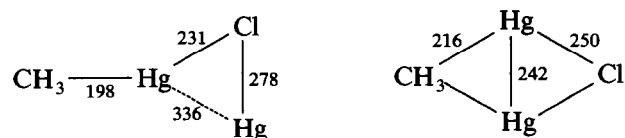
The structures **C** and **D** have an obvious resemblance with the structures of transition states postulated as two alternatives in mercury isotopic exchange (*vide supra*). The local minima of energy indicate that the structures **C** and **D** might be intermediates in the mercury exchange. The triangular structure appear to be more stable than the rhombic one in all cases studied. Furthermore, the fact that in structure **C** halogen atom, but not carbon, is involved in the "triangle" means that, in reaction 3b, the insertion of mercury atom will occur preferentially in the Hg–X bond.

Conclusions

The analysis of numerous experimental data as well as of theoretical calculations provides indirect evidence for the existence of organic calomels, RHgHgR and RHgHgX, although such compounds have not yet been isolated and studied because of their instability. Further theoretical studies of organic calomels and of other polymercury compounds (e.g. $R_4N^+Hg_5^-$ [19], mercury chain, mercury clusters [20] and similar polymetallic structures) would be of interest to obtain a more detailed information about their electronic structure and geometry.

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