EXCHANGE OF ORGANOMERCURY COMPOUNDS WITH MERCURY METAL

HI*. THE NATURE OF THE SUBVALENT SPECIES FORMED BY ORGANOMERCURY COMPOUNDS ON A MERCURY SURFACE

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Summary

A galvanostatic method has been employed to study the composition of adsorption layers which are formed on the surface of a mercury electrode (i) through adsorption of $EffgC_6F_5$ from water/methanol (9/1 v/v) solutions, (ii) through the simultaneous adsorption of Et_2Hg and $(C_6F_5)_2Hg$, (iii) during reduction of EtHgCl on mercury covered by a layer of $(C_6F_5)_2Hg$, and (iv) during the simultaneous one-electron reduction of EtHgCl and C₆ F₅ HgBr. The **compositions of the adsorbed layers have been analysed in terms of the cathodic charging curves (chronopotentiograms). The following organomercury com**pounds have been identified: Et_2Hg , $(C_6F_5)_2Hg$ and C_6F_5HgEt in run (iv), and Et_2Hg and $(C_6F_5)_2Hg$, but no C_6F_5HgEt , in runs (ii) and (iii). No evidence was obtained for the formation of Et_2Hg and $(C_6F_5)_2Hg$ in run (i). Both, polarographic and galvanostatic reduction of $C_6 F_5 H g E t$ indicate that charge transfer is preceded by a chemical reaction on the mercury surface, the reaction being the same as that observed in the adsorbed layer of $Et₂Hg$ and previously arbitrarily attributed to the equilibrium $R_2Hg + Hg \approx 2RHg$. The absence of cross-reactions between the different R_2Hg compounds on the **mercury surface [runs (i), (ii) and (iii)] demonstrates that the two RHg species present in this equilibrium are not kinetically independent. It is therefore concluded that the species formed in the reaction of RsHg with mercury has the** constitution R_2Hg_2 , i.e. corresponding to "organic calomel". This species ap**pears to be the intermediate present during mercury exchange between R₂Hg and mercury metal.**

* **For part II see ref. 1.**

Introduction

Polarograms of organomercury compounds usually show two waves, which nowadays are considered to correspond to two consecutive one-electron reduction steps [2 - 51 :

$$
RHgX + e^- \rightleftharpoons RHg \cdot + X^- \qquad \text{(1st wave)}
$$
\n
$$
RHg \cdot + e^- \xrightarrow{H^+} RH + Hg^0 \qquad \text{(2nd wave)}
$$
\n
$$
\tag{2}
$$

Electrolysis at controlled potentials on the plateaux ofthe first wave leads only to the reaction [2,5]:

$$
2 \text{ RHg} \rightarrow R_2 \text{Hg} + \text{Hg} \tag{3}
$$

If however the electrolysis is carried out at low temperatures, an unstable electrically-conducting material is obtained whose composition corresponds to RHg [6,7] _ **This substance exhibits no ESR signal and for this reason has been** assigned the "organometal" of formula $R_n Hg_n$.

The products of the one-electron reduction may also be observed during the pulse reduction of organomercury salts, especially when the rate of electrolysis is high [1,4,5,8] : **these may be reduced at potentials corresponding to the second polarographic wave for organomercury salts and are oxidized when the sign of the polarizing current is reversed_ The same products are also observed during the interaction of dialkylmercurials with a mercury metal surface** $[9,10]$.

Various structures may be proposed for the subvalent species generated by the one-electron reduction of RHgX or by the interaction of R_2 Hg with mer**cury metal; the most probable structures are those in which an organomercury radical is bonded to the mercury surface or that of "organic calomel", RHgHgR. Organic calomel has been postulated by Kreevoy and Walters [11] as an intermediate during mercury isotope exchange between organomercury cornpounds and labelled mercury metal. In the present study an attempt has been made to elucidate the true nature of the metastable intermediate compounds formed during the electrolysis of organomercury salts or formed by contact between dialkylmercurials and mercury. Studies have been made using galvanostatic methods of the behaviour of the following systems on mercury** surfaces: (i) EtHgC₆F₅, (ii) (C_6F_6) , Hg + Et₂Hg, (iii) EtHgCl + (C_6F_5) ₂Hg and (iv) **EtHgCl** + $C_6F_5HgBr.$

Results and discussion

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(i) EtHgC₆ F_5 .

Polarograms of ethylpentafluorophenylmercury in the system 1 *M* **EOAC-MeOH/H,O l/9 (v/v) exhibit two waves, the total limiting current being controlled by diffusion. The first wave varies in relation to the height of the mercury reservoir raised to the power of ca. 0.4 at 25°C and with a** negative temperature coefficient $(-0.5\%/^{\circ}C)$. Increasing the methanol content in the MeOH/H₂O mixture to $1/1$ (v/v), so that the solubility of the depolariser **is considerably increased led, to the disappearance of the first wave. These**

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observations suggest that the first wave is probably a kinetic wave corresponding to some surface chemical process. This chemical step precedes electron transfer because the latter is irreversible (vide infra). The half-wave potential, $E_{1/2}$, for the first wave is ca. -1.0 V (sce), i.e. close to the $E_{1/2}$ value for $(C_6F_5)_2Hg$ (ca. -0.9 V (sce)) [12].

The second wave has a half-wave potential $E_{1/2}$ of -1.41 V (sce). This wave apparently corresponds to the reduction of $Eff \mathbb{F}_5 , the first wave$ **being attributed to reduction of a more electrochemically active species formed** from EtHgC₆ F_5 . It is unlikely that this species is the organomercury radical, C_6 F_5 **Hg** or the symmetrical organic calomel C_6 F_5 **HgHgC₆** F_5 , since the second polarographic wave for C_6F_5HgBr (a wave which corresponds to the **reduction of such species [2]) lies towards more anodic potentials** $(E_{1/2} = -0.31)$ **V (see) [12]. The electrochemically active species corresponding to the first wave may therefore be** $(C_6 F_5)_2$ **Hg or the unsymmetrical organic calomel** E tHgHg C_6 F_5 .

The polarographic data reported above agree with galvanostatic measurements using the hanging mercury drop [9]. At high current densities, chronopotentiograms of ethylpentafluorophenylmercury exhibit a Faradaic delay at -1.55 to -1.65 V (see), corresponding to the reduction of this compound (Fig. 1, curve (a)):

 $C_6 F_5 HgEt + 2e^- \rightarrow C_6 F_5^- + Et^- + Hg^0$

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When the current density was decreased, another delay, besides that mentioned above, appeared at -1.1 to -1.2 V (sce) which corresponds to the first wave on **the polarogram (Fig. 1, curve (b)). If the delay corresponding to the reduction** of EtHgC₆ F₅ is termed "delay I" while that appearing at low current densities **is termed "delay II", then delay II corresponds to the reduction of some**

Fig. 1. Schematic representation of mercury charging curves in 1 *M* KOAc–MeOH/H₂O 1/9 (v/v) at 25°C. Curves (a) and (b); EtHgC₆F₅ (9 X 10⁻⁶ *M*), $E_i = -0.5 \text{ V}$ (sce); (c): $(C_6F_5)_2$ Hg (8 X 10⁻⁶ *M*) and Et₁ (a) and (e) were obtained at high current densities while curves (b) and (f) were obtained at low current **densities.**

species other than $E_t HgC_6 F_5$. Both delays are of a Faradaic nature and corre**spond to irreversible electrochemical processes; this follows from the fact that the reaction potentials (the potentials at which the delays arise) are dependent on the current densities (Fig. 2(a)). It should be noted that at all current densities delay II was observed ca. 120 mV towards higher cathodic potentials** than that corresponding to the reduction of $(C_6 F_5)$, Hg [12].

At **the same time as delay II appears, the length of delay I begins to decrease as the current density is decreased. The dependence of the lengths of both delays on the current densities are shown in Fig. 2(b). From this figure it can be seen that the length of delay II does not change at low current densities, but at higher current densities it decreases rapidly to zero. In contrast, the length of delay I increases with current density and reaches a maximum value when delay II disappears. The Tafel plots for both delays are shown in Fig. 2(a). Provided that the length of delay II is constant, the corresponding** Tafel plot is linear; decreasing the length of delay II leads to a deviation in the **Tafel plot towards the potential axis (corresponding to a transformation to a regime of limiting current). The Tafel plot for delay I contains two linear portions with different slopes one of which is responsible for the absence, and the other for the constancy in length, of delay II. The two linear parts of the plot are linked by a smooth transition.**

Fig. 2. Dependence of (a) the reduction potential and (b) the lengths of the delays I and 11 on the current density (i in A^{\cdot}cm⁻²) during the galvanostatic reduction of EtHgC₆F₅ (9 X 10⁻⁶ *M*), E_i =-0.5 V (sce) MeOH/H₂ O 1/9 (v/v), 1 M KOAc, adsorption time 2 min (without stirring the solution).

All the experimental data may be explained if the following equilibrium is assumed to occur in the adsorbed $E t H g C_6 F_5$ layer

$$
\mathrm{EtHgC}_{6} F_{5} \doteq \mathrm{(II)}
$$

with this equilibrium lying well to the left. Unless the current densities are higher than the rate of the reaction $(I) \rightarrow (II)$ only reduction of the initial **compound (I) is observed. At lower current densities, transfer of the first** electron is preceded by the conversion of $E t H g C_6 F_5$ to the more electrochem**ically active species (II). (Note that this is the situation which obtains in polarography.)** In addition to the reduction of $E_t H_gC_fF_s$, the E_t-H_g bond of **another compound should undergo an electrochemical reductive fission during** delay I; this compound has a structure from which the $C_6 F_5$ residue is absent*.

The experimental data discussed above thus throw some light on the nature of electrochemically active species (II). When EtHgC₆F₅ reacts with mercury metal all bonds of the type $R-Hg$ ($R = Et$ and C_6F_5) initially present **in the parent compound undergo some rearrangement with or without the participation of mercury metal. The resulting reactions may be depicted by the following equations**

$$
2 \text{ EtHgC}_6 F_5 \rightleftharpoons \text{Et}_2 \text{Hg} + (\text{C}_6 \text{F}_5)_2 \text{Hg}
$$
 (4)

or

$$
EtHgC_{6}F_{5} \rightleftharpoons EtHgHgC_{6}F_{5}
$$
\n
$$
\tag{5}
$$

From this it may be deduced that compound (II) is not the same as $(C_6 F_5)_2$. **Hg, since the latter undergoes reduction at higher anodic potentials than the former. Thus reaction (4) does not take place on a mercury surface and for this reason reaction (5) must be considered more likely. Another important observation is that the second polarographic wave of ethylmercury salts (at least in the initial portion of the wave where reduction is not so fast) and the greatest** cathodic delay in the chronopotentiograms of EtHgCl and $Et₂Hg [1,9]$, may **be attributed to the reduction of organic calomel, EtHgHgEt, but not to the reduction of organomercury radicals of the type** EtHg- **.**

It is possible that the electrochemical reduction of EtHgC_6F_5 and of the **products of the interaction of this compound with mercury may be written as follows:**

$$
C_{6} F_{5} H g E t + H g_{met} \stackrel{\text{G}}{\rightleftharpoons} C_{6} F_{5} H g H g E t
$$
\n
$$
2e^{-} \int_{a \text{ part of delay I}} a \text{ part of delay I} \qquad e^{-} \int_{c \text{ delay II}} d \text{elay II}
$$
\n
$$
C_{6} F_{5}^{-} + E t^{-} + H g \qquad C_{6} F_{5}^{-} + H g + \frac{1}{2} E t H g H g E t
$$
\n
$$
e^{-} \int_{a \text{ part of delay I}} d \text{day II}
$$
\n
$$
E t^{-} + H g
$$

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 $\sim 10^{11}$ m $^{-1}$.

^{*} The greatest cathodic delays of the compounds EtHgCl and EtHgC_c F_c overlap in chronopotentio**grams of mixtures of these compounds.**

At high current densities, when the electrochemical reduction rate is high, the resulting chronopotentiograms exhibit only delay I corresponding to the reduction of $E t H g C_6 F_5$ itself (Fig. 1, curve (a)) with the length of the delay being approximately constant (Fig. 2(b), curve I). Decreasing the current density re**sults in equilibrium (5) having sufficient time to shift to the right and a new delay, delay II, which corresponds to the reduction of organic calomel,** EtHgHgC₆ F_5 , appears on the chronopotentiograms, delay I now being due to the reduction of both the unchanged $\text{EtHgC}_6 F_5$ and the $\text{Et}-\text{Hg}$ bonds originally present in $\text{EtHgHgC}_6 F_5$ and retained in a non-reduced state during delay II. **At the lowest current densities, when the rate of the electrochemical reduction is small, equilibrium (5) now has sufficient time to shift completely to the right and delay I now corresponds only to the reduction of Et-Hg bonds, i.e. those** bonds retained in a nonreduced state after reduction of the C_6F_5 -Hg bonds in delay II (Fig. 1, curve (b)). Under these conditions the length of delay II is constant (Fig. 2(b), curve II). The decrease in length of delay I as the current **density is decreased (Fig. 2(b), curve I) may be readily explained if it is re**membered that the equilibrium $Et_2 Hg_2 \rightleftharpoons Et_2 Hg$ occurs on the mercury sur**face. When the system reaches the potentials corresponding to delay I at low** current densities, diethyldimercury, Et_2Hg_2 , which is formed during the reduc**tion of Ca FgHgHgEt in delay II, has sufficient time to partly transform into** diethylmercury and, because of the lack of Et₂Hg in the solution, to be desorbed off the mercury surface. (The desorption potential of $Et₂Hg$ is about -1.2 V (sce) [9] $).$

The above scheme is also in agreement with the following data. At a current density, *i*, of 10^{-5} A·cm⁻², ethylpentafluorophenylmercury cannot **accumulate on the mercury surface at potentials more cathodic than -1.1 V** (sce) although reduction of the compound only occurs at -1.4 V (sce). The obvious reason for this behaviour is that during the accumulation of $E t H g C_6 F_5$ **on the electrode at potentials more negative than -1.1 V this material trans**forms to organic calomel $EffgC_6F_5$, the latter compound undergoing reduc- $\frac{\text{tion at } -1.1 \text{ V (see)}*}{\text{.}}$

(ii) $(C_6 F_5)_2 Hg + Et_2 Hg$ *(Fig. 1, curve (c))*

The results obtained indicate that $E t H g C_6 F_5$ is not formed when $E t_2 H g$ and $(C_6 F_5)_2$ Hg are adsorbed together on a mercury surface $(E_i = -0.3$ to *-0.6* **V (see)). At all current densities studied, the chronopotentiograms obtain**ed show two Faradaic delays at -0.9 V and -1.4 to -1.6 V respectively and one capacity delay at -1.2 to -1.3 V (sce). The first Faradaic delay corresponds to the reduction of $(C_6 F_5)_2$ Hg, while the second delay, as shown above, corre**sponds to the reduction of diethyldimercury EtHgHgEt. The capacity delay is** due to the desorption of diethylmercury [9]. Addition of $E_{th}g₆$ F₅ to the **reaction mixture results in the appearance of a fourth delay at low current densities coincident with delay II obtained in run (i).**

 $\sim 10^7$

^{*} It should be noted that not only the delay attributable to Et, Hg but the delay associated with the reduction of *Et, Hg,* **(above scheme) is absent from the chronopotentiograms measured under such conditions. This is due to the transformation** *of* **diethyldhnercury into diethylmercury which ~cfm-s during potentiostatic adsorption of EtHgC,F, on the electrode at** *E =* **-1.1 V (see) (or** more negative values). **At these potentials. diethylmercury should be desorbed from the mercury electrode and mass into solution.**

These results indicate that the adsorbed layer contains none of the unsymmetrical compound $EffgC_6F_5$, which would have been formed if the initial compounds, Et_2Hg and $(C_6F_5)_2Hg$, had undergone any type of dissociation. **Thus the organomercurial molecule does not fragment on a mercury surface. Such a conclusion however does not rule out the possibility of the formation of** the organic calomel compounds EtHgHgC_6 F_5 and C_6 F_5 HgHgC_6 F_5 .

(iii) $(C_6F_5)_2Hg + EtHgCl$ *(Fig. 1, curve (d))*

Electrolysis of ethylmercury chloride at a mercury electrode in the presence of $(C_6 F_5)_2$ Hg leads, at potentials between -0.3 and -0.6 V, to the same **situation as that observed in run (ii); after the completion of electrolysis, the chronopotentiograms indicated that formation of the unsymmetrical compound EtHgCsFs had not occurred. The major electrolysis product is the** ethylmercury radical and the absence of adsorbed C_6F_5HgEt on the mercury **surface indicates either that this radical is not sufficiently reactive to undergo reaction with** $(C_6 F_5)_2$ **Hg or that its lifetime is very short so that it undergoes deactivation through some other reaction, which finally results in formation of diethylmercury. It is quite possible that a precursor of diethylmercury is diethyldimercury, EtHgHgEt.**

(iv) $EtHgCl + C_6F_5HgBr$ (Fig. 1, curves (e) and (f))

Quite different results have been obtained during the simultaneous electrolysis of the organomercury salts EtHgCl and C₆ F₅ HgBr. The half-wave potentials observed were -0.25 V for EtHgCl and -0.02 V for C₆ F₅ HgBr. In this **case the formation of the adsorbed layer was carried out at an initial potential** of -0.25 V (sce) to avoid the two-electron electrolysis of C_6F_5HgBr which takes place at -0.31 V [12].

Under such conditions, in addition to the capacity delay (corresponding to the desorption of diethylmercury), and the two Faradaic delays (corresponding to the reduction of $(C_6 F_5)$ ₂ Hg and Et – Hg bonds) which are observed at all current densities, at low current densities the chronopotentiograms also exhibit a delay corresponding to the reduction of $E tHgC_6F_5$ (Fig. 1, curve (f)). The **morphology, Tafel plot and appearance potentials,** *E,,* **of this delay coincide with those of delay II obtained in run (i) at all the low current densities investigated. The lengths of all these delays (to a first approximation the length of the Faradaic delay is proportional to the amount of substance adsorbed) show that the concentrations of the compounds in the adsorbed layer are approximately the same. At high current densities, the delay corresponding to** the reduction of EtHgC_6 F_5 coincides with that corresponding to the reduction **of Et -Hg bonds (Fig. 1, curve (e)). However, at low current densities another delay appears which corresponds to the species II mentioned in connection with run (i) (Fig. 1, curve (f)). Thus, when the simultaneous electrolysis of** EtHgCl and C_6 F_5 HgBr is undertaken under diffusion control, and when high **concentrations of organomercury radicals are generated, a cross-reaction between the various organomercury radicals in the system is possible:**

 C_6 \mathbf{F}_5 Hg⁺ + **EtHg⁺** \rightarrow C_6 \mathbf{F}_5 HgEt + Hg

The results described above indicate that organomercury compounds of the type R_2 Hg are not in chemical equilibria with organomercury radicals, **RHg.3** as **had been proposed earlier [1,8,9,13], but with "organic calomel" RHgHgR. Organomercury radicals generated during the electrolysis are converted to "organic calomel" by means of a very fast process. "Organic calomel" is** an unstable species which is transformed to a stable product*, R₂ Hg, during a period of ca. 10^{-2} s. The earlier reported values of the lifetimes of organomercury radicals of the type RHg· on a mercury surface (ca. 10^{-2} s for R = Alk⁻ 10^{-4} s for R = Ar and less than 10^{-4} s for R = PhCH₂ [1] and ca. 10^{-2} —10 **s for R = 3-pyridyl [4] should now be regarded as the lifetimes of diorganodi**mercury compounds of the type R_2Hg_2 . This is illustrated by the following **scheme.**

The principal feature of this scheme is that the primary product of the reduction of RHgX, the organomercury radical RHg-, transforms very rapidly to "organic calomel" RHgHgR (reactions (a) and (b) in the above scheme); however, the reverse process, the oxidation of RHgHgR to the organomercury salt, does not occur through the dissociation of "organic calomel" into these radicals but rather the direct oxidation of R_2Hg_2 occurs (reaction (d)). At **potentials more negative than those corresponding to the reduction of an organomercury salt to an "organic calomel", the latter is reduced to the carbanion (reaction (f)). This process does not appear to involve the predissociation of the "organic calomel" to the radicals** RHg- **. It cannot be ruled out however that at high current densities or at very negative potentials, when the rate of electrochemical reduction is greater than that of the dimerisation of the organomercury radical, direct reduction of the organomercury radical to the carbanion (reaction (h)) may occur. However, no data are at present available to confirm the existence of reaction (h).**

It is possible to verify the scheme given above by means of the concentration dependence of the reduction potentials of organomercury salts measured polarographically [2,3] and by the galvanostatic study of the one-electron reduction of 2-naphthylmercury acetate. Thus in Figure 3 plots are given of the

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 $2C_6F_5HgEt + 2Hg_{met} \rightleftharpoons 2C_6F_5HgHgEt$

 $2Hg + (C_6F_5)$ ₂ $Hg + Et_2Hg = 2C_6F_5Hg + 2EtHg'$

In addition, the dissociation of $R_2 Hg_2$ with the formation of two kinetically independent radicals, **RHg.. was not observed in these experiments. Inthis case the following cross-reactions could have occurred:**

Fig. 3. Dependence of the reaction potential on **the current density (i) for the galvanostatic reduction of** 2-naphthylmercury acetate (curves 1, 2, 3 and 4) and for the oxidation of the reduction product (curve 5) 2-naphthylmercury acetate: 4×10^{-5} M (1), 2×10^{-5} M (2 and 5), 1×10^{-5} M (3) and 5×10^{-7} M (4). MeOH/H₂ O 1/9 (v/v), 1 M KOAc, $E_i = 0.1$ V (sce), 25°C. Values of -F/RT (dln *i*/dE) are **given near the curves.**

various reaction potentials relative to the current densities for both the reduction of this salt and the oxidation of the reduction product. It is well known **that at low potentials the reduction of RHgX occurs via a one-electron process [2 - 53. Hence the steep slope of the Tafel plot at high current densities may be explained in terms of a fast second-order chemical reaction [16] which follows an initial reversible one-electron transfer. Such a reaction should lead to a slope of 2 for the Tafel plot equal to the order of the reaction, but since activities are not proportional to concentrations in concentrated adsorbed layers** [17] , **the experimental slope is less than 2.**

In Figure 3 the curve for the oxidation of the relatively stable product of the chemical reaction is also drawn-(curve 5). From this curve it can be seen that if the current densities are sufficiently high, the rate of oxidation of the **product is less than the density of the polarizing current. For this reason, the product cannot therefore be the organomercury radical RHg-. Experiments have shown that the electrolysis times correspond to high current densities, the instability of this product is not observable; the product oxidation process cannot include the same chemical reaction which determines the change of the organomercury salt reduction potential with current density. This latter reaction is responsible for the formation of a relatively stable product, and as discussed above, exhibits second-order kinetics as shown by the slope of the Tafel plot. In the above scheme, this reaction is represented by the equation** $2RHg \rightarrow R_2Hg$. The reason for the change in the order of the reaction when **electron transfer occurs at low current densities is at present under investigation.**

It may therefore be concluded that an equilibrium exists between R_2Hg and "organic calomel", R_2Hg_2 , on the mercury surface (reaction (c) in the **above scheme). This equilibrium results in an exchange of mercury between**

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RzHg and the metal. Reaction (c) probably represents the rate-determining step for the exchange. The nature of the kinetic steps which govern the rate of reaction (c) will be discussed in our next paper in this series.

Experimental

The electrochemical method and the technique employed as well as the methods used for solvent purification have been described earlier [9] _ Polarographic measurements were carried out using a thermostatted $(25 \pm 0.2^{\circ} \text{C})$ **25 ml cell supplied with a tube for nitrogen bubbling and an electrolyte bridge (1** *M* **KOAc) to connect the cell with the external water-saturated calomel** electrode. The solvent used was MeOH/H₂O $(1/9 \text{ v/v})$, the supporting electrolyte being 1 *M* KOAc. The mercury capillary had a dropping time $t = 3.7$ s and $m = 1.95$ mg·s⁻¹. Polarograms were recorded on an Electronic Polarograph **LP-60, the potential of the dropping electrode being controlled by means of a direct current potentiometer PPTV-1. Oxygen was removed from the cell by means of a flow of purified nitrogen. Concentrations of organomercury com**pounds used were 1×10^{-4} mol \cdot l⁻¹.

Organomercury compounds were prepared as described earlier [14] and had the reported constants [141. All compounds were recrystallized or distilled before use.

Ethylpen'cafluorophenylmercury was prepared in 25% yield by the method reported earlier for methylpentafluorophenylmercury [15]. The crude product was fractionated twice in vacuo; b.p. $112^{\circ}/15$ mmHg, m.p. $+6^{\circ}$ C, n_0^{17} **1.5139. No impurities were detected in the product by mass-spectral analysis. -Analysis: Found: C, 23.83, 23.98; H, 1.64, 1.78. CsHsFsHg calcd.: C,** *24.22:* **H, 1.72%.**

References

- **1 A.N. Kashin. A.B. Ershler. V.V. Strelets. K.P. Butin. I.P. Beletskaya and 0-A. Reutov. J. Organo**metal. Chem., 39 (1972) 237.
- **2 R.Benesh and R.E. Benesh. J. Amer. Chem. Sot.. 73 (1951) 3391.**
- **3 K.P. Butin. I.P. Beletskaya, A.K. Ryabtsev and O.A. Reutov. Elektrokhimiya. 3 (1967) 1318.**
- **4 C. Degrand and E. Laviron. Bull. Sot. Chim. Fr.. (1968) 2228.2233.**
- **5 R.E. Dessy. W. Kitching. T. Psarras. R. Salinger. A. Chen and T. Chiven. J. Amer. Chem. Sot.. 88 (1966) 460.**
- 6 G. Kraus, J. Amer. Chem. Soc., 34 (1913) 1732.
- **7 B.H.M. BiIlinge and G.B. Gowerdock. J. Chem. Sot.. (1962) 1201.**
- 8 A.N. Kashin, V.V. Strelets, K.P. Butin, I.P. Beletskaya, L.L. Knots, V.N. Alekseev and A.B. Ershler,
- Elektrokhimiya, 7 (1971) 1587.
9 K.P. Butin, A.N. Kashin, A.B. Ershler, V.V. Strelets, I.P. Beletskaya and O.A. Reutov, J. Organometal **Chem.. 39 (1972) 39.**
- **10 A.B. Ershler. V.V. Strelets, A.N. Kashin and K.P. Butin. Elektrokhimiya. 9 (1973) 423.**
- **11 M-M. Kreevoy and E.A. Walters. J. Amer. Chem. Sot.. 89 (1967) 2986.**
- **12 A.B. Ershler. A.N. Kashin. K.P. Butin and 1-P. Beletskaya. Elektrokhimiya. 7 (1971) 953.**
- **13 A.N. Kashin, V.V. Strelets, N.N. Ovsyannikov. KS. Butin. V.N. Alekseev, 1-P. Beletskaya. L.L. Knots, G.A. Tedoradze and A.B. ErshIer. EIektrokhimiya. 7 (1971) 1586.**
- **14 L.G. Makarova end A.N. Nesmeyanov, Metody Elementoorganicheskoi Khimii. Rtut'. Nauka Publishers. Moscow. 1965.**

الموالي التواصل

- **15 R.D. Chambers. G.E. Coates, J.G. Livingstone and W.K.R. Musgrave. J. Chem. Sot.. (1962) 4367.**
- 16 K.J. Vetter, Elektrochemische Kinetik, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1961.
17 M.I. Temkin, Zh. Fiz. Chim., 11 (1938) 169; 14 (1940) 1153; 15 (1941) 296.
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