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ISOTOPIC EXCHANGE AND ELECTROCHEMICAL STUDIES ON THE REDOX SYSTEM Ph_6Pb_2/Ph_3Pb^+

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SUMMARY

Electrochemical reversibility was found for the redox couple Ph_6Pb_2/Ph_3Pb^+ at a platinized platinum electrode. The overall reaction may be represented in the following way:

$$Ph_6Pb_2 \xrightleftharpoons{\text{Pt-black}} 2\ Ph_3Pb^{\bullet} \rightleftarrows 2\ Ph_3Pb^+ + 2\ e$$

Isotopic exchange between tagged hexaphenyldilead and triphenyllead ions supports the hypothesis of the formation of $Ph_3Pb^{\bullet}$ radicals at the surface of a platinized platinum foil.

INTRODUCTION

Many investigations have dealt with the problem of the dissociation into free radicals of homodimetallic compounds such as organodi-tins[1] and -leads[2]. At present several discrepancies about this subject exist. Moreover no experimental evidence for a homolytic dissociation has been found for hexaphenyldilead and many experimental findings indicate that spontaneous dissociation of this compound does not occur in solution[3,4]. The lack of isotopic exchange in benzene solution between hexaphenyldilead tagged with radio-active lead and triphenyllead chloride[5] is one argument supporting the above point of view.

Nevertheless, when the metal–metal bond of these homodimetallic compounds is cleaved by electrochemical reduction or oxidation, the formation of the respective species R_3M^- and R_3M^+ appear to be preceded by $R_3M^{\bullet}$ radicals as the intermediates in the scission of the metal–metal bonds[6,7].

So far the reversibility of redox systems of the type R_6Sn_2/R_3Sn^+ at the platinized platinum electrode has been attributed in our previous papers[8,9] to the ability of the platinum black to form $R_3Sn^{\bullet}$ radicals.

In the present paper we have verified the reversibility of the redox system Ph_6Pb_2/Ph_3Pb^+ at the platinized platinum electrode. In addition, isotopic exchange was observed between tagged hexaphenyldilead and triphenyllead ions in the presence of platinum black. This is evidence of an homolytic dissociation of the hexaphenyl compound in the presence of the catalyst.

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EXPERIMENTAL

Materials

Hexaphenyldilead and triphenyllead iodide were prepared according to the literature[10,11]. Radio-active hexaphenyldilead was prepared by the same method by using $PbCl_2$ tagged with radium D. $PbCl_2$ was prepared from RBS.1 lead 210 (radium D) as nitrate in 2.5 *N* nitric acid supplied by the Radiochemical Centre, Amersham, England.

Commercial methanol and benzene (Erba, Milano, Italy) were further purified. Commercial lithium nitrate was recrystallized and dried by the Joon's method[12]. Platinized platinum foils[13] (2.5 × 2 cm) were utilized for both electrochemical and isotopic exchange measurements.

Measurements of the equilibrium potentials of the system Ph_6Pb_2/Ph_3Pb^+

An appropriate quantity of a solution of triphenyllead ions (as nitrate) prepared by adding an equivalent amount of silver nitrate to triphenyllead iodide was mixed with a known amount of a solution of hexaphenyldilead and introduced into a half-cell. The assumed equilibrium potential at a platinized platinum electrode against SCE was measured at 25° for several ratios of reduced and oxidized forms of this system in methanol/benzene (50/50 v/v) 0.2 *M* $LiNO_3$ solution by means of a Solartron LM 1420 Electronic Digital Voltmeter. All the operations were made under dry nitrogen atmosphere.

We used the following relation:

$$E = E_0 + 0.0296 \log \frac{[Ph_3Pb^+]^2}{[Ph_6Pb_2]} \tag{1}$$

in order to calculate the formal standard potential E_0 from the observed equilibrium potentials E corresponding to different values of the ratio $[Ph_3Pb^+]^2/[Ph_6Pb_2]$.

Isotopic exchange

Benzene/methanol (50/50 v/v) solutions of triphenyllead ions and radioactive hexaphenyldilead were prepared. Proper amounts of them were mixed and kept at constant temperature (25°) in the presence or absence of a platinized platinum foil, smooth platinum or mercury. All these operations were carried out in the dark and under a dry nitrogen atmosphere. After a known time the solution was removed out and evaporated to dryness without heating. The solid residue was dissolved in a benzene/methanol mixture (95/5 v/v) and triphenyllead ions were precipitated as Ph_3PbF with a saturated aqueous KF solution. The precipitate was filtered off, well washed with benzene, water and methanol, suspended in methanol, transferred to a disk and counted to G.M.: measurements of the radioactivity of all samples (counts per min per mg) were made in the same way and under the same experimental conditions by means of a Philips Z 505 M Scaler Counter. The initial radioactivity of the hexaphenyldilead was determined (as Ph_3PbF).

RESULTS AND DISCUSSION

Seven runs were carried out for the redox system Ph_6Pb_2/Ph_3Pb^+ and Table 1

TABLE 1

CALCULATED VALUES OF E_0 FROM THE EXPERIMENTAL EQUILIBRIUM POTENTIALS E FOR THE SYSTEM Ph_6Pb_2/Ph_3Pb^+ AT 25°
Solvent methanol/benzene (50/50 v/v), 0.2 M $LiNO_3$.

$[Ph_6Pb_2]$ ($M \times 10^4$)	$[Ph_3Pb^+]$ ($M \times 10^4$)	E (V)	E_0 (V)
3.51	0.24	−0.272	−0.101
2.80	0.41	−0.259	−0.104
5.27	0.79	−0.248	−0.102
5.33	1.61	−0.232	−0.104
3.72	2.11	−0.219	−0.103
2.28	2.21	−0.209	−0.100
1.98	2.92	−0.202	−0.103

lists the results. The columns in the listed order show the molar concentration of the reduced and oxidized forms respectively, the experimental E-values and the calculated E_0-values on the basis of eqn. (1). These calculated values show good agreement among themselves. The average value of the formal standard potential E_0 is -0.102 ± 0.002 V. Treatment of the data by the least squares method, assuming a linear relationship between E and $\log(Ox^2/Red)$, gives intercept values of $E_0 = -0.102$ V *vs.* SCE and a slope value of 0.0296 V.

This system shows reversibility at the platinized platinum electrode similar to the redox couples R_6Sn_2/R_3Sn^+ (R=Me, Et, Bu and Ph) previously reported[9].

The ability of platinum black to promote the radical formation process at the platinum–solution interface:

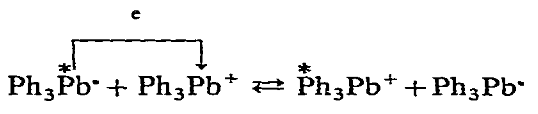
$$Ph_6Pb_2 \rightleftarrows 2\,Ph_3Pb^\bullet,$$

may be involved. It follows that the overall reaction may be represented in the following way:

$$Ph_6Pb_2 \underset{(a)}{\overset{\text{Pt black}}{\rightleftarrows}} 2\,Ph_3Pb^\bullet \underset{(b)}{\rightleftarrows} 2\,Ph_3Pb^+ + 2\,e$$

in which process (a) is the rate determining step.

Other evidence was therefore sought for the production of free radicals by platinum black. Any isotopic exchange between Ph_3Pb^+ and $Ph_3Pb^\bullet$ radical probably involves an electronic transfer mechanism of the following type:



$$Ph_3\overset{*}{Pb}{}^\bullet + Ph_3Pb^+ \rightleftarrows Ph_3\overset{*}{Pb}{}^+ + Ph_3Pb^\bullet \qquad (2)$$

Should hexaphenyldilead furnish radical species, an isotopic exchange between tagged Ph_6Pb_2 and Ph_3Pb^+ ions would be observed. In earlier work[5] no isotopic exchange was found in solution. This shows that hexaphenyldilead alone cannot dissociate homolytically in solution. However, in the presence of platinum black isotopic exchange is observed (*cf.* Table 2).

In our opinion these experiments strongly suggest that intermediate radical species are responsible for the observed electrochemical reversibility shown in Table 1.

TABLE 2

ISOTOPIC EXCHANGE BETWEEN TAGGED Pb_6Pb_2 AND Ph_3Pb^+ IN BENZENE/METHANOL (50/50 v/v) AT 25°

Run	Conditions	$[Ph_6Pb_2]$ ($M \times 10^3$)	$[Ph_3Pb^+]$ ($M \times 10^3$)	Time (h)	Initial activity ($counts \cdot min^{-1} \cdot mg^{-1}$)	Final activity ($counts \cdot min^{-1} \cdot mg^{-1}$)	Isotopic exchange (%)
1	Pt black	1.26	2.53	1	1106	500	90
2	Pt black	1.37	2.73	0.5	1106	540	98
3	Pt black	1.25	2.50	1.5	1106	521	94
4	Pt smooth	1.25	2.50	1.5	1106	16	2.9
5	Mercury	1.25	2.50	1.5	1106	20	3.6
6		1.25	2.50	1.5	1106	15	2.7

Further, it should be noted that only 3–4% isotopic exchange is observed when the reactants are mixed in the presence of mercury or smooth platinum, as in the case in homogeneous solution (see Table 2, runs 4, 5 and 6, respectively). This small apparent exchange is due probably to adsorption of hexaphenyldilead on the precipitated organolead fluoride.

Even if the electron exchange between the radical and the ion is slow, it is not possible to evaluate this point for two reasons. In the first place, the radicals are formed only on the platinum black surface, and are not evident in homogeneous solution. Secondly the platinum black would probably catalyze such a slow exchange. Because of the technique used we did not observe differences in isotopic exchange as a function of time.

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