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ON THE SUPPOSED EQUILIBRIUM $Ph_6Pb_2 \rightleftarrows Ph_4Pb+Ph_2Pb$ IN SOLUTION

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SUMMARY

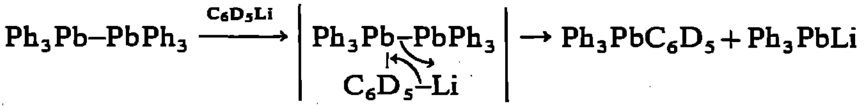
The reaction between pentadeuteriophenyllithium and hexaphenyldilead combined with new measurements of isotopic exchange between Ph_6Pb_2 (labelled with RaD) and Ph_4Pb, have shown that the dilead compound is undissociated in solution. These results cast doubt upon the previously reported equilibrium: $Ph_6Pb_2 \rightleftarrows Ph_4Pb+Ph_2Pb$.

The ready exchange of hexaphenyldilead labelled with radio-active lead and tetraphenyllead in benzene at 40° has previously been cited as evidence for the following rapid equilibrium[1]:

$$Ph_3Pb{-}PbPh_3 \rightleftarrows Ph_4Pb+Ph_2Pb \qquad (1)$$

Criticism of this hypothesis has been made on the basis of: (*a*) osmometric measurements which indicate that hexaphenyldilead (0.001 *M* solution in benzene) is not dissociated to a detectable extent[2] and (*b*) addition of tetraphenyllead to preparations believed to be diphenyllead which do not yield hexaphenyldilead. Furthermore, the hydrolytic stability of hexaphenyldilead argues against its facile dissociation into tetraphenyllead and diphenyllead since diphenyllead itself is readly hydrolyzed to lead oxide and benzene[3]. In addition, the lack of ^{14}C isotopic exchange[4] between hexaphenyldilead and tetraphenyllead, has recently called in question the experimental validity of the previous findings[1]. For these reasons we have reexamined the validity of reaction (1).

We have employed a variation of the well-known reaction between hexaphenyldilead and phenyllithium in THF[5], which yields tetraphenyllead and triphenylplumbyllithium in quantitative yield, thus the products of the reactions with pentadeuteriophenyllithium in place of phenyllithium are be expected to be triphenyl(pentadeuteriophenyl)lead and triphenylplumbyllithium if a nucleophilic attack on the dilead compound according to eqn. (2) is operative:



$$Ph_3Pb{-}PbPh_3 \xrightarrow{C_6D_5Li} \left| \begin{matrix} Ph_3Pb{-}PbPh_3 \\ C_6D_5{-}Li \end{matrix} \right| \rightarrow Ph_3PbC_6D_5+Ph_3PbLi \qquad (2)$$

On the other hand diphenyl(pentadeuteriophenyl)plumbyllithium and tetraphenyllead would be the reaction products if dissociation of Ph_6Pb_2 according to eqn. (1) is the first step followed by the reaction of Ph_2Pb with the lithium derivative (3):

$$Ph_2Pb+C_6D_5Li \rightarrow Ph_2C_6D_5PbLi \qquad (3)$$

established previously by Gilman *et al.*[6] to occur rapidly.

The products we obtained agree with scheme (2) which suggests that hexaphenyldilead does not dissociate to any great extent in solution. In order to confirm this result we reexamined the results previously reported on the isotopic exchange between hexaphenyldilead and tetraphenyllead, one species being labelled with radium D. We found that no significant exchange had taken place.

Furthermore we have examined, under the same experimental conditions, isotopic exchange between hexaphenyldilead and the following species, Ph_3Pb^+, Ph_2Pb^{2+} and Pb^{2+}, and have verified the existence of a slow isotopic exchange between hexaphenyldilead and Pb^{2+} ions.

Isotopic exchange for the system Ph_6Pb_2/Ph_4Pb takes place when traces of metallic lead are present and this fact probably, accounts for the erroneous results previously reported.

To conclude, on the basis of the foregoing evidence, the dissociation of Ph_6Pb_2 into Ph_4Pb and Ph_2Pb does not occur at low temperatures in the range at which Ph_6Pb_2 is stable.

EXPERIMENTAL AND RESULTS

Materials

Radio-active hexaphenyldilead was prepared according to the literature procedure[7,8] using $PbCl_2$ labelled with radium D.

$PbCl_2$ was prepared from RSB.1 lead-210 supplied as the nitrate in 2.5 *N* nitric acid by the Radiochemical Centre, Amersham, England.

$Pb(ClO_4)_2 \cdot 3H_2O$, purchased from K&K Laboratories (USA) was used without further purification.

C_6D_5Br, commercially available from Merck, was used to prepare C_6D_5Li[9]. Other reagents employed were all A.R. grade chemicals.

All the solvents employed were supplied by C. Erba (Milano) and were repurified.

Reaction of hexaphenyldilead with pentadeuteriophenyllithium

Hexaphenyldilead (12.5 g, 0.01425 mol) was dissolved in dry THF (50 ml) in nitrogen atmosphere. A THF solution of pentadeuteriophenyllithium (54 ml, 0.184 *M* 0.01 mol) was added at once at room temperature with stirring and the precipitate of $Ph_3PbC_6D_5$ (I), rapidly formed, was filtered off under nitrogen and was identified by comparison of IR and mass spectra (*cf.* Table 1) with those of Ph_4Pb (II).

The filtrate containing Ph_3PbLi was cooled to 5°, 1.8 g (0.01425 mol) benzyl chloride was added and the product, benzyltriphenyllead (m.p. 93–94°) was separated as previously reported[10].

The possible presence of other substances was ruled out by means of thin-layer chromatography.

The IR spectra of equimolar solutions of (I) and (II) in CS_2 (0.0155 *M*) showed

TABLE 1

MASS SPECTRA[a] OF Ph_3PbPh_D (Mass 521)

m/e	*Identification*[b]	*Intensity*[c]
208	$[Pb]^{\cdot +}$	100
285	$[PhPb]^+$	95
290	$[Ph_DPb]^+$	21
362	$[Ph_2Pb]^{\cdot +}$	1.3
367	$[PhPh_DPb]^+$	0.5
439	$[Ph_3Pb]^+$	43
444	$[Ph_2Ph_DPb]^+$	44

[a] Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer with 60 eV. Lead containing ions were identified by the isotopic composition. Pb 208/207/206/204 100/42/46/4. [b] Identification based upon lead-content. [c] Intensities of the main isotopic peak relative to the largest peak.

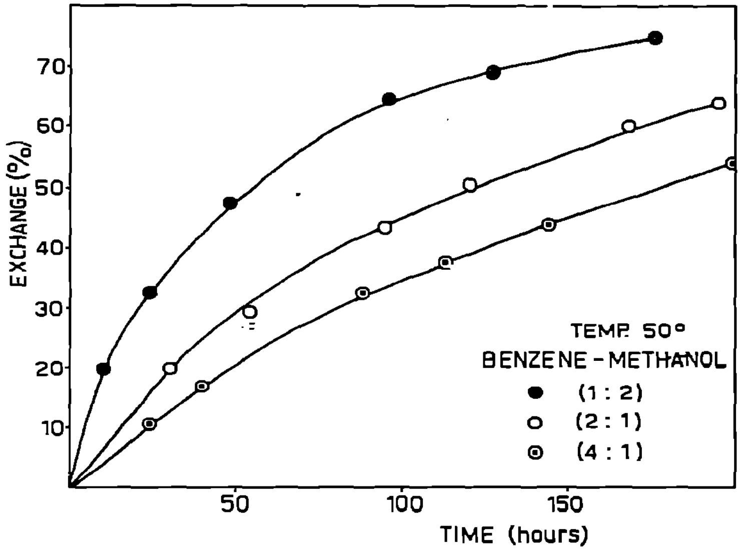


Fig. 1. Percent of exchanged radioactivity from hexaphenyldilead to Pb^{2+} ions *vs.* time.

absorbances at 990 cm^{-1} with δ(C–H) for (I) and (II), 0.198 and 0.276 respectively.

It can be inferred from these data that $Ph_3PbC_6D_5$ contains ca. 25% C_6D_5.

Isotopic exchange

(*a*). *Ph_6Pb_2/Pb^{2+} system.* The initial radioactivity of hexaphenyldilead and of the other products was determined as $PbCrO_4$.

Solutions of Ph_6Pb_2 and $Pb(ClO_4)_2 \cdot 3H_2O$ in benzene/methanol (various v/v ratios) were prepared, appropriate quantities were mixed and placed in a thermostatted bath at 35°. All the operations were carried out in the dark and under a dry nitrogen atmosphere. After an appropriate time interval (from 48 h to 10–20 days) known amounts of the solutions were withdrawn and added to water. The Pb^{2+} ions extracted into the aqueous layer were precipitated as $PbCrO_4$. The precipitate was filtered off, washed with benzene, water and methanol, suspended in methanol, transferred to a disk, desiccated and counted to G.M.

Measurements of the activity of all samples (c.p.m/180 sec) were made under the same experimental conditions using a Philips 2505 M Scaler counter.

From measurements at 25, 35 and 50°, a slow rate of exchange was observed. Figure 1 shows the percent of radio-active transfer from hexaphenyldilead to Pb^{2+} ions *vs.* the time at 50° for various benzene-methanol mixture ratios.

(*b*). *Ph_6Pb_2/Ph_4Pb system.* Radio-active hexaphenyldilead (0.268 g) and tetraphenyllead (0.315 g) were dissolved in the smallest amount of benzene and the solution was thermostatted at 40°. After a known time ($\approx$ 30 min) the solution was poured into a small volume of cold ethanol. Most of tetraphenyllead precipitated and was subsequently recrystallised from chloroform. The purity of the recovered material was assessed by its m.p. and IR spectrum.

Isotopic exchanges between labelled Ph_6Pb_2 and Ph_2Pb^{2+} and between labelled Ph_4Pb and Ph_3Pb^+, Ph_2Pb^{2+} and Pb^{2+} species were also performed in benzene/methanol (50.50 v/v) under the same conditions. No exchange was observed in any case.

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