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# GROUP IV ORGANOMETALLIC COMPOUNDS

## VI [†]. Kinetics of hydrogen chloride cleavage of hexaaryldileads

V.G. KUMAR DAS*, NG SEIK WENG and L.H. GAN
Department of Chemistry, University of Malaya,
Kuala Lumpur, Malaysia

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## Summary

The kinetics of the HCl cleavage of hexaphenyldilead has been examined at 30° and also at several temperatures in anhydrous dioxane as well as in chloroform and in 20% methanol-80% benzene. The effect of substituents on the benzene ring, the results of experiments with DCl and added salts and the observed second-order kinetics seem consistent with a four-centre mechanism involving preferential cleavage of the C-Pb bond by undissociated HCl.

## Introduction

A number of nucleophilic and weakly electrophilic reagents are known to cleave the lead-lead bond selectively in hexaphenyldilead [2]. Cleavage of the lead-carbon bond, however, has been considered to be rate-determining in the mechanisms proposed for the reactions of hexaaryldileads with acetic acid[3] and mercuric salts[4]. The reaction of these organolead substrates with hydrohalic acids however appears to have been

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[†] For Part V see Ref.[1]

only qualitatively investigated up to the present. Stoichiometric studies[5,6] in chloroform indicate that hexaalkyldileads follow equation (1),

$$R_6Pb_2 + 3HCl \rightarrow R_3PbCl + PbCl_2 + 3RH \qquad (1)$$

while the aryl derivatives[6-9] follow equation (2),

$$Ar_6Pb_2 + 4HCl \rightarrow Ar_2PbCl_2 + PbCl_2 + 4ArH \qquad (2)$$

The difference in stoichiometry was ascribed to the greater reactivity of the triaryllead chlorides towards acid.

However, hydrogen chloride in methanol solution, generated by the methanolysis of acyl chlorides, is reported[10] to convert $Et_6Pb_2$ to $Et_4Pb$ or $Et_3PbCl$ (equation 3).

$$\begin{tikzcd} Et_6Pb_2 + 2HCl \arrow[r] & Et_4Pb + PbCl_2 + 2C_2H_6 \arrow[d, "HCl"] & (3) \\ & Et_3PbCl & \end{tikzcd}$$

Willemsens and van der Kerk[11] have carefully reacted $Ph_6Pb_2$ with hydrogen chloride in a 1:1 molar ratio at low temperatures but have obtained no evidence for $Ph_4Pb$ in their stoichiometric study.

With mechanistic considerations in mind, we have carried out the present investigation to provide the first quantitative data on the hydrogen chloride cleavage of hexaaryldileads.

## Experimental

### 1. Materials

The hexaaryldileads were prepared according to published procedures[12]. The acid solution was prepared by passing dry HCl into anhydrous, peroxide-free dioxane. It proved expedient for the kinetic runs to prepare a stock solution of $5 \times 10^{-3}$M; the concentration of this was established by titration with tris(hydroxymethyl)aminomethane[13] in methanol, using the mixed indicator bromocresol green-alizarin red S[14]. Stock solutions of the acid in chloroform and 20% methanol-80% benzene were similarly prepared.

### 2. Kinetic runs

The rates were measured by following the decrease in absorbance of the hexaaryldileads at their previously determined $\lambda_{max}$ values in the near-ultraviolet[3]. A Durrum Stopped-Flow Model D-110 Spectrophotometer with temperature control facility was employed. In a typical run, equal volumes of the hexaarylidilead ($1.0 \times 10^{-4}$ M) and hydrogen chloride ($3.0 \times 10^{-4}$ M) solutions were forced rapidly from the drive syringes through the mixing chamber into the cuvette (observation chamber) of the stopped-flow spectrophotometer, pre-set at the $\lambda_{max}$ value associated with the dilead system. The absorbance changes during the course of the reaction were followed on a Heath-Schulumberger Recorder.

### 3. Product examination

A combination of thin layer chromatography[3,4] and the dithizone extraction method of Henderson and Snyder[15] was used to establish the product composition during reaction.

## Results and discussion

The first series of kinetic measurements in anhydrous dioxane were carried out with initial HCl to $Ph_6Pb_2$ ratio of 1/1, 2/1 and 3/1. Only in the latter case did the hexaphenyldilead completely react. A similar stoichiometric ratio was also employed in the mercuric chloride cleavage of hexaaryldileads[4], although in this case a detailed stoichiometric analysis was possible which indicated the ratio to be 2.85. The HCl cleavage follows second order kinetics, first order with respect to each reactant. A value of 16.8 $M^{-1}s^{-1}$ was obtained for the rate at 30°. Rate data were also procured using four-fold excess acid and the value

17.5 $M^{-1}s^{-1}$ was derived for the rate constant assuming a value $n = 3$ for the stoichiometry in the integrated rate expression (4).

$$\frac{1}{[Ph_6Pb_2]_o} \ln \frac{[HCl]_o - nx}{[Ph_6Pb_2]_o - x} = kt \tag{4}$$

where $[HCl]_o = 4\,[Ph_6Pb_2]_o$ ; $x = [Ph_6Pb_2]_t$

The rate constants were also determined at three other temperatures and the activation energy obtained from the Arrhenius plot is 28.9 kJ $mol^{-1}$ (Table 1).

Substituent effects on the rate are illustrated by the modified Hammett plot in Fig. 1 based on the Yukawa-Tsuno equation[16],

$$\log k/k_o = \rho\,[\sigma + r\,(\sigma^+ - \sigma)]$$

with $r = 0.6$ yielding the best linear fit. The $\rho$ value thus obtained

TABLE 1

Effect of temperature on the reaction $Ph_6Pb_2$ + 3HCl in dioxane:
$[Ph_6Pb_2]_o = 5 \times 10^{-5}$ M, $[HCl]_o = 1.5 \times 10^{-4}$ M

| Temperature ($^oC$) | k ($M^{-1}s^{-1}$)* | | |
|---|---|---|---|
| 30.0 ± 0.1 | 16.8 | $E_{act.}$ | = 25.8 kJ $mol^{-1}$ |
| 35.0 ± 0.1 | 19.8 | A | = $4.73 \times 10^5$ $M^{-1}s^{-1}$ |
| 40.0 ± 0.1 | 23.6 | $\Delta H^{\neq}$ | = 23.3 kJ $mol^{-1}$ |
| 45.0 ± 0.2 | 27.8 | $\Delta S^{\neq}_{30^o}$ | = -145 J $^oK^{-1}mol^{-1}$ |

* Each entry represents an average of 5 - 6 different determinations.

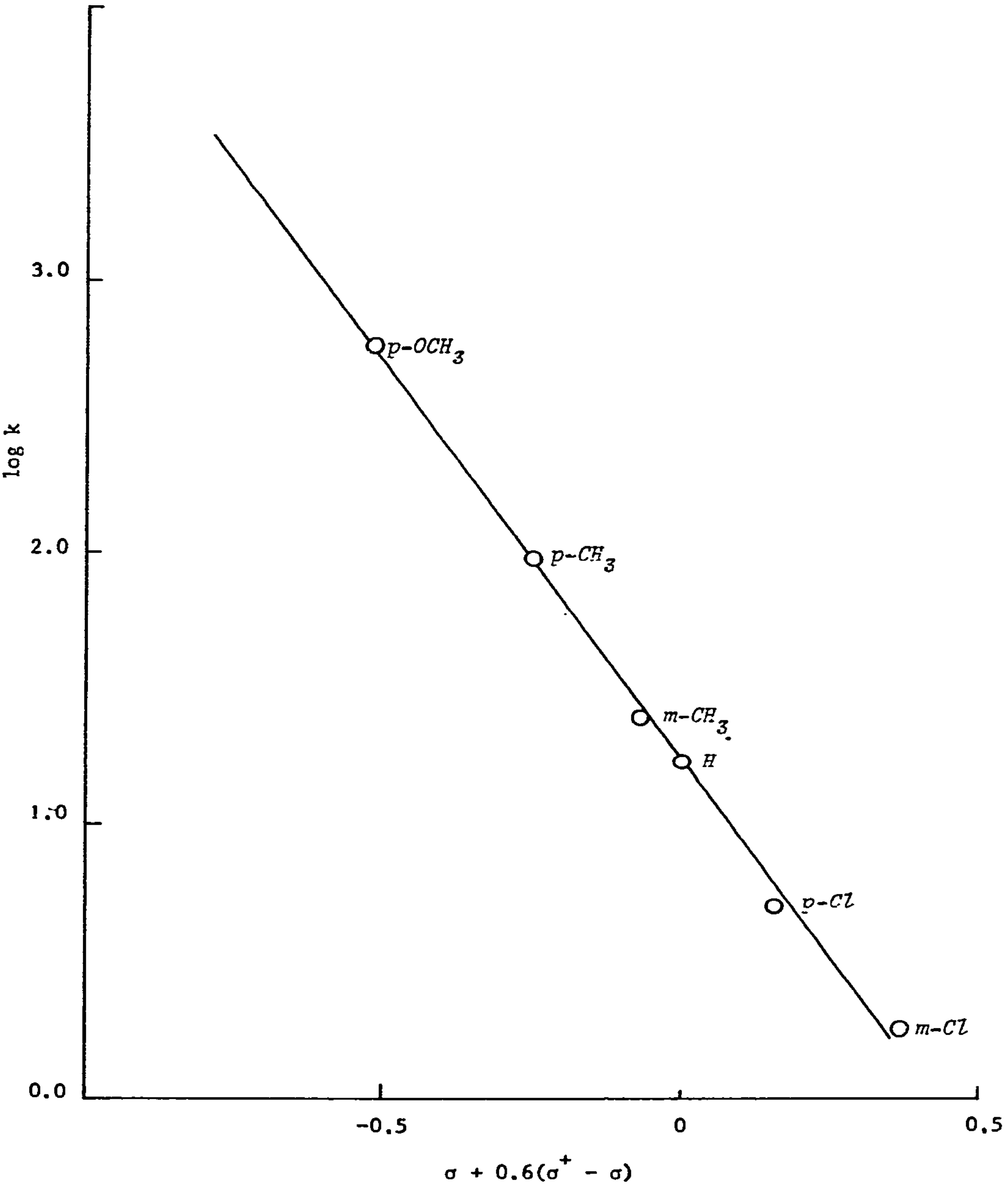


Fig. 1 - Plot of log k vs $|\sigma + 0.6\ (\sigma^{+} - \sigma)|$ for the reaction of some substituted hexaphenyldilead compounds with HCl in dioxane at 30°.

is −2.9, comparable with the value of −2.3 for the acetolysis of hexaaryldileads[3] and of −2.6 for the hydrogen chloride cleavage of tetraarylleads[1]. Electrophilic attack on carbon thus seems clearly indicated.

The addition of a stoichiometric amount of $Ph_4Pb$ (Table 2) is seen to have no effect upon the cleavage rate of hexaphenyldilead. This result together with the non-formation of $Ph_4Pb$ during the course of the reaction are in accord with our previous observations [3] strongly discounting the equilibrium, $R_6Pb_2 \rightleftharpoons R_4Pb + R_2Pb$, for the dilead substrates in solution.

The cleavage rate is however seen to decrease slightly in the presence of $LiClO_4$. This may be due to the kinetic salt effect which would be expected to be small for a reaction involving

TABLE 2

Effect of added compounds on the reaction $Ph_6Pb_2 + 3HCl$ in dioxane at 30°: $[Ph_6Pb_2]_o = 5 \times 10^{-5}$ M, $[HCl]_o = 1.5 \times 10^{-4}$ M

| Added compound | Concentration (M) | k ($M^{-1}s^{-1}$)* |
|---|---|---|
| $LiClO_4$ | $5 \times 10^{-4}$ | 16.1 |
| $LiClO_4$ | $1.5 \times 10^{-3}$ | 15.4 |
| $LiClO_4$ | $3 \times 10^{-3}$ | 14.8 |
| $Ph_4Pb$ | $5 \times 10^{-5}$ | 16.6+ |

* Each entry represents an average of 5 − 6 different determinations.

\+ The rate constant for the reaction $Ph_4Pb + HCl$ in dioxane at 30° is 1.35 $M^{-1}s^{-1}$ [Ref. 1].

uncharged species. HCl is considered to be negligibly ionized in dioxane and this is supported by the acidity function studies of Dessy and Kim [17]. There is however a slight possibility that the rate decrease may be a consequence of specific anion influence although this explanation was not favoured for the related HCl cleavage reaction of $Ph_4Pb$ in 20% methanol-80% benzene where LiBr and at low concentrations also LiCl produced rate lowerings while high concentrations of LiCl caused rate enhancement [1].

There is very little or no deuterium isotope effect in the cleavage of $Ph_6Pb_2$ as determined from the comparative rates of reaction with DCl and HCl. The cleavage rate using DCl containing $5 \times 10^{-3}$ M $D_2O$ is 17.1 $M^{-1}s^{-1}$ compared to 16.6 $M^{-1}s^{-1}$ using HCl containing $5 \times 10^{-3}$ M $H_2O$. The latter value is almost identical to that obtained in anhydrous dioxane. It has been reported [18] that the dissociation constant ($K_A$) of HCl at 35° changes from 0.006 to 0.0001 upon changing the composition of the dioxane-water medium from 70 to 82 weight % dioxane. $K_A$ is thus anticipated to be small in anhydrous dioxane and the dissociation equilibria to be not significantly affected by the presence of 0.005 M water. The deuterium isotope effect was also noted to be absent in the HCl cleavage of $Ph_4Pb$ in dioxane [1]. This indicates either molecular attack of HCl on hexaphenyldilead with little bonding of H to C in the transition state (slight bond making) or else an attack by ion-pair acid.

The rate constants for the HCl cleavage of $Ph_6Pb_2$ were also measured in chloroform and 20% methanol-80% benzene and the results are presented in Table 3. In the absence of more extensive experimental data a discussion of the trends is necessarily speculative. The decrease in rate upon changing the solvent from dioxane to the more polar methanol-benzene may be interpreted as a consequence of increased ionization of the acid in the latter medium (lesser undissociated acid) as much as of greater solvation of the undissociated acid (the attacking species) which results in a higher activation energy. In chloroform there

TABLE 3

Effect of solvent on the HCl cleavage of $Ph_6Pb_2$ at 30°

| Solvent* | Reactant ratio ($Ph_6Pb_2$/HCl) | k $M^{-1}s^{-1}$ | $E_a$ kJ $mol^{-1}$ | $\Delta H^{\neq}$ kJ $mol^{-1}$ | $\Delta S^{\neq}$ $J^{o}K^{-1}mol^{-1}$ |
|---|---|---|---|---|---|
| Dioxane (2.3) | 1/3 | 16.8 | 25.8 | 23.3 | -145 |
| Chloroform (4.8) | 1/4 | 172 | 31.7 | 29.2 | -97 |
| 20% methanol-80% benzene (28) | 1/3 | 0.48 | 31.2 | 28.7 | -156 |

* Dielectric constant values given in parenthesis are from Ref. 17.

is a large increase in rate although $\Delta H^{\neq}$ is similar in magnitude to that obtained in methanol-benzene. A possible explanation for this is indicated in the relatively large value of $\Delta S^{\neq}$ for the reaction in chloroform implying less effective solvation of the transition state in this medium.

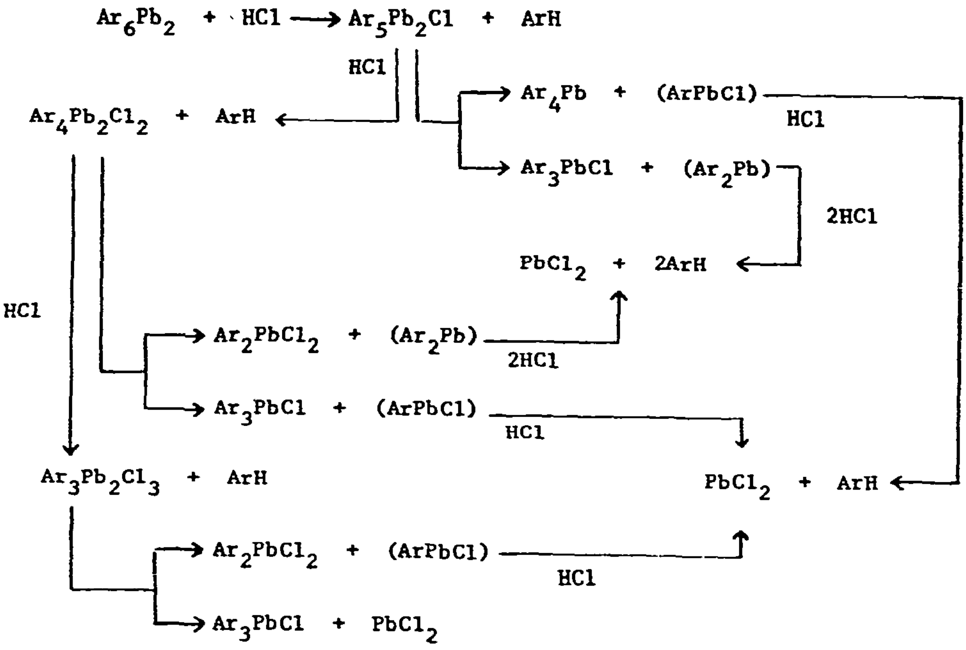
The present kinetic study indicates that in hexaphenyldilead the Pb-C bond cleaves in preference to the Pb-Pb bond. Initial cleavage of the Pb-Pb bond would lead to $Ph_3PbH$ and the most obvious subsequent reaction of the hydride would be,

$$Ph_3PbH + HCl \longrightarrow Ph_3PbCl + H_2 \qquad (7)$$

which is not observed.

The rate-determining Pb-C bond cleavage by the undissociated acid probably proceeds via a four-centre mechanism. The intermediary $Ar_5Pb_2Cl$

species which is formed may either rapidly disproportionate or suffer further Pb-C bond cleavage in the manner postulated by Willemsens and van der Kerk [11] as in the scheme below.



Little can be said at present about these breakdown patterns but considerations of stoichiometry as well as the absence of both $Ph_4Pb$ and $Ph_2PbCl_2$ even at the end of the reaction suggest that the steps leading to these products in the above scheme have a lower probability in dioxane.

We have previously suggested [1] for the reaction of HCl with $Ph_4Pb$ in both dioxane ($k_{30^o}$ = 1.35 $M^{-1}s^{-1}$) and 20% methanol-80% benzene ($k_{30^o}$ = 0.190 $M^{-1}s^{-1}$), a transition state structure in which Pb-Cl and C-H bond formations are relatively more advanced than breakage of H-Cl and Pb-C bonds. A similar description of the transition state also seems likely for the present cleavage reaction.

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