HEXAMETHYLDILEAD

I. PREPARATION, THERMAL DECOMPOSITION AND METHANOLYSIS

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Summary

The preparation, stability and storage of pure samples of hexamethyldilead is discussed. Thermal decomposition in hydrocarbon and carbon tetrachloride solutions is suggested to involve dimethyllead formation followed by a radical chain reaction in the case of carbon tetrachloride. Both catalysed and uncatalysed methanolysis have been found to proceed by initial protic cleavage of the Pb—CH$_3$ bond.

Introduction

As part of our general program of investigations of the relative reactivities of metal—metal and metal—carbon bonds in Group IVA organometallics, we chose to study hexamethyldilead, this being the simplest substrate at the most reactive end of the series. The first task was to obtain pure samples of the compound and examine its stability, particularly under reagent-free conditions of our subsequent experiments.

There have been several reports of the preparation and purification of this compound and other hexaalkyldileads [1,2,3]. Pure material has been obtained and various spectroscopic properties determined, however opinion seems to be that the compound is unstable. Most reactivity studies have been carried out on hexaethyldilead, in particular its thermal decomposition has been investigated [4—6]. There do not, however, appear to have been any previous reports on the methanolysis reaction.
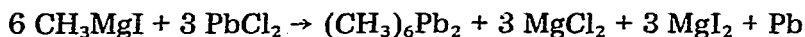
Experimental

Preparation and purification of hexamethyldilead
   The synthesis used followed the procedure of the original report by

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Calingaert and Soroos [1], with some modifications. The overall reaction is:

$$6 \, CH_3MgI + 3 \, PbCl_2 \rightarrow (CH_3)_6Pb_2 + 3 \, MgCl_2 + 3 \, MgI_2 + Pb$$

Methylmagnesium iodide was prepared from 35.9 g (0.25 mol) methyl iodide and 5.4 g (0.225 mol) magnesium in ca. 80 ml ether. A slowly passing nitrogen atmosphere was maintained necessitating the periodic addition of more ether. Freshly dried, finely-divided lead chloride (0.14 mol) was added in small portions over about an hour via a Schlenk solids addition funnel, while the suspension was vigorously stirred and the temperature maintained at between -5 and $-8°C$ with an ice/salt bath. The reaction is slightly exothermic and the temperature could be maintained in the desired range by controlling the rate of addition. Immediately a portion of lead chloride contacted the ether, a yellow-orange colour developed on the surface, before stirring dispersed the solid. The precipitation of lead metal appeared to commence soon after the first addition, and continued throughout. After most of the lead chloride had been added, the lead metal interfered with stirring, and further ether was required. The mixture was stirred for a further 30 minutes at $-5°C$, then small pieces of ice were added to hydrolyse excess Grignard reagent. (Usually there was only a minor reaction, with little evolution of methane.) Enough ice/water was then added, with stirring, to make the lead-containing water layer fairly mobile. The ether layer was decanted off, and three 50 ml portions of ether used to further extract the aqueous slurry. The cloudy, pale green ether extract was then quickly extracted twice with ice/water, producing a slightly cloudy solution. This solution was dried over anhydrous sodium carbonate, then filtered as rapidly as possible, minimizing contact with the atmosphere. Most of the ether was removed under vacuum, keeping the solution below room temperature. The product turned yellow and black at the surface, even when nitrogen was flushed through the rotary evaporator. The remaining ether and some tetramethyllead were pumped off at ca. 1 mmHg leaving a green/black solid. This mass was extracted thoroughly with three 5 ml portions of dry ether, filtered through a fine sinter, and the ether pumped off, keeping the flask cooled in ice. This usually produced a slightly off-white solid, which was normally stable at this stage, but sometimes decomposed rapidly even in the absence of air. Hexamethyldilead could be further purified by repetition of this technique, or by recrystallization at low temperature. M.p. 38°C (dec.) (lit. [1] 37—38°C). Hexamethyldilead is described as a cream or yellow solid, but it can be obtained as a white solid by crystallisation from ether, acetone or methanol. The compound is very soluble in ether even at 0°C, so the most convenient purification method is dissolution, filtration through a fine sinter or Celite filter aid, and removal of the ether and any tetramethyllead at below 1 mmHg, with cooling at 0°C. The problem with repeated use of ether is that it dissolves stopcock grease, which then becomes a contaminant. The presence of silicones does not seem to have any deleterious effects on the stability of the hexamethyldilead, but makes weighings inaccurate. This problem can be alleviated by using other solvents, in which the grease is insoluble, such as acetone. Hexamethyldilead is very soluble at room temperature, and insoluble at $-50°C$. Thus a crystallization can be performed in the absence of air, using Schlenk glassware, the product being precipitated

several times from the degassed acetone, with removal of the supernatant liquid by syringe, then removal of the remaining volatiles by pumping down to ca. 10^{-4} mmHg.

However, these methods sometimes failed to produce a stable product. The compound would rapidly liquify, becoming green and black, and resist further attempts at purification. On other occasions, the substance would remain solid, but quickly become completely black, then undergo no further visible change. On repurification the process would occur again. When repetition of the above methods failed to give a satisfactory sample, recrystallization from methanol was employed. This was generally avoided, since methanolysis takes place. However, if quickly dissolved in degassed methanol, white crystals would precipitate at $-50°C$ in a pure state free of the unidentified catalyst. Samples of the pure product were stored in a deep-freeze at $-20°C$ in a Schlenk tube, and dispensed in a stream of nitrogen.

Other materials

Methanol was AJAX UNIVAR "dried for non-aqueous titrations". Spectrograde acetone and isooctane were obtained from Eastman Chemicals. Benzene was AJAX UNIVAR reagent, carbon tetrachloride was Koch—Light puriss grade, toluene was from E. Merck, and anhydrous A.R. ether was from Mallinckrodt. Deuterated methanol was obtained from Stohler Isotope Chemicals or E. Merck. Lithium methoxide was prepared by dissolving lithium metal in methanol and was standardized by non-aqueous titration with benzoic acid in benzene/dimethylformamide. Lithium chloride was A.R. Merck, freshly dried before use.

Spectroscopic properties

The proton magnetic resonance spectrum of hexamethyldilead and a number of related compounds, summarised in Table 1, are much as previously reported for solutions in other solvents. As Fig. 1 indicates, these species are quite readily distinguished by this technique.

PMR spectra were recorded using Varian A-60, Varian EM-360, JEOL MH-100, or JEOL PS-100 spectrometers. The probe temperatures for the instruments were 36, 27.5, 20 and 28.5°C, respectively (all ±0.5°). In the majority of kinetic investigations, the MH-100 was employed, using the internal lock mode where possible, locked on a solvent signal. The internal lock mode was found to give superior reproducibility of peak heights, since field instability is the major cause of peak height variation, provided signals are not on the verge of saturation. A problem encountered in many of the systems described arises from precipitation during reaction which interferes with resolution and the lock signal.

UV spectra were recorded on either a Cary 14 or, in most cases, a Cary 17 recording spectrometer. The temperature of the cell compartment could not be controlled, but was found to be 22 ± 0.5°C. The concentration of hexamethyldilead was monitored by following the absorption maximum at 274 nm, ($\epsilon_{max} = 25\,400$ in isooctane). Mass spectra were recorded on an A.E.I. MS-902S mass spectrometer.
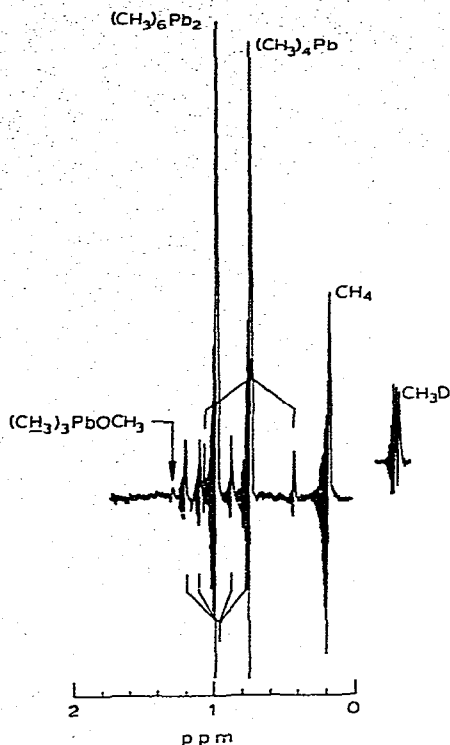
Fig. 1. PMR spectrum of $(CH_3)_6Pb_2$ during methanolysis

Preparation and decomposition of trimethyllead hydride in methanol solution

A solution of 5×10^{-5} mol trimethyllead chloride in 1 ml methanol at $-80°C$ was added to a slight deficiency of solid sodium borohydride in a cooled NMR tube. An instantaneous reaction occurred with evolution of gas, and precipita-

TABLE 1

PROTON RESONANCES FOR VARIOUS SOLUTIONS

	Chemical shifts [a] (coupling constants) [b]		
	CH_3OH	$C_6H_6/C_6H_5CH_3$	$CCl_4/CDCl_3$
$(CH_3)_6Pb_2$	0.97(43,23)	1.00(42,23) 1.01(42,23) [c]	0.96(42,23)
$(CH_3)_4Pb$	0.73(62.5)	0.72(62) 0.65(62) [d]	0.72(62)
$(CH_3)_3PbCl$	1.50(78) (79.5) [e]	(69.5) [f]	1.50(67) 1.63(70) [d]
$(CH_3)_3PbOCH_3$	1.27(78)		
$(C\underline{H}_3)_3PbH$	0.83(69)	0.85(66.7) [g]	
$(CH_3)_3Pb\underline{H}$	7.33(1.5) [h]	7.68(1.5) [g]	
CH_4	0.16(1.8) [i]		

[a] ppm positive to low field of TMS. [b] $J(^{207}Pb-{}^1H)$ in Hz. [c] Ref. 2. [d] Ref. 7. [e] Ref. 8. [f] Ref. 9. [g] Neat liquid, Ref. 10. [h] $J(H-Pb-CH_3)$. [i] $J(H-D)$ in CH_3D.
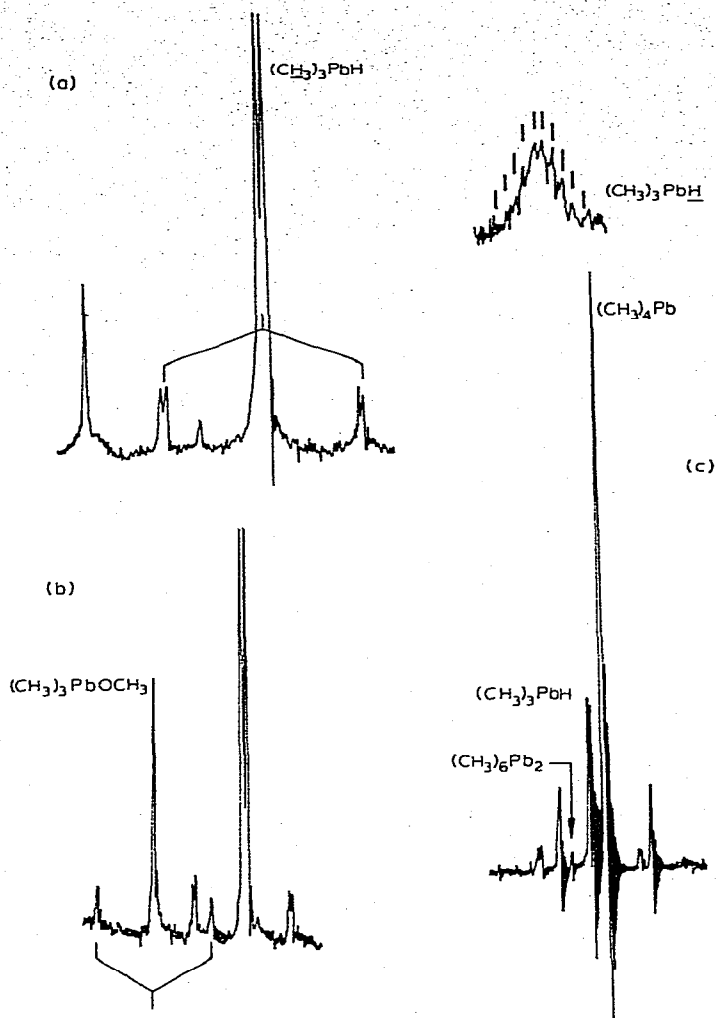
Fig. 2. PMR spectrum of $(CH_3)_3PbH$ in methanol at $-35°C$ (a) after 5 minutes; (b) after 2 hours; (c) after 24 hours.

tion of a small quantity of metallic lead. The NMR spectrum of the reaction mixture after 5 minutes at $-55°C$ is shown in Fig. 2a. A small quantity of trimethyllead chloride remained unreacted. The hydride decomposed slowly at $-35°C$, Fig. 2b showing the spectrum of the mixture after ca. 2 hours. The trimethyllead methoxide peak increased relative to the hydride doublet, and no methane was detected. Subsequent decomposition produced tetramethyllead, hexamethyldilead, and lead(II) salts, cf. Fig. 2c. The major decomposition pathway appeared to be methanolysis according to eq. 1 with little or no formation of methane.

$$(CH_3)_3PbH + CH_3OH \rightarrow (CH_3)_3PbOCH_3 + H_2 \tag{1}$$
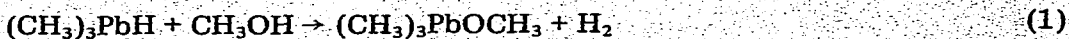
Thermal decomposition studies

Thermolyses were in all cases carried out in NMR tubes sealed on the vacuum line employing degassed solvents. The decomposition of solutions in benzene, toluene, chlorobenzene, chloroform, dichloromethane, dioxane and hexamethylphosphoric triamide (HMPT) were all found to conform to the stoichiometry shown in eq. 2, with the exception of the first few percent of

$$2 \ (CH_3)_6Pb_2 \rightarrow 3 \ (CH_3)_4Pb + Pb \tag{2}$$

reaction when some methane is produced. These were all slow reactions at room temperature except for the case of HMPT. Decompositions in carbon tetrachloride and acetone occur more rapidly and yield other products (see below).

Peak height measurements (h) in the PMR spectrum were employed for analysis with corrections for the spectral intensity missing from the central peaks due to coupling with active nuclei, i.e. ^{13}C and ^{207}Pb. Thus for hexamethyldilead (h_1) and tetramethyllead (h_2) $[(CH_3)_6Pb_2]_t/[(CH_3)_6Pb_2]_0 = 1.605h_1/(1.605h_1 + 1.306h_2) = r$ and $[(CH_3)_4Pb]_t/[(CH_3)_6Pb_2]_0 = 1.306h_2/(1.605h_1 + 1.306h_2)$ (the total intensity, $1.605h_1 + 1.306h_2$, remains constant when compared with an internal reference, e.g. cyclohexane).

The initial concentration of hexamethyldilead, ca. 0.1 M, could not be determined when this method of charging and sealing the tubes was employed, however, when the reactions followed first order kinetics this datum was not required. A small amount of silicone vacuum grease was always present as a contaminant and was responsible for a small singlet at ca. 0.0 ppm, but was otherwise of no consequence.

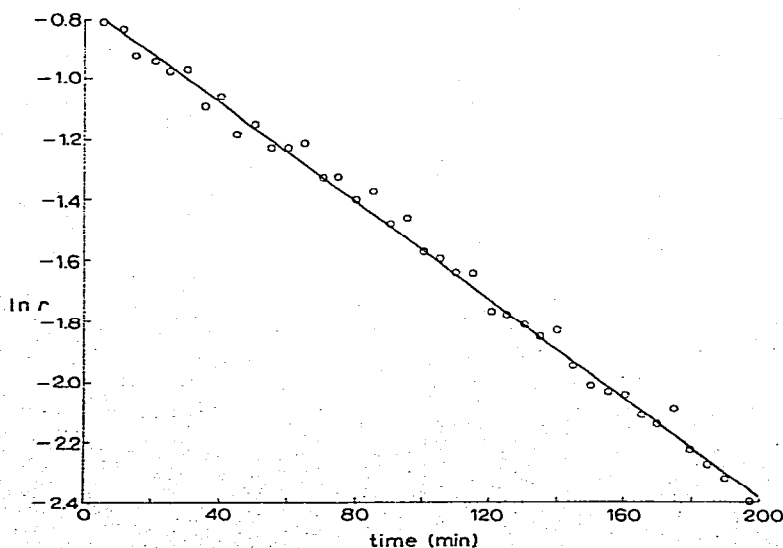Kinetic studies for toluene and benzene solutions was carried out over the

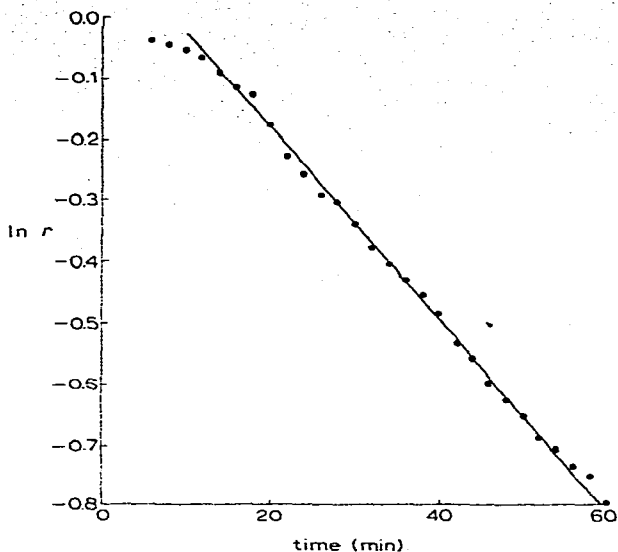Fig. 3. First order treatment of decomposition in toluene at 109°C.

Fig. 4. First order treatment of decomposition in CCl$_4$ at 36°C.

temperature range 78—109°C with the tubes heated in the probe of the spectrometer, or by suspending them in the condensing vapours of a suitable boiling liquid. The two methods gave essentially the same results and the brief period of removal required for analysis in the latter case did not appear to be significant. A typical kinetic run is illustrated in Fig. 3.

The decomposition in carbon tetrachloride solution at 36°C, illustrated in Fig. 4, is approximately first order after an induction period which varied from experiment to experiment. The linear region of Fig. 4 yields $k_{obs} = 3 \times 10^{-4}$ s^{-1} compared with 10^{-8} s^{-1} extrapolated from the toluene solution data. The major reaction product observed in the PMR spectrum is tetramethyllead formed in approximately equivalent amounts to the hexamethyldilead consumed. There are additional small variable features in the spectrum. One is trimethyllead chloride [δ 1.50 ppm; $J(^{207}\text{Pb}-^1\text{H})$ 67 Hz], one has δ 1.09 ppm; $J(^{207}\text{Pb}-^1\text{H})$ 64 Hz and another has δ 1.63 ppm; $J(^{207}\text{Pb}-^1\text{H})$ 70 Hz. The unknown compounds (CH$_3$)$_3$PbCCl$_3$ and (CH$_3$)$_3$PbCCl$_2$Pb(CH$_3$)$_3$ are likely candidates for these assignments. Dimethyllead dichloride (δ 2.5 ppm; $J(^{207}\text{Pb}-^1\text{H})$ 135 Hz in methanol) is extremely insoluble in carbon tetrachloride. There is a white precipitate, which appears to be largely lead chloride which was removed from a large scale experiment (ca. 0.1 g hexamethyldilead) by centrifugation and the supernatant liquid evaporated to yield a small amount of white product. When this product was introduced into the mass spectrometer on a heated probe at 100°C, ions arising from trimethyllead chloride and silicone grease were observed. On the other hand when introduced via the cold inlet a series of peaks typical of hexachloroethane were produced. The white precipitate yielded only very small amounts of trimethyllead chloride when extracted with acetone or with methanol in which it is readily soluble. Thus, excluding trace products, the stoichiometry of the reaction in carbon tetrachlo-

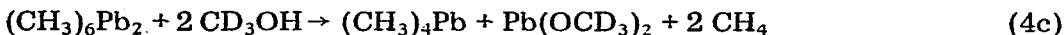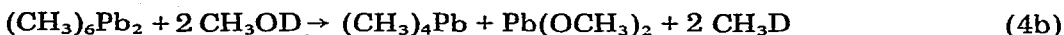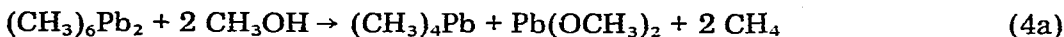ride approximately corresponds to eq. 3. Several modifications of the system

$$2 \ (CH_3)_6Pb_2 + 2 \ CCl_4 \rightarrow 3 \ (CH_3)_4Pb + PbCl_2 + C_2Cl_6 \hspace{2cm} (3)$$
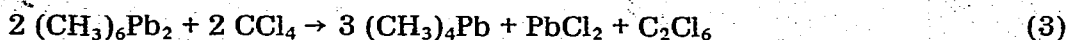
were studied but irreproducable kinetics were generally obtained. Added AIBN * reduced the first order rate constant by a factor of two without affecting the induction period, whereas benzoyl peroxide reduced the induction period and gave a subsequent slow reaction. Hydroquinone reduced the induction period and retarded the first order reaction by a factor of five. Saturation with air gave a fast initial reaction (oxidation) and then a slow reaction. Reaction in 1 : 1 carbon tetrachloride/toluene has a very long induction period (ca. 8 hours) with subsequent first order behaviour at a rate reduced by a factor of thirty. No products arising from radical attack on toluene were detected. Added *trans*-stilbene had no effect and no products of dichlorocarbene trapping were detected.

The major products of decomposition in acetone solution are tetramethyllead and lead as in the case of hydrocarbon solutions. The reaction is, however, more rapid ($k_{obs} \sim 5 \times 10^{-5} \ s^{-1}$ at 50°C). Furthermore, the precipitated lead metal always has associated with it small amounts of white material which could not be properly identified.

Methanolysis studies

Decomposition in methanol solution proceeds as follows:

$$(CH_3)_6Pb_2 + 2 \ CH_3OH \rightarrow (CH_3)_4Pb + Pb(OCH_3)_2 + 2 \ CH_4 \hspace{1cm} (4a)$$

$$(CH_3)_6Pb_2 + 2 \ CH_3OD \rightarrow (CH_3)_4Pb + Pb(OCH_3)_2 + 2 \ CH_3D \hspace{1cm} (4b)$$

$$(CH_3)_6Pb_2 + 2 \ CD_3OH \rightarrow (CH_3)_4Pb + Pb(OCD_3)_2 + 2 \ CH_4 \hspace{1cm} (4c)$$

The methane product was identified by its chemical shift and the characteristic (1 : 1 : 1) triplet of CH_3D obtained for solutions in CH_3OD or CD_3OD. Fig. 1 shows a typical PMR spectrum with the triplet pattern inset. (Spectra were usually run from high to low field to reduce interference between one of the satellites of hexamethyldilead and the central resonance of tetramethyllead.) Using an internal reference, either cyclohexane or the high field ^{13}C satellite of methanol, it was established that, after a brief initial period, the ratio of hexamethyldilead consumed to tetramethyllead formed was 1 : 1. A typical concentration vs. time curve for the species observed is shown in Fig. 5. The data shown for methane formation were obtained as twice the average of the hexamethyldilead consumed and the tetramethyllead formed. Early observation on the methane resonance agree with this measure, but the solution subsequently becomes saturated, and probably supersaturated, to various extents in different experiments after which this resonance has essentially constant intensity. Some lead methoxide remains in solution and some precipitates to varying extents depending presumably on a number of factors, e.g. area, cleanliness and regularity of the inside surface of the tube. Lead alkoxides are reported [11] to exist as polymeric chains linked by oxygen atoms. The extent of aggregation in solution is unknown.
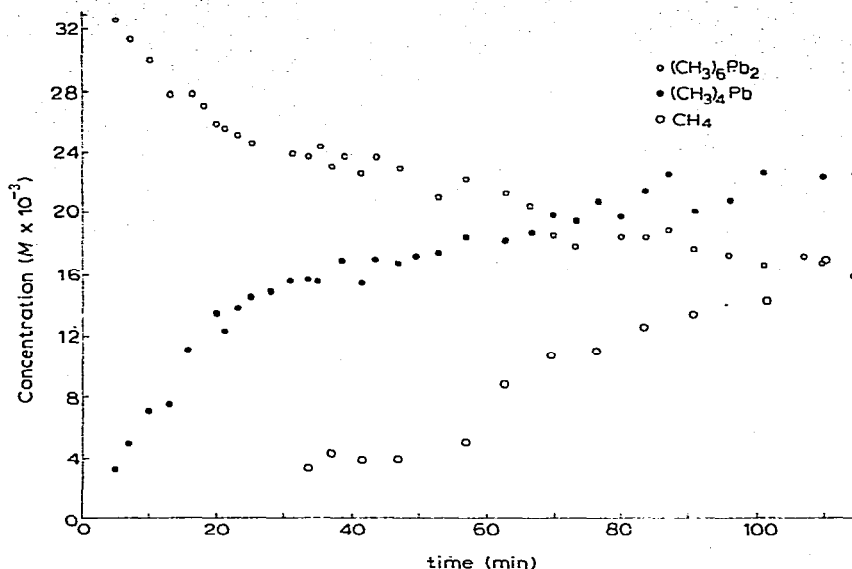
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* AIBN = azoisobutyronitrile.

Fig. 5. Concentration vs. time curves for $(CH_3)_6Pb_2$ in methanol.

Kinetic measurements were carried out by observation of the PMR spectrum or the UV spectrum at 274 nm. In both cases the reaction mixture was made up by adding the solvent, with any dissolved reagents, to a weighed amount of hexamethyldilead either in an NMR tube or a standard flask.

Results and discussion

Hexamethyldilead has an advantage over other hexaalkyldileads in being a solid at room temperature since decomposition occurs most readily in the liquid phase. Pure samples can be stored for long periods at moderately low temperatures if sealed. It is imperative, however, that the material be pure for otherwise decomposition leads to liquification and further decomposition. It is especially important that the commonest impurities trimethyllead salts be removed, cf. Part II [19].

Thermal decomposition

Thermal decomposition proceeds at a conveniently measurable rate in hy-

TABLE 2

FIRST ORDER RATE CONSTANTS FOR THERMAL DECOMPOSITION OF $(CH_3)_6Pb_2$

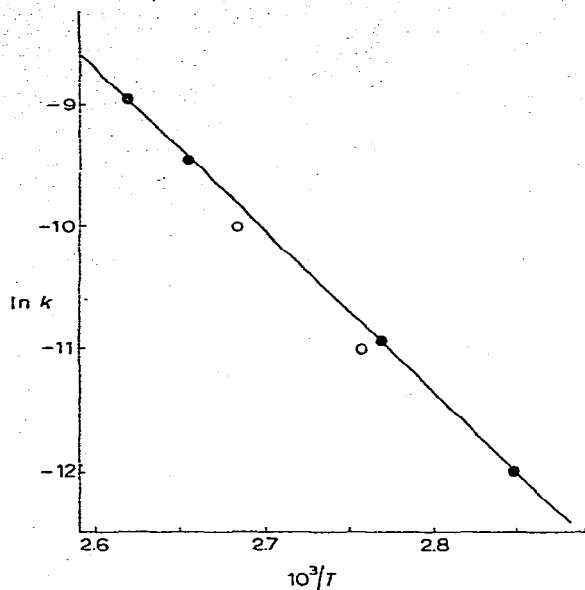| Solvent	$T(°C, ±0.5)$	$k(s^{-1})$
Benzene	89.5	$1.6(±0.1) \times 10^{-5}$
Benzene	99.5	$4.6(±0.1) \times 10^{-5}$
Toluene	78	$6.1(±0.1) \times 10^{-6}$
Toluene	88	$1.7(±0.1) \times 10^{-5}$
Toluene	104	$7.9(±0.1) \times 10^{-5}$
Toluene	109	$1.3(±0.1) \times 10^{-4}$

Fig. 6. Arrhenius plot for decomposition in toluene (solid circles) and in benzene (open circles).

drocarbon solutions at 78—109°C, but is sufficiently slow at ~30°C not to be of significance when solvolysis or other reactions are being carried out in methanol solutions. The first order thermolysis rate constants for toluene and benzene solutions are summarised in Table 2, and analysis of the data in terms of the Arrhenius equation is illustrated in Fig. 6. The stoichiometry is clearly that of eq. 2, i.e. all the methyl groups remain bonded to lead, and the first order rate constants for toluene solution are given by:

$$\log k_{dec} = 11.08(\pm 0.05) - 109.6(\pm 1.0) \text{ kJ mol}^{-1}/2.303 \, RT$$

There are no indications that a long chain reaction is involved here and the precipitated lead product does not affect the rate of decomposition.

Thermochemical results coupled with mass spectrometric studies lead to the following values for the bond dissociation energies:
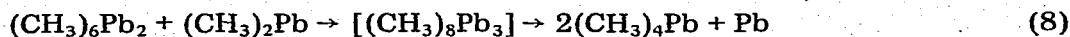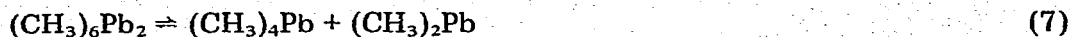
Pb—Pb in $(CH_3)_6Pb_2$ 229 kJ mol^{-1} Appearance potentials of $(CH_3)_3Pb^+$ [12]

Pb—C in $(CH_3)_4Pb$ 204 kJ mol^{-1}

207($\pm$4) kJ mol^{-1} Thermolysis of $(CH_3)_4Pb$ [13]

Both of these are about twice the activation energy reported above, so that neither reaction 5 nor reaction 6 seem likely to correspond to the measured rate of thermolysis. Methyl radicals are certainly not produced in the decom-

$(CH_3)_6Pb_2 \rightarrow 2(CH_3)_3Pb\cdot$ (5)

$(CH_3)_6Pb_2 \rightarrow (CH_3)_5Pb_2 + CH_3$ (6)

position since hydrogen abstraction from toluene would occur and methane would be a product.

The most reasonable decomposition pathway is as follows, with reaction 7 rate controlling and measured as $\frac{1}{2}k_{dec}$.

$$(CH_3)_6Pb_2 \rightleftharpoons (CH_3)_4Pb + (CH_3)_2Pb \tag{7}$$

$$(CH_3)_6Pb_2 + (CH_3)_2Pb \rightarrow [(CH_3)_8Pb_3] \rightarrow 2(CH_3)_4Pb + Pb \tag{8}$$

Reaction 8 could be a Pb—Pb or a Pb—C insertion and the decomposition of the transient octamethyltrilead can be envisaged as involving similar intramolecular bonding changes as those responsible for reaction 7.
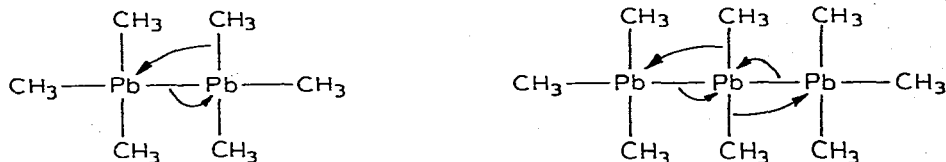
Diethyllead formation has also been suggested as the initial step in the thermolysis of hexaethyldilead [4—6]. In these experiments it is also reported that the reaction mixture becomes coloured (yellow-orange) as might be expected if significant quantities of polylead species were present. However, the overall stoichiometry reported is different from our findings, eq. 2, in that ethyl groups are lost from lead and appear as ethane (54.9%), ethene (42.3%), and butane (2.8%) as expected if ethyl radicals were formed and engaged in reactions other than combination and disproportionation. It is not clear to what extent the product tetraethyllead is undergoing concurrent thermolysis in these experiments, but this is known to yield ethyl radicals. Furthermore, the β-hydrogen containing ethyl group has available to its decomposition pathways, e.g.

$$C_2H_5 + C_2H_5PbR_3 \rightarrow C_2H_6 + \dot{C}_2H_4PbR_3 \rightarrow C_2H_4 + R_3Pb \cdot$$
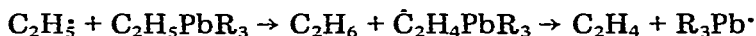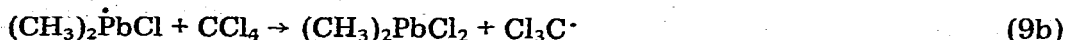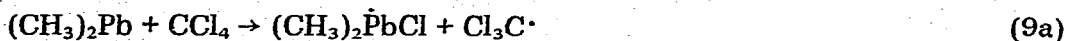
which are not important in the case of methyl groups.

The photolysis of hexamethyldilead in carbon tetrachloride and in pentane solutions has been studied [14], and the intermediacy of trimethyllead radicals presumed, although they could not be observed in the ESR spectrum. In pentane solutions containing alkyl halides the corresponding alkyl radicals are observable, lead is precipitated as in the normal thermolysis, and in some cases a white precipitate is reported. Both methyl radicals and trichloromethyl groups are observed by ESR in the case of carbon tetrachloride solutions, and trimethyllead chloride is claimed to be an important product on the basis of the mass spectrum of the acetone soluble part of the precipitate formed. Our experience is that traces of trimethyllead chloride are readily detected by this technique whereas hexachloroethane may be illusive.
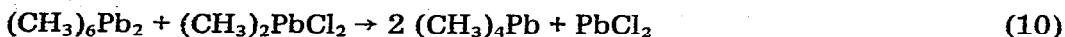
Thermolysis occurs considerably more rapidly in carbon tetrachloride than in most other solvents and takes a different course yielding chlorine containing products. As judged by the PMR spectrum each hexamethyldilead is converted into approximately 1.5 equivalents of tetramethyllead with traces of other species which could be the unknown compounds $(CH_3)_3PbCCl_3$ and $(CH_3)_3$-$PbCCl_2Pb(CH_3)_3$. Lead metal is not formed, and lead chloride is obtained as a

white precipitate. However, this precipitate also contains hexachloroethane and rather less trimethyllead chloride than at first sight appears to be the case. The kinetics are complex with the reaction displaying an induction period prior to an approximately first order loss of hexamethyldilead at a considerably greater rate than normal thermolysis.
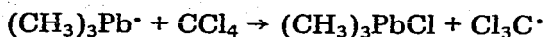
A chain reaction seems to be involved and the trichloromethyl radical is clearly implicated. Reaction 7 could be the initiating step followed by:

$$(CH_3)_2Pb + CCl_4 \rightarrow (CH_3)_2\overset{\cdot}{P}bCl + Cl_3C\cdot \tag{9a}$$

$$(CH_3)_2\overset{\cdot}{P}bCl + CCl_4 \rightarrow (CH_3)_2PbCl_2 + Cl_3C\cdot \tag{9b}$$

with dimethyllead dichloride rapidly consumed by

$$(CH_3)_6Pb_2 + (CH_3)_2PbCl_2 \rightarrow 2\ (CH_3)_4Pb + PbCl_2 \tag{10}$$

alternatively, the initiating process could be reaction 5 with

$$(CH_3)_3Pb\cdot + CCl_4 \rightarrow (CH_3)_3PbCl + Cl_3C\cdot$$

or reaction 6 with related reactions with carbon tetrachloride.

As far as may be judged the reaction

$$(CH_3)_6Pb_2 + 2\ (CH_3)_3PbCl \rightarrow 3\ (CH_3)_4Pb + PbCl_2 \tag{11}$$
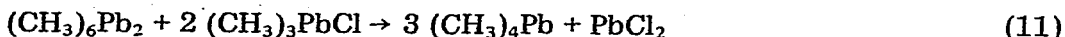
is rapid under these conditions [19].

Two series of chain reactions can be envisaged, one being:

$$(CH_3)_6Pb_2 + Cl_3C\cdot \rightarrow (CH_3)_3PbCCl_3 + (CH_3)_3Pb\cdot \tag{12a}$$

$$CCl_4 + (CH_3)_3Pb\cdot \rightarrow (CH_3)_3PbCl + Cl_3C\cdot \tag{12b}$$

and the other:

$$(CH_3)_3PbCCl_3 \rightarrow (CH_3)_3PbCl + Cl_2C \tag{13}$$
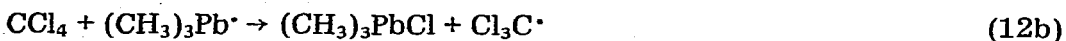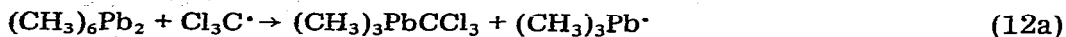
with ample precedents in the work of Seyferth [15], followed by

$$(CH_3)_6Pb_2 + Cl_2C \rightarrow (CH_3)_3PbCCl_2Pb(CH_3)_3 \tag{14a}$$

$$(CH_3)_3PbCCl_2Pb(CH_3)_3 \rightarrow (CH_3)_3Pb\overset{\cdot}{C}Cl_2 + (CH_3)_3Pb\cdot \tag{14b}$$

$$(CH_3)_6Pb_2 + (CH_3)_3Pb\overset{\cdot}{C}Cl_2 \rightarrow (CH_3)_3PbCCl_2Pb(CH_3)_3 + (CH_3)_3Pb\cdot \tag{14c}$$
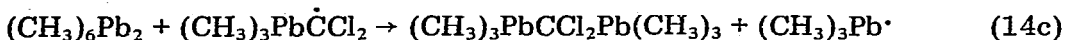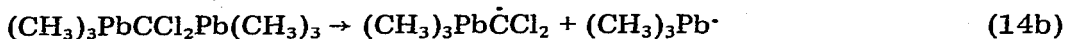
which has the branching capacity to compensate for chain termination by:

$$2\ Cl_3C\cdot \rightarrow C_2Cl_6 \tag{15}$$

After the induction period the rate of decomposition could be determined by substrate-independent steady-state concentrations of Cl_2C and/or $(CH_3)_3$-$Pb\overset{\cdot}{C}Cl_2$ and/or $Cl_3C\cdot$. Our inability to trap dichlorocarbene may be the result of its rapid reaction with hexamethyldilead.

Methanolysis

That hexamethyldilead should undergo methanolysis was not totally unexpected since this also occurs in the case of hexaaryldileads bearing electron-withdrawing substituents [16,17].

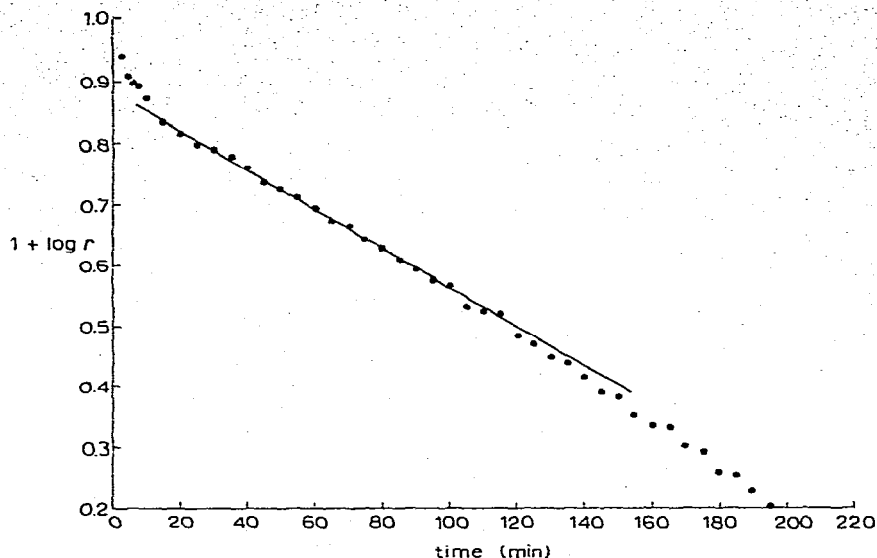Examined as a first order reaction, cf. Fig. 7, a three part curve is obtained.

Fig. 7. First order treatment of methanolysis.

In the first region there is a small, rapid destruction of the substrate. This region typically lasts for fifteen minutes, but its duration and the extent of reaction varies considerably. It is minimised by the use of degassed methanol but could not be totally eliminated. It clearly corresponds to reaction of the oxygen and other minor reactive components either in the methanol or the hexamethyldilead. After this "clean-up" period there is a first order region. This, however, is of short duration since autocatalysis sets in. Table 3 lists first order rate constants obtained for the several sets of experiments. The autocatalysis is most reasonably ascribed to the lead methoxide product since the only other product, tetramethyllead, has no effect of the reaction. Independently produced lead methoxide apparently has a different solid state structure because it is insoluble in methanol, as is the precipitated product of methanolysis. (The

TABLE 3

FIRST ORDER RATE CONSTANTS FOR METHANOLYSIS UNDER VARIOUS CONDITIONS AT 30°C

$k_{obs} \times 10^{-5} \text{ s}^{-1}$	Reaction conditions
9.5	CH_3OH (not degassed)
11.2	CH_3OH (not degassed)
8.2	CH_3OH (not degassed)
7.9	CD_3OH
5.8	CH_3OH (degassed)
5.7	CH_3OH (degassed)
5.5	CH_3OH (degassed, sealed)
4.6	CH_3OH (degassed, sealed)
4.7	CD_3OD (not degassed)
5.1	CD_3OD (not degassed)
4.6	CD_3OD (not degassed)

first order rate constants are similarly larger for systems that were not degassed since the initial oxygen reaction will yield lead methoxide.)

A set of kinetic runs were carried out with particular attention to exclusion of oxygen. In these degassed solvents and substrates were introduced into the tube under nitrogen in a glove-box and the tubes sealed on the vacuum line. Initial concentrations were indeterminate and the initial ten minutes of reaction unobservable. The reactions were first order $k_{obs} = 5.1(\pm 0.5) \times 10^{-5}$, and became autocatalytic as before.

The approximate rate constant in the first order region for non-degassed methanol (and CD_3OH) is $9(\pm 1) \times 10^{-5}$ s^{-1}, whereas in CD_3OD it is $4.8(\pm 0.2) \times 10^{-5}$ s^{-1}. Thus the reaction involves protic cleavage with a kinetic isotope effect of ca. 2. This kinetic isotope effect is considerably less than the maximum observable for a symmetrical transition state. It is consistent with a poorly developed C—H bond in the transition state as might be expected for a protolysis with substantial nucleophilic assistance.

Lithium methoxide is a particularly good catalyst for methanolysis. Apart from the first few percent of reaction, the reaction is cleanly first order without showing autocatalytic behaviour provided that $[LiOCH_3] > 0.01$ M, i.e. well below that of the substrate (0.05 M). The observed rate constants are given by

$$k_{obs} = 12(\pm 4) \times 10^{-5} + 2.3(\pm 0.1) \times 10^{-2} \,[LiOCH_3]\ \text{s}^{-1}$$

which means that if the rate processes are given by $k_m\,[(CH_3)_6Pb_2]$

$[CH_3OH]^2$ and $k'_m\,[(CH_3)_6Pb_2][CH_3OH][LiOCH_3]$, then $k'_m/k_m \simeq 4500$.

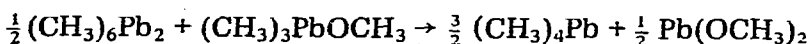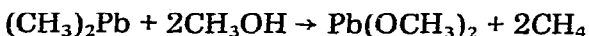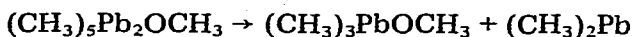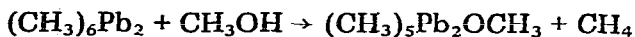Lithium chloride is a much less effective catalyst which at a concentration of 0.5 M increases the rate by a factor of two. (Such an increase is brought about by ca. 0.01 M lithium methoxide). Potassium cyanide is quite effective and at a concentration of 0.25 M the reaction is essentially complete in twenty minutes. Pyridine (1 M) caused no detectable rate change and lithium perchlorate (0.5 M) was without detectable effect.

A possible mechanism of the methanolysis involves Pb—Pb bond cleavage yielding trimethyllead hydride as an intermediate (eq. 16). However, this species
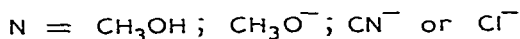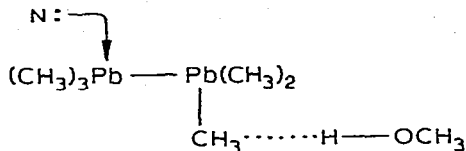
$$(CH_3)_6Pb_2 + CH_3OH \rightarrow (CH_3)_3PbOCH_3 + (CH_3)_3PbH \tag{16}$$
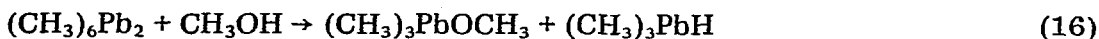
in methanol does not yield methane but rather produces hydrogen.

The initial step therefore must be electrophilic Pb—CH$_3$ cleavage. This could yield a pentamethyldilead methoxide intermediate which subsequently decomposes, or there could be a concerted Pb—Pb cleavage.

$(CH_3)_6Pb_2 + CH_3OH \rightarrow (CH_3)_5Pb_2OCH_3 + CH_4$

$(CH_3)_5Pb_2OCH_3 \rightarrow (CH_3)_3PbOCH_3 + (CH_3)_2Pb$

$(CH_3)_2Pb + 2CH_3OH \rightarrow Pb(OCH_3)_2 + 2CH_4$

$\frac{1}{2}(CH_3)_6Pb_2 + (CH_3)_3PbOCH_3 \rightarrow \frac{3}{2}(CH_3)_4Pb + \frac{1}{2}Pb(OCH_3)_2$

overall $\quad \frac{3}{2}(CH_3)_6Pb_2 + 3\,CH_3OH \rightarrow \frac{3}{2}(CH_3)_4Pb + \frac{3}{2}Pb(OCH_3)_2 + 3\,CH_4$
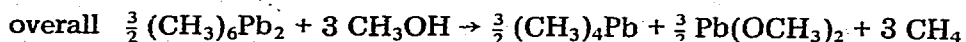
We favour the concerted process since the reaction is very much faster than the undetectable methanolysis of tetramethyllead. (Acetolysis of hexamethyldilead

occurs at a rate comparable with its rate of dissolution in acetic acid, i.e. $k \gg 10^{-1}$ s^{-1}, whereas acetolysis of tetramethyllead is much slower $k = 1.2 \times 10^{-5} s^{1}$ [18].) Nucleophilic assistance is then envisaged to take place at the distant lead atom thus

$$N : \rightharpoondown$$
$$(CH_3)_3Pb \longrightarrow Pb(CH_3)_2$$
$$CH_3 \cdots \cdots H \longrightarrow OCH_3$$

$$N = CH_3OH ; \quad CH_3O^- ; \quad CN^- \quad \text{or} \quad Cl^-$$

Methanolysis of dimethyllead is anticipated to be quite rapid, and the reaction between hexamethyldilead and trimethyllead methoxide is known to be fast [19].

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