Thermal Decomposition of Hexamethyldilead

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Summary Hexamethyldilead undergoes first order thermolysis in toluene and in benzene solutions with $k = 1{\cdot}2 \times 10^{11} \exp\{-110\ \text{kJ mol}^{-1}/RT\}\text{s}^{-1}$; dissociation to tetramethyl-lead and dimethyl-lead, the latter being a transient intermediate, is suggested.

The appearance potential of Me_3Pb^+ from hexamethyldilead ($9{\cdot}02 \pm 0{\cdot}14$ eV) is larger than that from tetramethyl-lead ($8{\cdot}77 \pm 0{\cdot}16$ eV), corresponding to a bond dissociation energy difference of 25 kJ mol^{-1} (6 kcal mol^{-1}),[1] Thus, if the bond dissociation energy of Pb–C in hexamethyldilead is similar to that in tetramethyl-lead, then, instead of the anticipated thermal decomposition (1), reaction (2) may in fact be preferred.

$$Me_6Pb_2 \rightarrow 2Me_3\dot{P}b \qquad (1)$$

$$Me_6Pb_2 \rightarrow Me_3Pb\dot{P}bMe_2 + M\dot{e} \qquad (2)$$

Recent studies[2] of the thermal decomposition of tetramethyl-lead in the presence of toluene show an activation energy of 207(±4) kJ mol^{-1} (49·5 kcal mol^{-1}) closely similar to the Pb–C bond dissociation energy (204 kJ mol^{-1}) calculated from the appearance potential data.[1] The activation energy for reaction (1) is hence expected to be *ca.* 230 kJ mol^{-1}.

To ascertain whether reaction (1) or reaction (2) is the dominant mode of thermal decomposition for hexamethyldilead, we examined degassed solutions of this compound in benzene or toluene at several temperatures, and found that the reaction proceeds cleanly according to the stoicheiometry of equation (3), and in particular, yields no methane nor bibenzyl when conducted in toluene solution. Decomposition does not therefore occur by way of reaction (2) since methyl radicals would certainly abstract hydrogen from the solvent. The rate of reaction, monirored by ^{1}H n.m.r. spectroscopy, is satisfactorily first order in hexamethyldilead. It shows no indications of reversibility, nor suppression by tetramethyl-lead. There is no induction period and the reaction appears unaffected by the presence of the film of lead formed on the walls of the reaction vessel. The first order rate constant is given by $k = 1{\cdot}2 \times 10^{11} \exp\{-110\ \text{kJ mol}^{-1}/RT\}\text{s}^{-1}$, and is essentially the same for benzene and toluene solutions as indicated by the rate constants given in the Table.

$$2Me_6Pb_2 \rightarrow 3Me_4Pb + Pb \qquad (3)$$

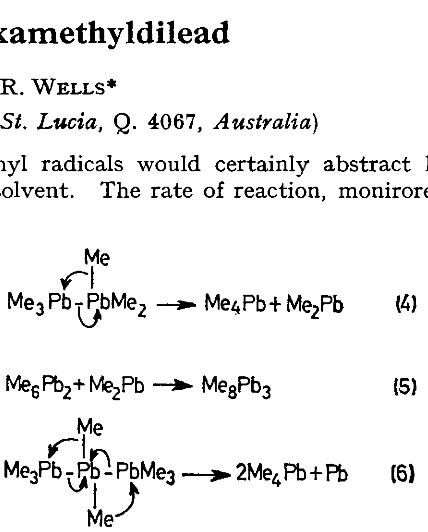

Table. First order thermal decomposition of hexamethyldilead

Solvent	Temp/K	Rate constant/s^{-1}
Toluene	351	$6{\cdot}1\ (\pm 0{\cdot}1) \times 10^{-6}$[a]
Toluene	361	$1{\cdot}75\ (\pm 0{\cdot}1) \times 10^{-5}$[a]
Toluene	377	$7{\cdot}9\ (\pm 0{\cdot}1) \times 10^{-5}$[a]
Toluene	382	$1{\cdot}3\ (\pm 0{\cdot}1) \times 10^{-4}$[a]
Benzene	362·5	$1{\cdot}6\ (\pm 0{\cdot}1) \times 10^{-5}$
Benzene	372·5	$4{\cdot}6\ (\pm 0{\cdot}1) \times 10^{-5}$

[a] $A = 1{\cdot}21\ (\pm 0{\cdot}14) \times 10^{11}\ \text{s}^{-1}$, $E_{act} = 110\ (\pm 1)$ kJ mol^{-1}

If a non-chain decomposition were initiated by reaction (**1**), its activation energy would be at least the corresponding bond dissociation energy (*ca.* 230 kJ mol^{-1}). We find no evidence for chain decomposition nor can we write an acceptable chain mechanism conforming to our kinetic and stoicheiometric observations. Thus reaction (1) is almost certainly not involved.

We suggest that decomposition is initiated by reaction (4) which produces dimethyl-lead as a reactive intermediate.

This species inserts into a hexamethyldilead molecule (5) to yield octamethyltrilead, which could rapidly decompose by an intramolecular mechanism (6) similar to the one by which dimethyl-lead is produced.

Certainly dimethyl-lead does not dissociate to yield methyl radicals, nor does it undergo intramolecular decomposition leading to ethane.

Dissociation by reaction (4) has also been suggested by Razuvaev *et al.*[3] for the liquid-phase decomposition of hexaethyldilead and it was claimed that diethyl-lead is observable in this system. Most reasonably the coloured intermediate present may have been octaethyltrilead or some other catenated species. There are also in this case hydrocarbon products, but these may have arisen from the concurrent decomposition of tetraethyl-lead.

Related investigations[4] have shown that the corresponding reaction (4) accompanies decomposition to trimethylsilyl radicals in the corresponding silicon compounds.

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