ALKYLATION AS A ROUTE TO REDUCTION OF COPPER(II) BY TETRAALKYLLEAD

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SUMMARY

The mechanism of the facile reduction of copper(II) complexes by tetraalkyllead compounds is explored. Two processes are considered: the first involving the alkylation of copper(II), followed by subsequent homolysis of the alkylcopper(II) species, and the second involving an electron transfer to form a tetraalkyllead cation radical. The pattern of methyl/ethyl reactivities in several electrophilic alkylations are compared with those in the copper(II) reduction. Selectivities in the mass spectral cracking patterns of various tetraalkyllead compounds are used as models for the selective cleavages of cation radicals. Since the selectivities for cleavage of CH_3-Pb and CH_3CH_2-Pb bonds are different for the two processes, it is concluded that the rate-limiting step in the reduction of copper(II) chloride by tetraethyllead occurs by a trans-alkylation process.

INTRODUCTION

Tetraethyllead is rapidly oxidized by various copper(II) complexes even at very low temperatures in protic as well as aprotic media[1]. Ethyl radicals appear to be prime intermediates in reactions carried out in acetic acid[2]. The reaction sequence (Eqs. 1, 2) has been presented to account for the variety of products obtained with different copper(II) oxidants:

$$Et_4Pb + Cu^{II}X_2 \rightarrow Et_3PbX + Cu^IX + Et \cdot \tag{1}$$

$$Et \cdot + Cu^{II}X_2 \xrightarrow{\text{fast}} Et_{ox} + Cu^IX \tag{2}$$

in which Et_{ox} represents Et–X or other products of oxidation such as alkene, etc.

The observation of a homolytic process involving alkyl radicals under these mild conditions is rather unique among organometallic systems[3]. Furthermore, organolead compounds are desirable agents for studying the alkylation of a variety of transition metal complexes and their importance gains impetus from the recent increased interest in this aspect of organometallic processes.

There are essentially two mechanisms by which copper(II) can be reduced by tetraethyllead in reaction (1)[2]. An outer-sphere electron transfer given in Eq. 3 of Scheme 1 can be followed by fragmentation (Eq. 4) of the tetraethyllead cation radical.

Scheme 1

$$Et_4Pb + Cu^{II}X_2 \rightarrow Et_4Pb^{\ddagger} + Cu^{I}X_2^{-} \tag{3}$$

$$Et_4Pb^{\ddagger} \rightarrow Et_3Pb^{+} \quad Et\cdot, \text{ etc.} \tag{4}$$

Alternatively, an inner-sphere process presented in Scheme 2 involves alkyl transfer from tetraethyllead to copper(II) as given in Eq. 5, and ethyl radicals are generated by subsequent homolysis of a metastable ethylcopper(II) intermediate.

Scheme 2

$$Et_4Pb + Cu^{II}X_2 \rightarrow Et_3PbX + EtCu^{II}X \tag{5}$$

$$EtCu^{II}X \rightarrow Cu^{I}X + Et\cdot, \text{ etc.} \tag{6}$$
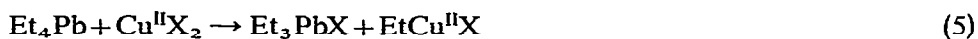
A mechanistic distinction between Schemes 1 and 2 can be made by an examination of the intramolecular competition involving several alkyl groups. Thus, the foregoing study[7] established that electrophilic cleavage of an alkyllead bond follows the order: methyl > ethyl, and the magnitude of the difference in rates depends on the electrophile. On the other hand, the mass spectral cracking pattern of organolead compounds, particularly at low ionizing voltages, should reflect selectivities in the fragmentation of alkyllead bonds in the tetraalkyllead cation radical[5]. In this instance the homolysis of the weaker alkyl–Pb bond is favored, *i.e.*, ethyl > methyl. In this report we used these diametrically opposed reactivity patterns as diagnostic probes for the mechanism of radical production during the reduction of copper(II) by tetraalkyllead compounds.

RESULTS AND DISCUSSION

The reduction of Cu^{II} chloride by tetraethyl- and tetramethyl-lead

Copper(II) chloride is only partially soluble in acetic acid, but can be readily solubilized as the chlorocuprate by the addition of lithium chloride.

$$Cu^{II}Cl_2 + n \text{ LiCl} \rightleftharpoons Li_nCu^{II}Cl_{2+n} \qquad n = 1, 2 \tag{7}$$
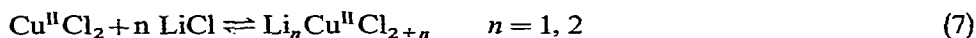
Tetraethyllead (in excess) reacts on mixing, with either Cu^{II} chloride present as a suspension or chlorocuprate in solution to produce one-half mole of ethyl chloride for each Cu^{II} chloride[2]* :

$$Et_4Pb + 2 Cu^{II}Cl_2 \rightarrow Et_3PbCl + EtCl + 2 Cu^{I}Cl \tag{8}$$
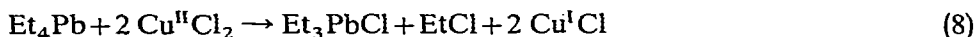
The dramatic discharge of the color indicates that the reactions given in Table 1 are essentially complete in 5 minutes at 20°, and additional ethyl chloride is not produced on further standing. Moreover, the same reaction (8) occurs rapidly when Cu^{II} chloride is employed in two-fold excess. In the latter case, additional ethyl chloride is formed only in a much slower reaction probably due to a further dealkylation reaction (Eq. 9)**.

$$Et_3PbCl + 2 Cu^{II}Cl_2 \rightarrow Et_2PbCl_2 + EtCl + 2 Cu^{I}Cl \tag{9}$$

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* The reaction then proceeds to produce alkane, (*vide infra*) but in the absence of copper(II) no more alkyl chloride is formed.

** The reactive chlorocopper(II) species in Eq. 7 will be referred to hereafter generally as copper(II) chloride and written CuCl$_2$.

TABLE 1

REDUCTION OF COPPER (II) CHLORIDE BY TETRAETHYL- AND TETRAMETHYL-LEAD [a]

R_4Pb	$Cu^{II}X_2$ (10^2 mmoles)		$R\text{-}X$ (10^2 mmoles)	$2RX/Cu^{II}$
$(CH_3CH_2)_4Pb$	$CuCl_2$	9.24^b	4.59	0.99
$(CH_3CH_2)_4Pb$	$CuCl_2$	4.50^c	2.11	0.95
$(CH_3)_4Pb$	$CuCl_2$	4.50^c	2.16	0.96

[a] In solutions (3.0 ml) of 0.15 M R_4Pb in acetic acid at 20°. [b] Suspension. [c] Also contains 0.439 mmole LiCl, homogeneous solution.

Tetramethyllead also reacts with Cu^{II} chloride under the same conditions to produce methyl chloride in excellent yields (Table 1).

$$(CH_3)_4Pb + 2\ Cu^{II}Cl_2 \rightarrow (CH_3)_3PbCl + CH_3Cl + 2\ Cu^{I}Cl \tag{10}$$
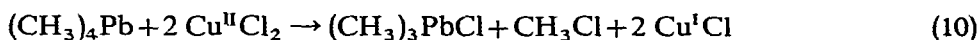
The reduction of a solution of copper(II) chloride by tetraethyl- or tetramethyl-lead in acetic acid leads to a colorless solution of chlorocopper(I) species. The latter is an efficient catalyst for the production of ethane or methane from tetraethyl- or tetramethyl-lead, respectively, by a process described previously[4].

$$R_4Pb + HOAc \xrightarrow{\ Cu^{I}Cl\ } R_3PbOAc + R\text{-}H \tag{11}$$

As a result, alkane and alkyl chloride are formed simultaneously when copper-(II) chloride reacts with tetraalkyllead. The catalyzed protonolysis (Eq. 11), however, does not affect the reduction (Eq. 8), since the latter proceeds at much faster rates. The formation of alkyl chloride can, thus, be used directly to measure the reduction of copper(II) chloride by tetraalkyllead.
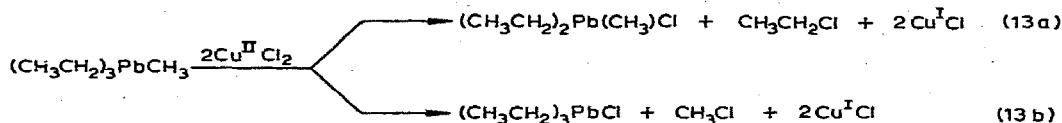
The addition of molecular oxygen does not inhibit the copper(I)-catalyzed formation of ethane[2]. This observation is consistent with the relatively slow autoxidation of chlorocopper(I) species previously observed in aqueous solutions[6].

$$2\ LiCu^{I}Cl_2 + O_2 \rightarrow (LiCu^{II}Cl_2)_2O_2\ ,\ \text{etc.} \tag{12}$$
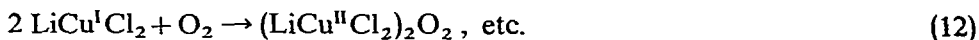
It is clear, moreover, that chlorocopper species are oxidized by oxygen, since additional ethyl chloride is generated only after the addition of oxygen. The relatively slow rate of formation of ethyl chloride under these circumstances must directly reflect the rate of autoxidation of chlorocopper(I), since the reduction of copper(II) chloride by tetraalkyllead is fast.

Reaction of mixed methyl/ethyl lead compounds with copper(II) chloride

A mixture of methyl chloride and ethyl chloride is formed when either triethyl-methyllead or trimethylethyllead reacts with copper(II) chloride. The combined yields of alkyl chlorides formed coincided with one-half of the number of equivalents of copper(II) chloride used (Table 2). This stoichiometry is in accord with that found for the symmetrical tetraalkyllead compounds (Eqs. 8 and 10) and relates to the loss of methyl and ethyl groups, e.g.,

$$(CH_3CH_2)_3PbCH_3 \xrightarrow{2Cu^{II}Cl_2} \begin{cases} (CH_3CH_2)_2Pb(CH_3)Cl + CH_3CH_2Cl + 2Cu^ICl \quad (13a) \\ \\ (CH_3CH_2)_3PbCl + CH_3Cl + 2Cu^ICl \quad\quad\quad (13b) \end{cases}$$

Such an intramolecular competition during the cleavages of CH_3-Pb and CH_3CH_2-Pb bonds by copper(II) chloride is measured by the yields of methyl chloride and ethyl chloride, respectively. The last column in Table 2 represents the rate of cleavage of a methyl group relative to an ethyl group after normalization for the number of alkyl groups contained in the reactant.
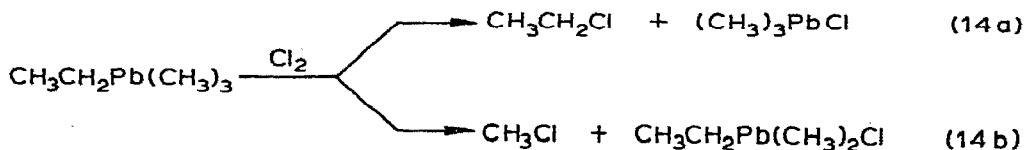
TABLE 2

INTRAMOLECULAR COMPETITION IN THE OXIDATIVE CLEAVAGE OF METHYL AND ETHYL GROUPS IN TETRAALKYLLEAD BY COPPER(II) CHLORIDE

$R_3PbR'^a$ (mmoles)		$CuCl_2$ (mmoles)	$LiCl$ (mmoles)	Products (mmoles)			Reactivity[c] CH_3/CH_3CH_2
				CH_3Cl	CH_3CH_2Cl	$\Sigma(\%)^b$	
$(CH_3CH_2)_3PbCH_3$	0.553	0.396	4.29	0.164	0.0113	99	43
$(CH_3CH_2)_3PbCH_3$	0.553	0.429	4.29	0.187	0.0137	94	41
$(CH_3CH_2)_3PbCH_3$	0.553	0.860	0^d	0.123	0.288	96	1.3
$(CH_3CH_2)_3PbCH_3$	0.553	0.494	0^d	0.0681	0.155	91	1.3
$(CH_3CH_2)_2Pb(CH_3)_2$	0.535	0.405	4.29	0.179	0.0038	90	47
$CH_3CH_2Pb(CH_3)_3$	0.538	0.412	4.29	0.212	0.00154	100	46
$CH_3CH_2Pb(CH_3)_3$	0.202	1.03	0^d	0.0415	0.0049	91	2.8

^{a} Reactions carried out in 3 ml glacial acetic acid. ^{b} Based on stoichiometry in Eq. 13. Sum of CH_3Cl and CH_3CH_2-Cl yields. ^{c} Normalized for alkyl groups. ^{d} Heterogeneous.

The results in Table 2 show that cleavage of the CH_3-Pb bond by copper(II) chloride is much faster than that of the CH_3CH_2-Pb. Interestingly, the selectivity decreases drastically when the oxidative cleavage is carried out under heterogeneous conditions (*vide supra*). The latter make mechanistic deductions difficult and these results were not considered further.

The competitive chlorinolysis of methyl and ethyl groups in triethylmethyllead and trimethylethyllead is given in Table 3.

$$CH_3CH_2Pb(CH_3)_3 \xrightarrow{Cl_2} \begin{cases} CH_3CH_2Cl + (CH_3)_3PbCl \quad\quad\quad (14a) \\ \\ CH_3Cl + CH_3CH_2Pb(CH_3)_2Cl \quad (14b) \end{cases}$$

The different reactivity ratios in Table 3 from those listed in Table 2 indicates the molecular chlorine formed possibly by disproportionation (Eq. 15)

$$2\ CuCl_2 \rightleftharpoons 2\ CuCl + Cl_2 \tag{15}$$

is not responsible for the reactivity pattern obtained during cleavage of tetraalkyllead

TABLE 3

COMPETITIVE CHLORINOLYSIS OF TETRAALKYLLEAD[a]

R_3PbR' (mmoles)		Products (mmoles)		Reactivity[b] CH_3/CH_3CH_2
		CH_3Cl	CH_3CH_2Cl	
$(CH_3CH_2)_3PbCH_3$	0.553	0.214	0.101	6.4
$(CH_3CH_2)Pb(CH_3)_3$	0.202	0.0615	0.00182	11

[a] In 3 ml glacial acetic acid at 20°. [b] Corrected for number of alkyl groups, subject to errors discussed in the text.

with copper(II) chloride. However, an accurate determination of the relative reactivities of methyl and ethyl groups in chlorinolysis from this data is made difficult by the known facility with which chlorine replaces more than one alkyl group in tetra-alkyllead.

$$R_3PbCl + Cl_2 \rightarrow R_2PbCl_2 + RCl \tag{16}$$

Nonetheless, it is clear from the results in Tables 2 and 3, that methyl cleavage is always favored over ethyl cleavage during oxidation with copper(II) chloride or chlorinolysis.

For comparison, the relative rates of cleavage of CH_3-Pb and CH_3CH_2-Pb bonds were also determined by intermolecular competition. An excess of an equimolar mixture of tetramethyllead and tetraethyllead was treated with copper(II) chloride, and the methyl chloride and ethyl chloride determined (Table 4).

TABLE 4

INTERMOLECULAR COMPETITION IN THE OXIDATIVE CLEAVAGE OF METHYL AND ETHYL GROUPS FROM TETRAALKYLLEAD.

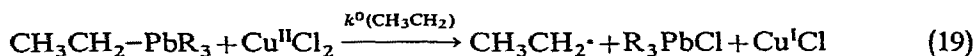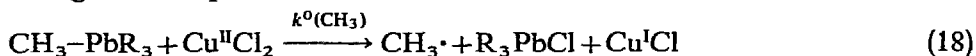| Organolead	Oxidant (mmoles)		Product (mmoles)		Reactivity CH_3/CH_3CH_2
			CH_3Cl	CH_3CH_2Cl	
$(CH_3)_4Pb + (CH_3CH_2)_4Pb$	$CuCl_2$ LiCl	0.430 4.29	0.175	0.036	4.9
$(CH_3)_4Pb + (CH_3CH_2)_4Pb$	Cl_2	0.176	0.095	0.085	1.1

Intrinsic rates of oxidative cleavage of methyl and ethyl groups in tetraalkyllead by copper(II) chloride

The relative rates of cleavage of methyl and ethyl groups determined by intermolecular and intramolecular competition are summarized in Table 5 for each methyl-/ethyl-lead combination.

The differences in the values of $k(CH_3)/k(CH_3CH_2)$ among various tetraalkyllead combinations in Table 5 reflect the influence of the departing trialkyllead moiety on the rate of oxidative cleavage. It was shown in the foregoing study[7] that the intrinsic value R_0 for the relative rates of methyl and ethyl cleavage under conditions of constant leaving group is given by:

$$R_0^4 = \prod_i \left(\frac{k(CH_3-Pb)}{k(CH_3CH_2-Pb)} \right)_i \tag{17}$$

where the right hand term is the product of all the reactivity ratios (intra- and inter-molecular) given in Table 5. We calculate, on such a basis, that a CH_3-Pb bond is oxidatively cleaved by copper(II) chloride 26 times faster than a CH_3CH_2-Pb bond under equivalent circumstances. In other words, $R_0 = k^0(CH_3)/k^0(CH_3CH_2) = 26$ for the process given in Eqs. 18 and 19.

$$CH_3-PbR_3 + Cu^{II}Cl_2 \xrightarrow{k^0(CH_3)} CH_3\cdot + R_3PbCl + Cu^ICl \tag{18}$$

$$CH_3CH_2-PbR_3 + Cu^{II}Cl_2 \xrightarrow{k^0(CH_3CH_2)} CH_3CH_2\cdot + R_3PbCl + Cu^ICl \tag{19}$$

where $PbR_3 = Pb(CH_3CH_2)_n(CH_3)_{3-n}$

The value of the reactivity parameter S (1.8) in Eq. 23 is typical of that for other electrophilic cleavage processes[7], and it is a measure of the susceptibility of the relative cleavage rates R_0 to substitution of an ethyl group for a methyl group in the departing trialkyllead cationic leaving group.

TABLE 5

RELATIVE RATES OF CH_3-Pb AND CH_3CH_2-Pb CLEAVAGE BY COPPER(II) CHLORIDE

Combination	$k(CH_3)/k(CH_3CH_2)$
$(CH_3)_4Pb + (CH_3CH_2)_4Pb$	4.9
$(CH_3)_3PbCH_2CH_3$	46
$(CH_3)_2Pb(CH_2CH_3)_2$	47[a]
$CH_3Pb(CH_2CH_3)_3$	42

[a] Results by H. Gardner.

Mass spectra of tetramethyllead and tetraethyllead

The examination of the mass spectra of tetraalkyllead compounds was under-

TABLE 6

VARIATIONS IN THE RELATIVE ABUNDANCES OF IONS IN THE MASS SPECTRA OF TETRA-ALKYLLEAD COMPOUNDS AND MIXTURES AT DIFFERENT IONIZING VOLTAGES
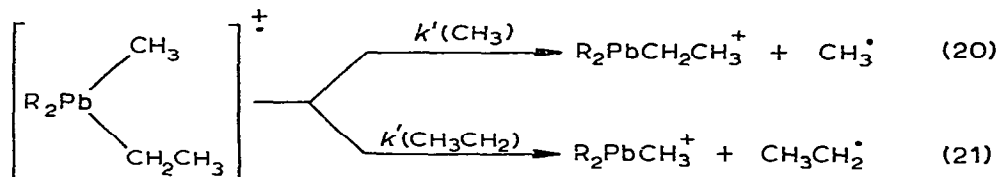
Tetraalkyllead compound or mixture	Relative abundance $\dfrac{P-CH_3}{P-CH_2CH_3}$[b]				
	Ionizing voltage (eV)[c]				
	70	45	25	20	15
$CH_3Pb(CH_2CH_3)_3$	0.21	0.21	0.12	0.08	0.05[d]
$(CH_3)_2Pb(CH_2CH_3)_2$	0.17	0.16	0.15	0.14	0.07
$(CH_3)_3Pb(CH_2CH_3)$	0.19	0.19	0.18	0.16	0.12[d]
$Pb(CH_3)_4 + Pb(CH_2CH_3)_4$[a]	0.66	0.61	0.64	0.67	0.60

[a] Equimolar mixture. [b] Ratio of methyl cleavage *vs* ethyl cleavage from parent molecular ion. Normalized for number of alkyl groups present. [c] Nominal values (uncalibrated). [d] At 17.5 eV.

taken in order to obtain information on the relative bond dissociation processes involving CH_3–Pb and CH_3CH_2–Pb scission[5]. The formation of the radical cation $R_4Pb^{\ddot{+}}$ in the step preceding fragmentation[8,9,10] allows mass spectroscopy to be a useful diagnostic tool for studying the oxidative cleavage of tetraalkyllead compounds involved in Scheme 1 (Eq. 4). The relative rates of cleavage of methyl and ethyl groups, for example, can be compared to the intensities of the peaks for $P-CH_3$ ($P=$ the parent molecule-ion) and $P-CH_2CH_3$.

Lead has three principal isotopes, with nominal masses of 206, 207 and 208. The intensities of the peaks corresponding to trialkyl–^{208}Pb resulting from the loss of one methyl group and the loss of one ethyl group are compared in Table 6, for three unsymmetrical tetraalkyllead compounds as a function of the electron energy.

We attribute the competitive cleavage to arise from selectivity in the fragmentation of the parent molecule-ion (Eqs. 20 and 21).

$$\left[R_2Pb\begin{matrix} \diagup CH_3 \\ \diagdown CH_2CH_3 \end{matrix} \right]^{\ddot{+}} \begin{matrix} \xrightarrow{k'(CH_3)} R_2PbCH_2CH_3^+ + CH_3^{\cdot} & (20) \\ \\ \xrightarrow{k'(CH_3CH_2)} R_2PbCH_3^+ + CH_3CH_2^{\cdot} & (21) \end{matrix}$$

Intermolecular competition in the fragmentation of CH_3–Pb and CH_3CH_2–Pb bonds was obtained from an equimolar mixture of tetramethyllead and tetraethyllead. The relative abundance of $P-CH_3$ and $P-CH_2CH_3$ is almost constant over the range of electron energies studied as also shown in Table 6.

The inherent differences between the formation of radical cations in the gas phase from highly energetic processes, and those carried out by chemical means in solution, however, make the quantitative treatment of competitive cleavage processes somewhat tenuous. Nonetheless, the qualitative trends in the data are clear. That is, ethyl cleavage of the parent molecule-ion predominates over methyl cleavage. A more complete discussion of the mass spectra is given in the Experimental Section.

Mechanism of the oxidative cleavage of tetraalkyllead by copper(II) chloride

The foregoing studies have clearly established two divergent patterns for the relative reactivity of a CH_3–Pb compared to a CH_3CH_2–Pb linkage in tetraalkyllead compounds during the reduction of copper(II) chloride compared to the mass spectral cracking pattern of the cation radical. Thus, the greater reactivity of methyl groups (by a factor of 26) during the reduction process follows the pattern previously established for electrophilic cleavages of alkyl–Pb bonds[7]. On the other hand, the fragmentation of the tetraalkyllead cation radical favors ethyl cleavage (by a factor of about 6, see Experimental Section) in accord with expectations based on differences in bond strengths of ethyl and methyl compounds. The CH_3/CH_3CH_2 selectivities in these two processes are listed in Table 7.

In both processes a trialkyllead cation(oid) is formed,

$$R_4Pb + Cu^{II}Cl_2 \xrightarrow{-(RCuCl_2^-)} R_3Pb^+ \xleftarrow{-(R^{\cdot})} R_4Pb^{\ddot{+}} \qquad (22a,b)$$
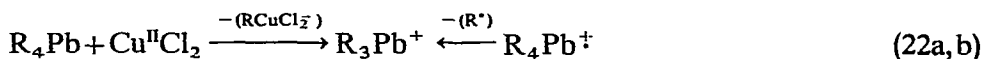
and the rates are influenced by the pattern of alkyl substitution on R_3Pb^+. If we apply

TABLE 7

INTRINSIC REACTIVITIES OF CH_3–Pb AND CH_3CH_2–Pb BONDS IN TETRAALKYLLEAD CATION RADICALS AND IN COPPER(II) REDUCTIONS

Processes	R_0	S
$Cu^{II}Cl_2$ Reduction	26	1.8
Mass Spectrum	0.25^a	0.72^a

[a] See Experimental.

the concept of competitive cleavage (Eqs. 20 and 21)[7], the effect of each ethyl group on Pb in accelerating the rate of cleavage is given by the constant multiplicative term S, in Eq. 23, where the term on the

$$S \cdot R_0 = [k(CH_3)/k(CH_3CH_2)]_{M_{4-n}E_n} \tag{23}$$

right side of the equation represents the relative rates of methyl and ethyl cleavage determined by intramolecular competition during the cleavage of $(CH_3)_{4-n}$Pb-$(CH_2CH_3)_n$. The value of S in Table 7 for the reduction of copper(II) chloride is similar to those of other electrophilic processes. However, S in the mass spectral fragmentation is less than that in the copper(II) reduction, as may be expected for a highly energetic process*.

We conclude from these selective studies that the alkylation Scheme 2 (Eq. 5) pertains to the facile reaction of tetraalkyllead compounds with copper(II) chloride. The formation of alkyl radicals during the reduction of copper(II) is then associated with the ready homolysis of an alkylcopper(II) intermediate in a subsequent step (Eq. 6).

EXPERIMENTAL

Materials

Anhydrous copper(II) chloride was prepared from the dihydrate by desiccation in a vacuum oven at 100°. Lithium chloride was anhydrous reagent grade material obtained from the Lithium Corporation of America. The other materials were the same as those used in the foregoing study[7]. Tetraethyllead was prepared from ethyl-magnesium bromide, plumbous chloride and ethyl iodide according to the procedure described by Gilman and Jones. Gas chromatographic analysis indicated the purity to be >98%.

Reaction of copper(II) chloride with tetraalkyllead

To a 25 ml flask containing weighed amounts of copper(II) chloride and lithium chloride, a known volume of acetic acid was added and the mixture stirred magnetically until homogeneous. The solution was equilibrated at 20°, and a measured amount of tetraalkyllead was added by means of a micro-hypodermic syringe. For kinetic runs, the marker gas, isobutane, was added prior to the addition of tetraalkyllead and the yields of alkyl chlorides determined by gas chromatography. The progress of the reaction was followed by periodically extracting small volumes of the gas (< 0.01%) from the flask for GLC analysis.

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* Differences in solvation between the gas phase and solution processes also preclude a quantitative comparison.

Analysis

Methyl and ethyl chlorides were determined quantitatively by gas chromatography using the internal standard (isobutane) method. A procedure was developed for the analysis of the alkyl chlorides by calibration under the same conditions as those used in the reactions. Analyses were also carried out with columns with liquid phases of different polarity (Porapak Q, FFAP and silicone). Analyses were generally reproducible to $\pm 2\%$.

The mass spectra were determined on a Varian MAT CH-7 mass spectrometer. The electron voltages are nominal values and uncorrected and are intended to be used for comparative purposes. The mass spectra of tetraethyllead were also compared on a AEI MS-9 at various electron energies and substantially the same results were obtained. We thank Mr. H. Gardner for carrying out this comparison.

Mass spectra of tetraalkyllead compounds

The mass spectral clastograms of tetramethyllead and tetraethyllead were generally in agreement with those in the literature[8,9,10]. The ion of greatest abundance in the mass spectrum of tetramethyllead at 70 eV is $(CH_3)_3Pb^+$ [8,9,10]. The parent molecule ion $(CH_3)_4Pb^+$ has a diminishingly low relative abundance. On the other hand, $CH_3CH_2Pb^+$ is the base peak* in the mass spectrum of tetraethyllead under the same conditions[9,10]. The other principal ions in the mass spectra of tetramethyllead
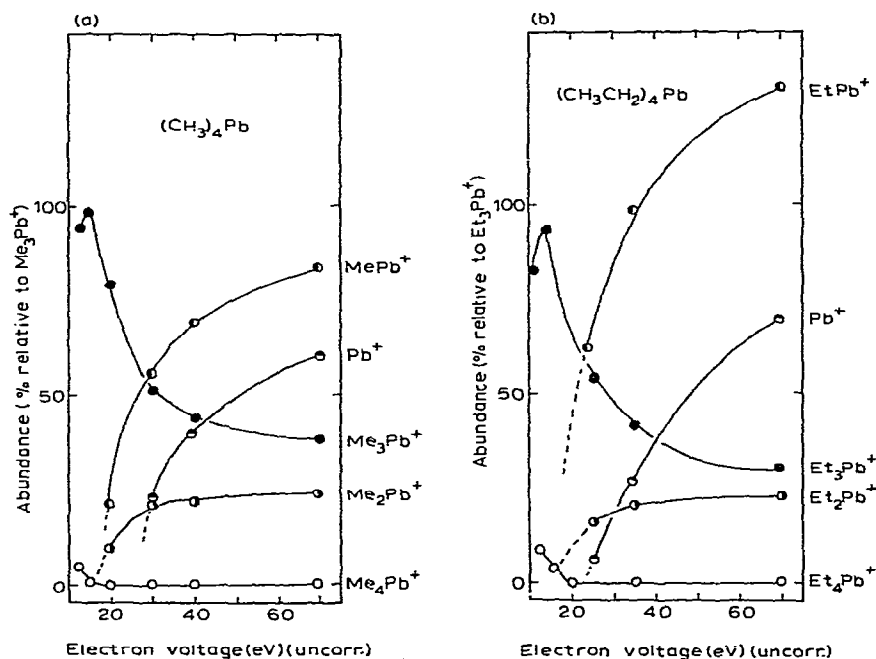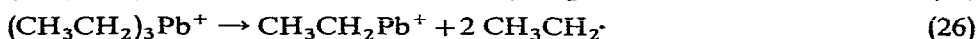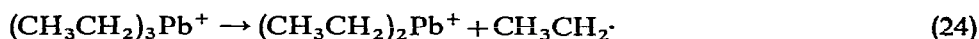

Fig. 1. Clastograms for (a) tetramethyllead and (b) tetraethyllead. R_3Pb^+ (●) plotted as % of total ion current. Others plotted as % of R_3Pb^+.

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* Elimination of ethylene units to form ethyllead hydrides is an energetically favored process at high ionizing voltages.

and tetraethyllead at 70 eV are shown in Figs. 1a and b, respectively.

Fragmentation processes (Eqs. 24–27) involving R–Pb scission have been assigned on the basis of metastable transitions in tetraethyllead and tetramethyllead[9], e.g.,

$$(CH_3CH_2)_3Pb^+ \rightarrow (CH_3CH_2)_2Pb^+ + CH_3CH_2 \cdot \tag{24}$$

$$(CH_3CH_2)_2Pb^+ \rightarrow CH_3CH_2Pb^+ + CH_3CH_2 \cdot \tag{25}$$

$$(CH_3CH_2)_3Pb^+ \rightarrow CH_3CH_2Pb^+ + 2\ CH_3CH_2 \cdot \tag{26}$$

$$(CH_3)_3Pb^+ \rightarrow CH_3Pb^+ + 2\ CH_3 \cdot \tag{27}$$

In the mass spectrum of tetramethyllead, the principal fragment ion $(CH_3)_3Pb^+$ is formed by loss of a methyl radical subsequent to ionization of the parent molecule, which has an ionization potential of 8 eV[8].

$$(CH_3)_4Pb \xrightarrow{8eV} (CH_3)_4Pb^+ \rightarrow (CH_3)_3Pb^+ + CH_3 \cdot \tag{28a,b}$$
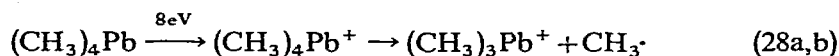
ΔH_f (kcal·mol^{-1})   32.6   217   206

The clastogram in Fig. 1a showing the variation of the abundance of each ion of the mass spectrum as a function of the electron energy (between the ionization potential and 70 eV) is in accord with this formulation[*]. Thus, the relative abundances of both the parent molecule ion and the first fragment increase with decreasing ionizing voltages and become the only species of importance at less than 15 eV. A similar pattern is established for tetraethyllead as shown in Fig. 1b. If the mass spectrum of an equimolar mixture of tetraethyllead and tetramethyllead is taken under these conditions, the relative abundances of $(CH_3CH_2)_3Pb^+$ and $(CH_3)_3Pb^+$ is a measure of the relative ionization efficiencies (cross sections) of tetraethyllead and tetramethyl-

TABLE 8

SELECTIVITY IN THE MASS SPECTRAL CRACKING PATTERN OF UNSYMMETRICAL TETRAALKYLLEAD AT 70 eV[a]

$(CH_3)_nPbR_{4-n}$	R	API[a]	$\dfrac{P-CH_3{}^b}{P-R}$	$\Delta H_f^0(R\cdot)^d$ (kcal/mole)	$D(R-H)^e$
$(CH_3)_3PbR$	CH_3	—	—	34.2 + 1	104.1
$(CH_3)_3PbR$	CH_3CH_2	1298	0.18$_5$ (0.19)	25 ± 1	97.4
$(CH_3)_3PbR$	$CH_3CH_2CH_2CH_2$	1300	0.23	22.6 + 2	99.3
$(CH_3)_3PbR$	$CH_3CH_2(CH_3)CH$	1301	0.098	13	95
$(CH_3)_3PbR$	$(CH_3)_3C$	1302	0^c	8.2 ± 1	92.4
$(CH_3)_2PbR_2$	CH_3CH_2	1299	0.18$_5$ (0.17)		
CH_3PbR_3	CH_3CH_2	1303	0.31 (0.21)		

[a] Selected Mass Spectral Data, American Petroleum Institute, Texas A and M University, College Station, Texas, 1969. [b] Corrected for the number of alkyl groups present. Number in parentheses, this work. [c] No peak for loss of methyl reported. [d] Heat of formation of R· radical (D. M. Golden and S. W. Benson, Chem. Rev., 69 (1969) 125.) [e] Bond dissociation energy of R–H. See ref. 13.

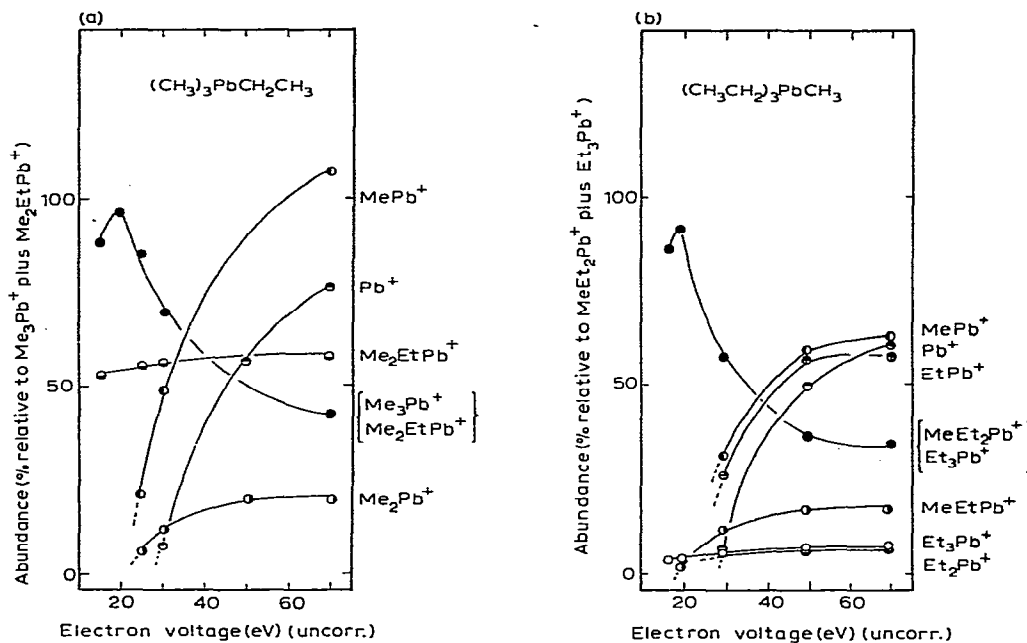[*] For mass-spectral studies of other alkylmetals see ref. 11.

Fig. 2. Clastograms for (a) $(CH_3)_3PbCH_2CH_3$ and (b) $CH_3Pb(CH_2CH_3)_3$. First-daughter ions (●) in brackets plotted as % of total ion current; others plotted as % of first-daughter ions.

lead, respectively. Interestingly, this ratio increases only slowly with increasing ionizing voltages. The relative abundances of the daughter ions also vary little under the same conditions.

Mass spectra of unsymmetrical tetraalkyllead compounds

Intramolecular competition in the fragmentation of alkyl–Pb bonds in unsymmetrical tetraalkyllead compounds by electron impact at 70 eV is collected in Table 8[12]. The trend is clearly established for selective cleavage to occur with increasing substitution at the α-carbon, and is in accord with the bond dissociation energies expected for the CH_3–Pb *versus* the CH_3CH_2–Pb bonds in tetraalkyllead compounds. These bond strengths can be estimated from the bond dissociation energies in tetramethyllead (36.5 ± 1 kcal·mole^{-1}) and tetraethyllead (30.8 ± 2 kcal·mole^{-1})[8b]. The data for the stabilities of the alkyl radicals are also collected in Table 8. The preferential fragmentation of an ethyl group relative to a methyl group in an intramolecular competition is not highly sensitive to the substitution pattern in the tetraalkyllead compound (Table 8, column 4). The selectivity also remains relatively invariant with the ionizing voltage as shown in the clastograms for trimethylethyllead and triethylmethyllead in Fig. 2a and b. Extrapolation to the ionization potentials of the organolead compounds was not possible with our instrumentation.

The data clearly show, however, that ethyl cleavage is favored over methyl cleavage by a factor of 5–6 in trimethylethyllead and triethylmethyllead under conditions (< 20 eV) in which secondary fragmentations are suppressed. The relative rates of the two modes of fragmentation in Eqs. 20 and 21 should be dependent also on the

stability of the trialkyllead cation, (i.e., the substitution pattern of alkyl groups remaining on the lead nucleus after scission) like that found in the electrophilic cleavage described earlier (cf. Table 5 and ref. 7).

Under these circumstances, the intrinsic selectivity in the fragmentation of a CH_3–Pb bond compared to a CH_3CH_2–Pb bond (under conditions in which the same trialkyllead cation departs) can only be obtained from absolute rate measurements. However, in the absence of experimental techniques for the determination of the latter, we resort to an (tenuous) approximation in which we assume that the intermolecular results in Table 6 parallel the relative rates of fragmentation of the molecule-ions of tetramethyl- and tetraethyl-lead. Equation (29) is then applicable, from which the intrinsic selectivity R_0' is obtained for the fragmentation of the radical-ion from the data in Table 6.

$$R_0' = k^{0\prime}(CH_3)/k^{0\prime}(CH_3CH_2) = (0.6)(0.19)(0.17)(0.21)^{\frac{1}{2}} = 0.25 \qquad (29)$$

The value of R_0' obtained in this manner, leads to a value for S of 0.72.

Although it is interesting to obtain estimates of the relative rates of alkyl cleavage in the tetraalkyllead cation by the foregoing analysis, they must be accepted with reservations since there are serious assumptions made in their derivation.

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