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SELECTIVITY FACTORS IN THE ELECTROPHILIC CLEAVAGES OF TETRAALKYLLEAD COMPOUNDS

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SUMMARY

The rates of electrophilic cleavage of CH_3–Pb and CH_3CH_2–Pb bonds in various methyl/ethyl tetraalkyllead compounds are examined. The reactivity of a given alkyl–Pb linkage is highly dependent on the substitution pattern on the cationic trialkyllead leaving group, in which an ethyl group is approximately twice as effective as a methyl group in enhancing the rate. A method is developed for obtaining the relative reactivity of CH_3–Pb and CH_3CH_2–Pb bonds to electrophilic cleavage under conditions of constant leaving group from competition studies.

INTRODUCTION

The cleavage of alkyl–metal bonds is important to an understanding of the variety of alkylation reactions occurring in organometallic systems. Foremost among these is the mechanism of electrophilic processes, which have been studied extensively with metal alkyls, especially mercury and tin[1–7].

The reactivity of a particular alkyl–metal bond to electrophilic cleavage depends on the electrophile, the alkyl group, the metal and other ligands associated with the metal. Although the last factor has been recognized as significant in the reactivity of organometals[3], its importance has not been assessed quantitatively.

Tetraalkyllead compounds possess a number of desired qualitites for the quantitative study of the reactivity of the alkyl–Pb linkage in electrophilic reactions[8]. In this report we have used the complete set of tetraalkyllead methyl/ethyl derivatives to show the quantitative relationship between the reactivities of CH_3–Pb and CH_3CH_2–Pb bonds and the substitution pattern on the lead leaving group.

RESULTS

Acetolysis of tetramethyl- and tetraethyl-lead

Solutions of tetramethyllead and tetraethyllead in glacial acetic acid at 20° afforded methane and ethane, respectively, according to the following stoichiometry:

$$R_4Pb + HOAc \longrightarrow R_3PbOAc + RH \qquad (1)$$

$(R = CH_3, CH_3CH_2)$

The product of alkane could be monitored continuously and quantitatively by gas chromatography using the internal standard method.

The formation of methane and ethane followed first order kinetics at low conversions ($< 10\%$) of the tetraalkyllead precursor[9]. The pseudo first order rate constants k'_R given in Table 1 are in good agreement with those obtained by Robinson under slightly different conditions[10].

$$+\frac{d(RH)}{dt} = k'_R\,(R_4Pb)$$

$$\text{where} \qquad k'_R = k_R\,(HOAc) \tag{2}$$

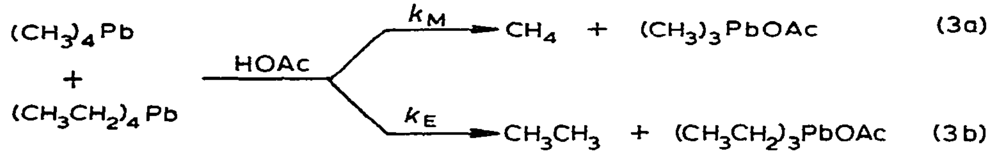
TABLE 1

ACETOLYSIS OF TETRAMETHYL- AND TETRAETHYL-LEAD AT 20°

Alkyllead compound	*Conc. (M)*	*Alkane RH*	*Rate constant, k'_R (10^6 sec^{-1})[a]*	k_M/k_E
$(CH_3)_4Pb$	0.10	CH_4	7.3	1.5
$(CH_3CH_2)_4Pb$	0.067–0.10	CH_3CH_3	4.9	
$(CH_3)_4Pb$ +	0.053–0.10	CH_4 +	7.2	1.5
$(CH_3CH_2)_4Pb$	0.038–0.10	CH_3CH_3	4.7	
$(CH_3)_3PbOAc$	0.10	CH_4	0.56	—
$(CH_3CH_2)_3PbOAc$	0.10	CH_3CH_3	4.6	—

[a] An average of at least 3 determinations. The standard deviation is $\leqslant 2\%$ of the observed rate constant.

Acetolysis of mixtures of tetramethyllead and tetraethyllead were also carried out in order to test for possible difficulties associated with trace metal and other adventitious catalysis.



The first order rate constants (Table 1) obtained under these conditions were in accord with those obtained separately. These results also indicate that redistribution reactions (Eqs. 4 and 5) or disproportionation processes (Eq. 6) were not significant under reaction conditions (*vide infra*).

$$(CH_3)_4Pb + (CH_3CH_2)_4Pb \rightleftharpoons (CH_3)_{4-n}(CH_3CH_2)_nPb + (CH_3CH_2)_{4-n}(CH_3)_nPb \tag{4}$$

$$(CH_3)_3Pb^+ + (CH_3CH_2)_4Pb \rightleftharpoons (CH_3)_3(CH_3CH_2)Pb + (CH_3CH_2)_3Pb^+,\ \text{etc.} \tag{5}$$

$$(CH_3)_3Pb^+ + (CH_3CH_2)_3Pb^+ \rightleftharpoons (CH_3)_3(CH_3CH_2)Pb + (CH_3CH_2)_2Pb^{2+},\ \text{etc.} \tag{6}$$

$n = 3, 2, 1$

Acetolysis of mixed methyl- and ethyl-lead compounds

Trimethylethyllead (M_3E) and triethylmethyllead (E_3M) were prepared in high purity by the reaction of the corresponding trialkyllead acetates with Grignard reagents.

$$R_3PbOAc + R'MgBr \rightarrow R_3PbR' + MgBr(OAc) \tag{7}$$

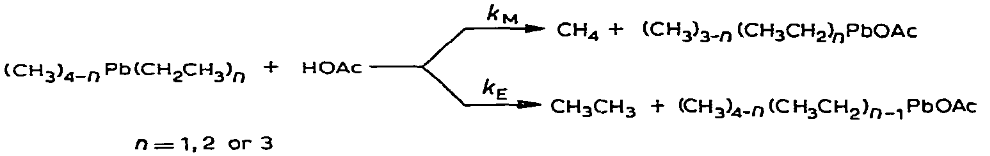
Other procedures examined were less suitable since the desired alkyllead compounds were adulterated by products of redistribution[11]. Dimethyldiethyllead (M_2E_2) was prepared from methylmagnesium iodide and diethyllead dibromide which was generated by controlled brominolysis of tetraethyllead. We were less successful in

$$(CH_3CH_2)_2PbBr_2 + 2CH_3MgI \rightarrow (CH_3CH_2)_2Pb(CH_3)_2 + 2MgIBr$$

preparing diethyllead dichloride by protonolysis with hydrogen chloride or by chlorinolysis[12].

The purity of all of these tetraalkyllead compounds were determined by gas chromatographic and mass spectral analyses. The five methyl and ethyl organolead compounds were separated on a polyethyleneglycol–Quadrol column[13]. Furthermore, a mixture of pure tetraethyllead and tetramethyllead did not undergo redistibution on this column. Examination of the mass spectra showed no indication of the presence of ions other than those derived from the parent ($R_{4-n}R'_nPb$) and first daughters. However, the low abundances of the parent molecule-ion even at very low ionizing voltages makes this technique somewhat wanting as an accurate method of analysis for these compounds.

The acetolyses of M_3E, M_2E_2 and ME_3 were carried out using the same procedure employed for tetramethyl- and tetraethyl-lead. Although the mixtures of trialkyllead acetates were not quantitatively analyzed further, the results with trimethyl- and triethyl-lead acetates separately (see Table 1) indicated that they could not have contributed significantly to the amounts of RH formed if the protonolysis was carried out to low conversion.



$$(CH_3)_{4-n}Pb(CH_2CH_3)_n + HOAc \xrightarrow{k_M} CH_4 + (CH_3)_{3-n}(CH_3CH_2)_nPbOAc \tag{8a}$$

$$(CH_3)_{4-n}Pb(CH_2CH_3)_n + HOAc \xrightarrow{k_E} CH_3CH_3 + (CH_3)_{4-n}(CH_3CH_2)_{n-1}PbOAc \tag{8b}$$

$n = 1, 2$ or 3

The rates of formation of methane and ethane each followed first order kinetics to low conversions ($< 10\%$). The pseudo first order rate constants k_M and k_E in Eq. 8 for the cleavage of methyl and ethyl groups, respectively, from M_3E, M_2E_2, and ME_3 are listed in Table 2.

Protonolysis of tetraalkyllead compounds with trifluoromethanesulfonic acid

Trifluoromethanesulfonic (triflic) acid is one of the strongest acids available[14], and it is an ideal protonic source since it is nonoxidizing, can be made anhydrous and the triflate (OTf) anion is poorly coordinated to many metal nuclei[15]. Triflic acid reacted rapidly with tetramethyl- and tetraethyl-lead in acetic acid according to Eq. 9.

TABLE 2

ACETOLYSIS OF MIXED METHYL–ETHYL-LEAD COMPOUNDS AT 20°

$R_{4-n}R'_nPb$	Conc. (M)	RH	(Yield)[b]	Rate constant[c] [k_R, 10^6 sec^{-1}]	k_M/k_E[a]
$(CH_3)_3PbCH_2CH_3$	0.083–0.097	CH_4	(97.9)	10	16
		CH_3CH_3	(2.1)	0.21	
$(CH_3)_2Pb(CH_2CH_3)_2$	0.078–0.12	CH_4	(93.6)	13	15
		CH_3CH_3	(6.4)	0.88	
$CH_3Pb(CH_2CH_3)_3$	0.076–0.093	CH_4	(84.0)	11	16
		CH_3CH_3	(16.0)	2.1	

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[a] Normalized for number of alkyl groups in reactant. [b] Relative yields. [c] An average of at least 3 determinations. Standard deviation is < 3% in rate constant.

$$R_4Pb + HOTf \xrightarrow[HOAc]{} R_3PbOTf + RH \qquad (9)$$

$$R = CH_3,\ CH_3CH_2$$

The protonolysis occurred at rates too fast to measure accurately at 20° by our analytical procedures. In the presence of excess tetraalkyllead, reaction 9 and the much slower acetolysis reaction (Eq. 1) occurred concurrently. The two processes could be readily separated by extrapolation of the acetolysis reaction to zero time. The half-life of triflic acid was estimated after the correction for the acetolysis reaction. The pseudo first order rate constant k_H in Eq. 10 for its disappearance obtained in this manner is listed in Table 3.

$$-\frac{1}{[R_4Pb]_0}\frac{d(R_4Pb)}{dt} = k_H(HOTf) \qquad (10)$$

TABLE 3

PROTONOLYSIS OF TETRAALKYLLEAD COMPOUNDS WITH TRIFLIC ACID.

$R_{4-n}R'_nPb$	Conc. (M)	RH	Half-life[a] or yield (%)[c]	$\frac{k_H(Me)}{k_H(Et)}$[b,d,e]
$(CH_3)_4Pb$		CH_4	< 10 sec	—
$(CH_3CH_2)_4Pb$		CH_3CH_3	~30 sec	—
$(CH_3)_4Pb +$	0.10–0.20	CH_4	89.5	8.5[d,e]
$(CH_3CH_2)_4Pb$	0.10–0.20	CH_3CH_3	10.5	
$(CH_3)_3PbCH_2CH_3$	0.20	CH_4	96.6	81[d,e]
		CH_3CH_3	0.41	
$(CH_3)_2Pb(CH_2CH_3)_2$	0.20	CH_4	98.8	84[d,e]
		CH_3CH_3	1.2	
$CH_3Pb(CH_2CH_3)_3$	0.20	CH_4	96.7	89[d,e]
		CH_3CH_3	3.3	

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[a] Corrected for acetolysis reaction. [b] Normalized for number of alkyl groups in reactant. [c] Relative yields. [d] In 3 ml HOAc containing 0.068 mmol triflic acid. [e] An average of at least 2 determinations, estimated reproducibility, ±10%.

The relative rates of protonolysis of tetramethyl- and tetraethyl-lead by triflic acid was determined by intermolecular competition in the protonolysis of an excess of a mixture of tetramethyl- and tetraethyl-lead with triflic acid in acetic acid solutions. The relative yields of methane and ethane were normalized by the composition of the mixture of tetraalkyllead compounds employed.

$$\begin{matrix} (CH_3)_4Pb \\ + \\ (CH_3CH_2)_4Pb \end{matrix} \xrightarrow{HOTf} \begin{cases} CH_4 + (CH_3)_3PbOTf & (11a) \\ CH_3CH_3 + (CH_3CH_2)_3PbOTf & (11b) \end{cases}$$

The relative rates of protonolysis of tetramethyllead and tetraethyllead obtained in this manner are listed in Table 3.

Intramolecular competition in the protonolysis of methyl and ethyl groups bonded to lead were also studied with M_3E, M_2E_2, and ME_3 using the same procedure described above. As shown in Table 3, the selectivity in the relative intramolecular rates of protonolysis are approximately ten times larger than the intermolecular rates. It should be emphasized that the reliability of the relative rates measured in this manner are subject to errors, which are magnified in proportion to the magnitude of the ratio due to the difficulty in measuring (by gas chromatography)small amounts of one alkane component. In addition, the relative rates are very sensitive to the purity of the tetraalkyllead compound and to the triflic acid concentration.

$$\begin{matrix} (CH_3)_{4-n}Pb(CH_2CH_3)_n \\ n = 1, 2 \text{ or } 3 \end{matrix} \xrightarrow{HOTf} \begin{cases} CH_4 + (CH_3CH_2)_n(CH_3)_{3-n}PbOTf & (12a) \\ CH_3CH_3 + (CH_3)_{4-n}(CH_2CH_3)_{n-1}PbOTf & (12b) \end{cases}$$

Electrophilic cleavage of tetraalkyllead compounds by copper(I)

The decomposition of tetraethyllead in acetic acid solutions is markedly catalyzed by various copper(I) complexes, and the stoichiometry in Eq. 1 is the same as that described for acetolysis. Previous studies[9] showed that the catalysis by copper-(I) acetate proceeds via the following mechanism in which the step (Eq. 13) involving alkylation of copper(I) is rate determining.

$$R_4Pb + Cu^IOAc \xrightarrow{k_c} R_3PbOAc + RCu^I \qquad (13)$$

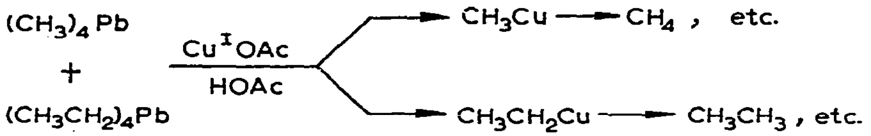
$$RCu^I + HOAc \rightarrow RH + Cu^IOAc, \text{ etc.} \qquad (14)$$

The kinetics of the copper-catalyzed decomposition of tetraethyllead in acetic acid is described by

$$\frac{d(EtH)}{dt} = k_R'(Et_4Pb) + k_c[CuOAc][Et_4Pb]$$

where k_R' and k_c represent the pseudo first order rate constant for acetolysis and the second order rate constant for the copper-catalyzed process, respectively.

The formation of methane and ethane from the copper catalyzed decomposition of a mixture of tetramethyllead and tetraethyllead, respectively, affords a measure of the relative rates of electrophilic cleavage of these compounds by copper(I).



(15a)

(15b)

The results obtained from an intermolecular competition are listed in Table 4.

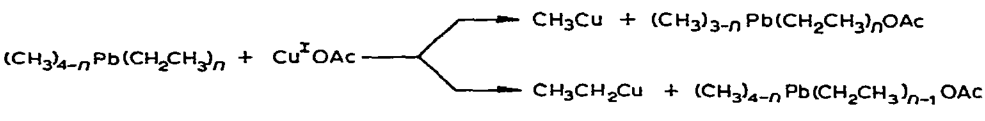
TABLE 4

ELECTROPHILIC CLEAVAGE OF TETRAALKYLLEAD COMPOUNDS BY COPPER(I)

$R_{4-n}R'_nPb$	*Conc.*[a] *(M)*	*RH*	*Relative Yield (%)*	*$k_c(Me)/k_c(Et)$*
$(CH_3)_4Pb$ +	0.17	CH_4	89.6	8.8
$(CH_3CH_2)_4Pb$	0.17	CH_3CH_3	10.4	
$(CH_3)_3PbCH_2CH_3$	0.20–0.34	CH_4	99.7_5	130[b]
		CH_3CH_3	0.2_5	
$(CH_3)_2Pb(CH_2CH_3)_2$	0.20–0.24	CH_4	99.0_6	100[b]
		CH_3CH_3	0.9_4	
$CH_3Pb(CH_2CH_3)_3$	0.20–0.27	CH_4	96.7_7	90[b]
		CH_3CH_3	3.2_3	

[a] Determined in a saturated solution of CuOAc in 3 ml of acetic acid. [b] An average of 2 determinations. Estimated reproducibility, ±15%.

The relative rates of electrophilic cleavage were also determined by intramolecular competition employing the mixed alkyllead compounds, M_3E, M_2E_2, and ME_3, *e.g.*,



(16a)

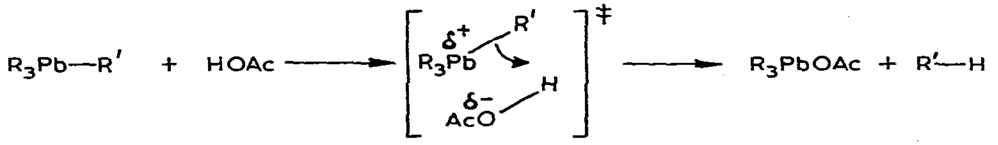
(16b)

The selective cleavage of a methyl group as shown in Table 4 occurs almost to the exclusion of ethyl cleavage.

DISCUSSION

Acetolysis of the alkyl–lead bond

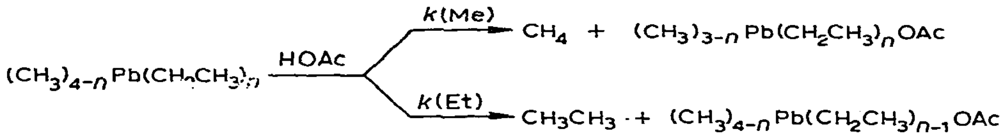
The acetolysis of tetraalkyllead can be considered as an electrophilic cleavage of the alkyl–lead linkage as follows:



(17)

The results of the intermolecular and intramolecular competitions listed in Tables 1 and 2 show a large discrepancy in the relative rates of cleavage of a methyl–lead compared to an ethyl–lead bond. The absolute rates of cleavage of a CH_3–Pb or CH_3CH_2–Pb bond by acetic acid also varies considerably with the constitution of the tetraalkyllead compound. The results listed in Table 5 for the rates of acetolysis have been normalized for the number of methyl and ethyl groups present in the reactant.

The trends in Table 5 indicate that the rates of acetolysis of a particular alkyl–Pb bond increases as the methyl groups are successively replaced with ethyl groups in the trialkyllead leaving group. Thus, the reactivity of an ethyl–lead bond is the greatest in tetraethyllead and the least in ethyltrimethyllead. Similarly, the CH_3–Pb bond is the least reactive in tetramethyllead and most reactive in methyltriethyllead. In fact, a constant multiplicative factor S separates the rates of acetolysis between any two contiguous members in the series $(CH_3)_{4-n}Pb(CH_2CH_3)_n$ (where $n = 0, 1, 2, 3, 4$) as listed in the fifth column of Table 5.



(18)

(19)

The value of S is essentially constant at 1.84 for methyl cleavage (Eq. 18) and 1.75 for ethyl cleavage (Eq. 19) as a comparison between the figures in column 5

TABLE 5

RATES OF ACETOLYSIS OF CH_3–Pb AND CH_3CH_2–Pb BONDS AT 20°

Bond *R–Pb*	*Compound* *$(CH_3)_{4-n}Pb(CH_2CH_3)_n$*	*Rate Constant* (10^6 *sec*$^{-1}$)		*Relative rate*[b]	
		k	*k′*[a]	*Found*	*Calcd.*[c]
CH_3–Pb	$(CH_3)_4Pb$	7.3	1.8	1.00	1.00
CH_3–Pb	$(CH_3)_3PbCH_2CH_3$	10	3.3	1.8	1.8
CH_3–Pb	$(CH_3)_2Pb(CH_2CH_3)_2$	13	6.5	3.6	3.4
CH_3–Pb	$CH_3Pb(CH_2CH_3)_3$	11	11	6.1	6.2
CH_3CH_2–Pb	$(CH_3CH_2)_4Pb$	4.9	1.2	1.00	1.00
CH_3CH_2–Pb	$(CH_3CH_2)_3PbCH_3$	2.1	0.70	0.56	0.57
CH_3CH_2–Pb	$(CH_3CH_2)_2Pb(CH_3)_2$	0.88	0.44	0.35	0.33
CH_3CH_2–Pb	$CH_3CH_2Pb(CH_3)_3$	0.21	0.21	0.17	0.18

[a] Normalized for each alkyl group. [b] Per alkyl group based on $R_4Pb = 1.00$. [c] Constant multiplicative factor of 1.84 for CH_3–Pb and 1.75 for CH_3CH_2–Pb.

and 6 of Table 5 indicates. This correlation represents a linear free energy relationship in which the factor S is the sensitivity of the particular alkyl–Pb cleavage to methyl or ethyl substitution in the departing trialkylplumbonium ion, *i.e.*:

$$k(\mathrm{R}) = k_0(\mathrm{R})S^m = k_0(\mathrm{R})\exp(m\Delta\Delta F^{\ddagger}/RT) \qquad (20)$$

$$\mathrm{R}=\mathrm{CH_3},\ \mathrm{CH_3CH_2}$$

where $k_0(\mathrm{R})$ represents the cleavage rate of R_4Pb, m the number of ethyl groups [$m=n$ in Eq. 18 and $m=n-1$ in Eq. 19] and $\Delta\Delta F^{\ddagger}$ the change in the free energy of activation as a result of an ethyl substitution. In particular, the replacement of each methyl group by an ethyl group leads to doubling the rate of acetolysis or lowering the free energy of the transition state by about 0.4 $\mathrm{kcal \cdot mole^{-1}}$.

The correlation of rates (with ethyl substitution) in Eq. 20 is contrary to that expected if steric effects were sizeable in the transition state of this process. Thus, the effect of the different alkyl groups is largely electronic in origin.

The ability of ethyl groups to stabilize the incipient trialkylplumbonium ion in preference to methyl groups is also indicated by comparison with the carbon analog, in which the first order solvolysis (S_N1) of t-alkyl halides listed in Table 6[16] represents a model (Eq. 21) for comparative purposes.

$$\mathrm{R_3C{-}Cl} \rightarrow [\mathrm{R_3C^{\delta+}}\ldots\mathrm{Cl^{\delta-}}]^{\ddagger} \rightarrow \mathrm{R_3C^+} + \mathrm{Cl^-},\ \text{etc.} \qquad (21)$$

TABLE 6

SOLVOLYSIS OF TERTIARY ALKYL CHLORIDES IN 80% AQUEOUS ETHANOL AT 25°

Alkyl chloride	*Rate constant* (h^{-1})	*Relative rate*	
		Found	*Calcd.*
$(CH_3)_3C{-}Cl$	0.033	1.00	1.00
$(CH_3)_2(CH_3CH_2)C{-}Cl$	0.055	1.67	1.67
$CH_3(CH_3CH_2)_2C{-}Cl$	0.086	2.61	2.59
$(CH_3CH_2)_3C{-}Cl$	0.099	3.00	4.65

The replacement of one methyl group in t-butyl chloride by an ethyl group increases the rate constant by a factor of 1.67. A second ethyl group increases the rate constant further by a factor of 2.59 or 1.67^2. However, the last ethyl group does not contribute as effectively as the others, probably due to steric crowding, which is not as serious a factor in the larger lead nucleus. The preferential stabilization of cations by an ethyl compared to a methyl group can be attributed largely to differences in the inductive effect since it is highly dependent on conformation[17].

The high sensitivity of the alkyl–lead bond to the presence of other groups on the lead nucleus does complicate a mechanistic analysis of the acetolysis process. However, the relative reactivity of methyl and ethyl groups can be compared under conditions of constant leaving group (R_3Pb^+). For example, we find that the ratios of rates of methyl and ethyl cleavage obtained under these circumstances are more or less invariant as shown in Table 7. Such a result is consistent with the previously proposed formulation which suggested that the differences between methyl and ethyl

TABLE 7

RELATIVE RATES OF ACETOLYSIS OF CH_3–Pb AND CH_3CH_2–Pb BONDS UNDER CONDITIONS OF CONSTANT LEAVING GROUP

Compound (pair)	*Rate constant*[a] *(sec^{-1})*	*k(Me)/k(Et)*[b]
CH_3–$Pb(CH_3)_3$	1.8×10^{-6}	8.6
CH_3CH_2–$Pb(CH_3)_3$	2.1×10^{-7}	
CH_3–$Pb(CH_3)(CH_2CH_3)_2$	6.5×10^{-6}	9.3
CH_3CH_2–$Pb(CH_3)(CH_2CH_3)_2$	7.0×10^{-7}	
CH_3–$Pb(CH_3)_2(CH_2CH_3)$	3.3×10^{-6}	7.5
CH_3CH_2–$Pb(CH_3)_2(CH_2CH_3)$	4.4×10^{-7}	
CH_3–$Pb(CH_2CH_3)_3$	1.1×10^{-5}	9.2
CH_3CH_2–$Pb(CH_2CH_3)_3$	1.2×10^{-6}	

[a] Rate per alkyl group. [b] Rate ratio per alkyl group.

groups on the incipient R_3Pb^+ is largely electronic in origin. Under these circumstances the logarithms of the relative rate constants k(Me)/k(Et) reflect differences in free energy terms (*cf.* Eq. 20) which largely cancel each other*. Such an additivity is not expected if steric effects are important.

For the relative rates of acetolysis of CH_3–Pb and CH_3CH_2–Pb bonds under equivalent circumstances we let,

$$R_0 = \frac{k[CH_3\text{–}PbM_3]}{k[CH_3CH_2\text{–}PbM_3]} \cong \frac{k[CH_3\text{–}PbM_2E]}{k[CH_3CH_2\text{–}PbM_2E]} \cong \frac{k[CH_3\text{–}PbME_2]}{k[CH_3CH_2\text{–}PbME_2]}$$

$$\cong \frac{k[CH_3\text{–}PbE_3]}{k[CH_3CH_2\text{–}PbE_3]} \cong 8.6\ (\text{avg.}) \qquad (22)$$

The rate ratio R_0 represented in Eq. 22 measures the intrinsic difference between the rate of CH_3–Pb and CH_3CH_2–Pb cleavage.

The values of R_0 can also be obtained under conditions in which the absolute rate constants k(R) are unknown or unobtainable (*e.g.*, due to reactions too fast to measure). Thus, the following four relative rates can be obtained from studies involving three intramolecular comparisons together with one intermolecular competition listed in Table 8.

It can be readily shown from Eq. 22 and Table 8 that,

$$(R(M_4E_4))(R(ME_3))(R(M_2E_2))(R(M_3E)) = R_0^4 \qquad (23)$$

The value of R_0 for the acetolysis of methylethyllead compounds listed in Table 8 computed in this manner is $[(15)(16)(16)(1.5)]^{\frac{1}{4}} = 8.7$, which is in good agreement with the value obtained from the absolute rate measurements in Table 7.

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* Provided that no wide variation exists in the degree of bond breaking in the transition states of CH_3–Pb and CH_3CH_2–Pb cleavages. The assumption does not necessarily apply to other alkyl groups, particularly those with α-branching.

TABLE 8

INTERMOLECULAR AND INTRAMOLECULAR RELATIVE RATES OF ACETOLYSIS OF CH_3–Pb AND CH_3CH_2–Pb BONDS

Compound	*Competition*	*Rate constant (ratio)*	*R*
$(CH_3)_4Pb+(CH_3CH_2)_4Pb$	Intermolecular	$\frac{k(CH_3\text{–}PbMe_3)}{k(CH_3CH_2\text{–}PbE_3)} = R(M_4E_4)$	1.5
$CH_3Pb(CH_2CH_3)_3$	Intramolecular	$\frac{k(CH_3\text{–}PbE_3)}{k(CH_3CH_2\text{–}PbME_2)} = R(ME_3)$	16
$(CH_3)_2Pb(CH_2CH_3)_2$	Intramolecular	$\frac{k(CH_3\text{–}PbME_2)}{k(CHCH_2PbM_2E)} = R(M_2E_2)$	15
$(CH_3)_3PbCH_2CH_3$	Intramolecular	$\frac{k(CH_3\text{–}PbM_2E)}{k(CH_3CH_2\text{–}PbM_3)} = R(M_3E)$	16
		$\frac{k(CH_3\text{–}PbR_3)}{k(CH_3CH_2\text{–}PbR_3)} = R_0$	8.7

TABLE 9

RELATIVE RATES OF PROTONOLYSIS (TRIFLIC ACID) AND ELECTROPHILIC CLEAVAGE BY COPPER(I) OF CH_3–Pb AND CH_3CH_2–Pb BONDS

R_4Pb	*Competition*	*Relative rates of cleavage*	
		HOTf	*Cu^IOAc*
$(CH_3)_4Pb+(CH_3CH_2)_4Pb$	Intermolecular	8.5	8.8
$(CH_3)_3PbCH_2CH_3$	Intramolecular	81	130
$(CH_3)_2Pb(CH_2CH_3)_2$	Intramolecular	84	100
$CH_3Pb(CH_2CH_3)_3$	Intramolecular	89	90
R_0		48	~56

Intrinsic rates of cleavage of tetraalkyllead compounds by triflic acid and copper(I) acetate.

The procedure outlined in Eq. 23 can also be used to obtain intrinsic values for the relative rates of cleavage R_0 for the protonolysis of methyl–lead and ethyl–lead bonds, since the rate of reaction with triflic acid (Eq. 9) is too fast to measure accurately. The same method can be applied to the electrophilic cleavage of tetraalkyllead by copper(I) during the catalyzed acetolysis (Eqs. 13 and 14). Both results are included in Table 9.

Selectivity factors in the electrophilic cleavage of tetraalkyllead compounds

Acetic acid, triflic acid and copper(I) acetate represent three electrophiles with different structural and chemical properties. Reactivity parameters for the re-

TABLE 10

INTRINSIC REACTIVITIES OF CH_3–Pb AND CH_3CH_2–Pb BOND IN ELECTROPHILIC CLEAVAGES

Electrophile	*Rate constant*[a] (*l·mol^{-1}·sec^{-1}*)	R_0[b]	S[c]
HOAc	2.8×10^{-5}	8.7	1.80
HOTf	$>2 \times 10^{-1}$	48	1.77
Cu^IOAc	3.3×10^{-2}[d]	~56	1.85

[a] For reaction of tetraethyllead. [b] See Eq. 23. [c] See Eq. 20 and/or 24. [d] See ref. 9.

lative rates of CH_3–Pb and CH_3CH_2–Pb cleavage are summarized in Table 10 for these electrophiles.

The effect of each ethyl group (on the departing trialkyllead cation) in accelerating the rate of electrophilic cleavage is obtained from absolute rate measurements and given by the constant multiplicative factor S in Eq. 20. In the absence of kinetic data, the value of S can also be obtained from competition studies using the relationship:

$$S \cdot R_0 = [k(CH_3)/k(CH_3CH_2)]_{M_{4-n}E_n} \qquad (24)$$

where the term in brackets is the relative rates of cleavage of methyl and ethyl groups in $(CH_3)_{4-n}Pb(CH_2CH_3)_n$ by intramolecular competition. The corollary for intermolecular competition is given by:

$$S^{-3} \cdot R_0 = [k(CH_3)/k(CH_3CH_2)]_{M_4E_4}$$

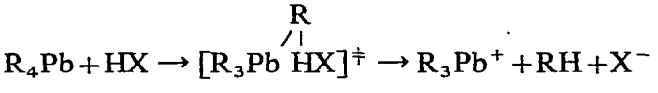
where the term on the right side represents the relative rates of cleavage of methyl and ethyl groups from tetramethyllead and tetraethyllead. Values of S (Table 10) are approximately the same for all three electrophiles.

Triflic acid like perchloric acid behaves as a strong electrolyte in acetic acid and is present as acetacidium ions and ion-pairs[14,18,19]:

$$CF_3SO_3H + CH_3CO_2H \rightleftharpoons [CF_3SO_3^- \quad CH_3CO_2H_2^+] \rightleftharpoons CF_3SO_3^- + CH_3CO_2H_2^+$$

Under these conditions the electrophile is $CH_3CO_2H_2^+$, whereas it is CH_3CO_2H in acetic acid. Glacial acetic acid supports ionization only poorly, [the dissociation constant of triflic acid is $1.26 \cdot 10^{-5}$][14] and salts are also highly ion-paired in this medium[20].

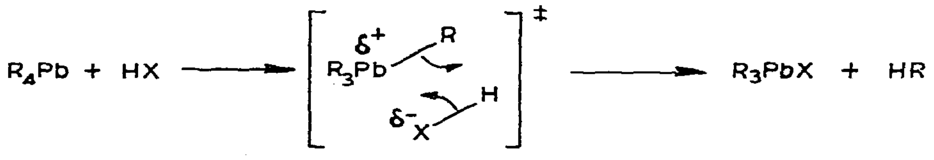
The change of electrophile from CH_3CO_2H to $CH_3CO_2H_2^+$ is accompanied by a large increase in rate (Table 10), but there is also a parallel increase in selectivity. This trend is opposite to that expected on the basis of a direct proton transfer from the acid to the tetraalkyllead moiety via an open transition state as (I).



$$R_4Pb + HX \rightarrow [R_3\overset{R}{Pb}\,HX]^{\ddagger} \rightarrow R_3Pb^+ + RH + X^- \qquad (25)$$

(I)

According to the Hammond postulate[21], the stronger acid in such a formulation should lead to a decrease in selectivity relative to the weaker acid, since bond making (*i.e.*, R...H) will not have progressed as far in the transition state. From such a basis, we propose that the conjugate base X must also be involved directly in the proton transfer process. A closed four-centered transition state such as (II) may be one such possibility.



(26)

(II)

This mechanism is readily designated as a S_E2i process, according to the mechanistic categories developed for the cleavage of alkyl–metal bonds[22].

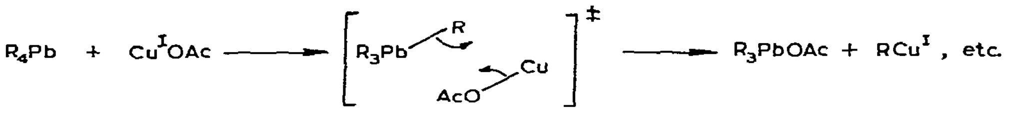
The formulation in Eq. 26 derives part of its driving force from the formation of the bond between Pb and X. The latter is an incipient acetate ion when acetic acid is the electrophile, whereas it is a less nucleophilic species when acetacidium ion is the proton donor. The triflate ion itself is a poor nucleophile and is probably incorporated into the product in a subsequent step, *e.g.*

$$R_4Pb + AcOH_2^+ \rightarrow R\text{–}H + R_3PbOAcH^+ \quad (27)$$

$$R_3PbOAcH^+ + OTf^- \rightarrow R_3PbOTf + HOAc \quad (28)$$

The much faster rates observed with $CH_3CO_2H_2^+$ compared to CH_3CO_2H indicates that the driving force is derived predominantly by proton transfer in comparison to a nucleophilic component (*e.g.*, a S_ECi process[22])*. We also conclude that the selectivity in the bond cleavage of CH_3–Pb *versus* CH_3CH_2–Pb is inversely related to the degree of interaction between Pb and X.

The high selectivity observed in the electrophilic cleavage of tetraalkyllead by copper(I) acetate is interesting. We presume a cyclic transition state also pertains to this electrophile, although selectivity studies were not carried out with copper(I) triflate. This view assumes that in the transition state (III), the nucleophilicity of the incipient acetate ion is diminished in CuOAc compared to HOAc.



(29)

(III)

The value of *S* in Table 10 suggests that a closed transition state such as III can accommodate a copper nucleus without serious steric difficulties.

Steric effects are not important in the ground states of tetraalkyllead compounds containing only methyl and ethyl groups. Thus, Calingaert and Beatty[23] found that

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* The study of the kinetic (deuterium) isotope effects would aid in the further probing of the transition state for protonolysis.

equilibration of a mixture of tetramethyllead and tetraethyllead led to a random mixture of $(CH_3)_{4-n}Pb(CH_2CH_3)_n$ compounds. The relative rate factor S presented earlier in Eq. 19 represents the effect which an alkyl substituent (on the departing trialkyllead moiety) has on the rate of cleavage. The constancy of S in the reactions of a series of methylethyllead compounds with electrophiles also indicates the minor importance of steric effects in the transition states.

The absence of a significant steric difference between methyl and ethyl groups is not inconsistent with a closed transition state such as (II) or (III). The relatively large covalent radius of lead should also enable it to accommodate primary alkyl groups of increasing chain length without serious steric compression as studies with tin indicate[3]. Preliminary experiments, however, indicate that the same approximation will not be valid with the larger secondary and tertiary alkyl groups.

Conclusions

The rates of electrophilic cleavage of alkyl groups on lead are highly dependent on the alkyl groups remaining on the departing trialkyllead cation. Conclusions based on either intramolecular or intermolecular comparisons of rates alone are, therefore, invalid for the determination of the relative reactivity R_0 of a particular alkyl–lead bond. Methods for the determination of the latter are described based on studies carried out with leaving groups of the same structure. The effect of alkyl groups on the leaving group is determined by a parameter S when steric effects are unimportant.

EXPERIMENTAL SECTION

Materials

Tetraethyllead was prepared from ethylmagnesium bromide, plumbous chloride and ethyl iodide according to the procedure described by Gilman and Jones[24]. Tetramethyllead was prepared by the same method using methylmagnesium iodide and methyl iodide. Triethylmethyllead was prepared from 3.5 g triethyllead acetate (Alfa Products Ventron Corp.) in 20 ml tetrahydrofuran (THF) solution (30 ml of 1.65 M). The mixture was stirred for two hours under nitrogen and heated to reflux. The mixture was then poured into slightly acidic water, extracted with ether and the ethereal solution washed further and dried. Removal of the ether afforded a clear oil which was steam distilled and redistilled under vacuo; b.p. 90° (30 mm). Trimethylethyllead was prepared from 5 g trimethyllead acetate (Alpha Products) and 50 ml of approximately 1 M solution of ethylmagnesium bromide in ether. B.p. 56–58° (55 mm).

Diethyldimethyllead was prepared by a two-step procedure from tetraethyllead. Low temperature controlled brominolysis of tetraethyllead following the method of Willemsens and Van der Kerk[25] yielded diethyllead dibromide in nearly quantitative yield. Diethyllead dibromide (80 mmol) was added under nitrogen to a solution of 200 mmol of methylmagnesium iodide in 200 ml of ether at ice temperature. A vigorous reaction ensued with each addition of diethyllead dibromide. After addition was complete (15 min), the mixture was stirred for 40 min and then allowed to stand overnight. The mixture was quenched by pouring it in an ice-cold solution of dilute hydrochloric acid. The aqueous solution was re-extracted with ether and the combined ethereal extracts washed with water and dried over anhydrous calcium chloride. Vacuum distillation of the clear oil (22.5 g) remaining after removal of the solvent afforded diethyldimethyllead, b.p. 58–59° (18 mm).

Acetic acid was redistilled after refluxing with acetic anhydride. The results were the same when Mallinckrodt reagent grade material was used as such. Trifluoromethanesulfonic acid from 3M Corp. (Minneapolis) was redistilled (b.p. 162°) before use.

Copper(I) acetate was prepared from copper(I) oxide[27] by the method of Weller and Mills[28] by refluxing it with a mixture of acetic acid/acetic anhydride under either hydrogen or nitrogen. The colorless precipitate of copper(I) acetate was washed repeatedly with dry, deaerated acetic acid until the wash solution was colorless.

Acetolysis of tetraalkyllead compounds

A 25 ml flask containing 3 ml of acetic acid was sealed with a gas-tight rubber serum cap. The flask was equilibrated at $20.0 \pm 0.1^\circ$ and a measured volume of isobutane was added as a marker gas by means of a hypodermic syringe. The reaction was initiated by adding a known amount of the tetraalkyllead compound (or a prepared mixture) with a micro-syringe to the magnetically stirred solution. The acetolysis of tetraethyllead proceeded at the same rate independently of whether the atmosphere was air or flushed with argon.

Reactions involving triflic acid were carried out as described above, except 3 ml of standard solution of triflic acid in acetic acid was added. For reactions with copper(I) acetate, the vessel was evacuated initially and 3 ml of a saturated solution of copper(I) acetate was added with a hypodermic syringe.

Analysis

The tetraalkyllead compounds were analyzed by gas chromatography on a 2-meter copper column containing 10% wt polyethyleneglycol 400 and 1% wt Quadrol on non-acid washed Chromosorb W[13]. This column did not induce redistribution of the tetraalkyllead compounds since a mixture of pure tetraethyllead and tetramethyllead showed no evidence of forming mixed alkyl compounds. Analysis indicated that all the tetraalkyllead compounds were of 97% minimum purity. The mass spectra at low ionizing voltages (< 20 eV) afforded similar results[26].

Methane and ethane were analyzed by gas chromatography on a 6 ft Porapak Q column at 80° using isobutane as the internal standard. Quantitative analysis was effected by carefully calibrating the system with known amounts of these gases under reaction conditions. Kinetics were determined by periodically extracting a small volume ($< 0.01\%$) of the equilibrated gas phase as described earlier[9].

The kinetics of acetolysis was followed for a period of approximately 2 hours, during which time 10 to 15 samples of gas were extracted. When the data were plotted, the yields of alkanes usually followed first order kinetics to within 5%. For reactions with triflic acid and copper(I) acetate, the relative yields of methane and ethane were determined in two ways: (1) since the reaction with either triflic acid or copper(I) acetate occurred much more rapidly than the acetolysis reaction, the relative rates could be determined by extrapolation to zero time. (2) Sampling of the reaction mixture during the first few minutes minimized the contribution from the slower acetolysis reaction.

The concentration of copper(I) acetate was determined in acetic acid solutions by oxidation to copper(II) acetate with oxygen. The latter was determined spectroscopically by its absorption at 680 nm ($\varepsilon_{app} = 176$ cm$^{-1} \cdot M^{-1}$)[15a]. At 20°, the solubility of copper(I) acetate in acetic acid[9] is 1.19×10^{-3} M.

Acetate was determined by titration with a standard solution of trifluoromethanesulfonic acid in acetic acid using copper(II) acetate as a visual indicator[9]. At the endpoint, the color of the solution changed abruptly from a deep blue green color of copper(II) acetate to a pale blue color of copper(II) triflate. The method was standardized with samples of alkali metal acetates and should be generally applicable to the determination of other carboxylate salts in acetic acid solutions.

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