**702.** *The Reaction of Tetramethyl-lead and Trimethyl-lead Chloride with Alkali Metals in Liquid Ammonia.*

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Alkali metals in liquid ammonia produce fission of one Pb–C bond in $PbMe_4$, giving $PbMe_3^-$ ions and methyl radicals; the latter yield methane and ethane. The $PbMe_3^-$ ions are then solvolysed; in presence of potassium all the methyl groups are removed to give lead imide, while with sodium or lithium only one is removed, giving dimethyl-lead. With trimethyl-lead chloride, $PbMe_3^-$ is first formed; some of this suffers fission of all Pb–C bonds, some forms the ion $PbMe_3^-$ (which is then solvolysed), and some undergoes disproportionation.

In a previous paper[1] it was shown that potassium and a tetra-alkylammonium ion in liquid ammonia give a tertiary amine and a hydrocarbon; the mechanism suggested was:

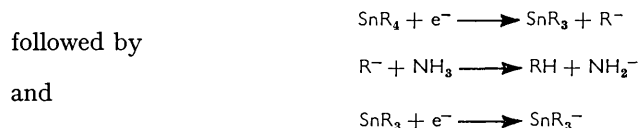$$NR_4^+ + e^- \longrightarrow NR_3 + R$$
$$R + e^- \longrightarrow R^-$$
$$R^- + NH_3 \longrightarrow RH + NH_2^-$$
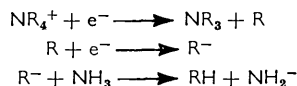
When R = Me, a small amount of ethane was also formed, by combination of two methyl radicals or by a reaction $NMe_4^+ + Me^- \longrightarrow NMe_3 + C_2H_6$. It seemed that, if reaction of a metal–ammonia solution with a neutral molecule of type MMe_4 could yield ethane, then radical combination must be operative; hence a study of the reaction of tetramethyl-lead has been undertaken.

Reductions of lead tetra-alkyls in liquid ammonia have been considered in a review by Gilman;[2] the overall reaction suggested is:

$$PbR_4 + 2e^- + NH_3 = PbR_3^- + RH + NH_2^-$$
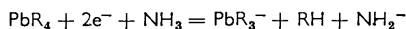
Most studies of these systems have however been concerned primarily with the use of ions PbR_3^- in synthesis of unsymmetrical lead tetra-alkyls; the hydrocarbon products have not been investigated quantitatively, nor has solvolysis of the products been examined. Moreover it is not certain that only PbR_3^- ions are formed initially; Kraus and Sessions,[3] studying SnR_4 compounds, postulated reactions:

$$SnR_4 + e^- \longrightarrow SnR_3 + R^-$$

followed by

$$R^- + NH_3 \longrightarrow RH + NH_2^-$$

and

$$SnR_3 + e^- \longrightarrow SnR_3^-$$

If PbR_3 radicals are in fact formed then these may lose further alkyl groups, or disproportionate to lead and lead tetra-alkyls. It was therefore considered that studies of metal–ammonia reactions with trialkyl-lead halides should also be made, since the initial reaction would then be $PbR_3^+ + e^- = PbR_3$ and further products would be those originating from PbR_3 radicals.

In previous work,[1] only potassium was used; in the present work, sodium and lithium are found to yield different results from potassium, because of differences in the solubilities of the amides in liquid ammonia.

Experimental

Metal–ammonia solutions were handled, and gaseous and volatile products were analysed, in a vacuum.[1] Tetramethyl-lead and trimethyl-lead chloride were prepared by conventional methods and analysed. The lead compound and alkali metal in liquid ammonia were allowed to react in a sealed tube until the blue colour disappeared. At the usual temperature of

[1] Hazlehurst, Holliday, and Pass, *J.*, 1956, 4653.
[2] Gilman, *Chem. Rev.*, 1954, **64**, 114.
[3] Kraus and Sessions, *J. Amer. Chem. Soc.*, 1925, **47**, 2361.

reaction, —78°, tetramethyl-lead was insoluble, and reaction was slow; trimethyl-lead chloride was soluble at this temperature, so reaction was much faster. The solutions continued to evolve hydrocarbon after disappearance of colour; this part of the reaction was completed by refluxing under a cold finger (—78°). Volatile products (including any tetramethyl-lead) and solvent were then removed, and the solid residue analysed for lead (as chromate), potassium if present (as potassium tetraphenylboron), and alkalinity (corresponding to amide content [1]). It was not found possible to determine tetramethyl-lead, whether unchanged or formed as a product.

Results.—These are given in Tables 1 and 2; only results for complete experiments carried out under reproducible conditions are quoted. The experiments are numbered for convenience in discussion; units are mmoles unless otherwise stated. Hydrogen, " initial " methane, and ethane were evolved before the colour vanished; "final" methane was that evolved on subsequent ammonolysis, and the amide and lead readings were taken on the solid residues.

TABLE 1. *Experiments with tetramethyl-lead at* —78°.

Expt. no.	1	2	3	4	5	6	7
PbMe$_4$ added	2·74	1·60	1·81	2·14	1·28	2·28	2·30
Metal	K	K	K (at —33°)	Na	Na	Li	Li
Amt. added	2·91	3·77	2·78	2·57	3·88	3·04	2·40
Products: H$_2$	—	0·34	—	—	0·64	—	—
CH$_4$ (initial)	1·26	1·41	1·02	1·09	1·10	1·40	1·05
C$_2$H$_6$	0·14	0·08	0·15	0·14	0·12	0·11	0·11
CH$_4$ (Final)	4·70	4·55	3·94	1·38	1·32	1·32	1·37
NH$_2^-$	2·72	3·50	2·45	2·73	3·72	2·75	2·30
Pb	1·61	1·51	1·31	0·69	0·63	0·74	0·65
Time (hr.)	4	100	1·3	23	—	6	6

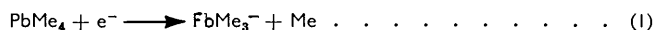TABLE 2. *Experiments with trimethyl-lead chloride (at* —78°).

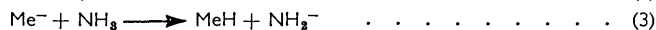| Expt. no.	8	9	10	11	12	13
Me$_3$PbCl added	0·40	0·20	0·21	0·47	0·45	0·20
Metal	K	K	K	K	Li	Li
Amt. added	0·79	0·38	0·51	2·93	0·98	0·29
Products: H$_2$	—	—	—	0·83	—	—
CH$_4$ (initial)	0·16	0·11	0·20	0·49	0·41	0·17
C$_2$H$_6$	—	—	—	—	—	—
CH$_4$ (final)	0·69	0·18	0·29	0·93	0·14	0·07
NH$_2^-$	0·44	0·17	0·21	2·37	0·51	0·23
Pb	0·29	0·12	0·15	0·43	0·25	0·09
Time (hr.)	0·16	0·16	0·16	164	0·25	0·25

DISCUSSION

The results for the potassium–tetramethyl-lead reactions suggest that the reaction ratio is 2 : 1; when potassium in excess is added (expt. 2), hydrogen is evolved, the amount indicating that the excess has reacted thus:

$$K + NH_3 = KNH_2 + \tfrac{1}{2}H_2$$
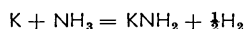
It is then reasonable to postulate that the first step in the reaction is

$$PbMe_4 + e^- \longrightarrow FbMe_3^- + Me \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

followed by

$$Me + e^- \longrightarrow Me^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$Me^- + NH_3 \longrightarrow MeH + NH_2^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or

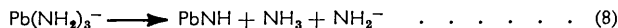$$Me + Me \longrightarrow C_2H_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$
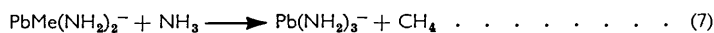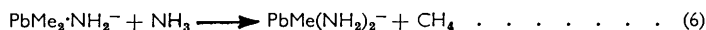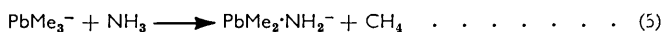
In agreement with this scheme, the approximate relation [Initial CH$_4$ + 2 × C$_2$H$_6$] = Pb holds for each experiment. The production of ethane would not be expected if reaction (1) were written

$$PbMe_4 + e^- \longrightarrow PbMe_3 + Me^-$$

Moreover, in expt. 2, where the initial electron concentration is high, the ratio C$_2$H$_6$/initial CH$_4$ falls, as is to be expected since high electron concentration will favour reaction (2) at the expense of (4). Increase of temperature (expt. 3) causes increased solubility of

tetramethyl-lead; there is a small increase in the C_2H_6/initial CH_4 ratio here, perhaps because of the greater extent of reaction (1).

On the above hypothesis, only one methyl radical is removed by electron attack, and the ion $PbMe_3^-$ remains in solution. Hence there is the possibility that three more methyl groups can be removed by solvent attack, and it appears that this does occur, since the relation [Final CH_4] = [3 × initial CH_4 + 6 × C_2H_6] holds in each experiment, even when excess of potassium is present. The solvolysis can be written stepwise thus:

$$PbMe_3^- + NH_3 \longrightarrow PbMe_2{\cdot}NH_2^- + CH_4 \quad \cdots \cdots \cdots \quad (5)$$

$$PbMe_2{\cdot}NH_2^- + NH_3 \longrightarrow PbMe(NH_2)_2^- + CH_4 \quad \cdots \cdots \cdots \quad (6)$$

$$PbMe(NH_2)_2^- + NH_3 \longrightarrow Pb(NH_2)_3^- + CH_4 \quad \cdots \cdots \cdots \quad (7)$$

$$Pb(NH_2)_3^- \longrightarrow PbNH + NH_3 + NH_2^- \quad \cdots \cdots \cdots \quad (8)$$

Evidence for the intermediate steps (5) and (6) is considered below; reactions (5), (6), and (7) together yield the observed amount of methane. The final reaction (8) is postulated because (*a*) the residue obtained was an orange solid, with a tendency to decompose explosively (characteristic of lead imide), and (*b*) formation of a further equivalent of amide ion is required to explain the observed approximate equality between added metal and amide ion produced.

When sodium or lithium is used instead of potassium (expts. 4—7), the total amount of methane (relative to the amount of metal added) is reduced, as is also the amount of residual lead. The ratio final CH_4/initial CH_4 is also decreased. The results of expt. 5, in which hydrogen is produced by the excess of sodium, suggest that the reaction ratio Na : $PbMe_4$ is 2 : 1, as with potassium. If this is true in the other experiments also, then it can be assumed that reactions (1)—(4) occur as with potassium, yielding methane and ethane; this assumption is supported by the observed equality Na(or Li) = 2[Initial $CH_4 + C_2H_6$]. If the first solvolysis (5) now follows, it alone yields sufficient final methane since it is seen that Final CH_4 = Initial $CH_4 + C_2H_6$ = $PbMe_3^-$. The product of reaction (5), $PbMe_2{\cdot}NH_2^-$, instead of undergoing further solvolysis, reacts with sodium (or lithium) ions, thus:

$$PbMe_2{\cdot}NH_2^- + Na^+ \longrightarrow PbMe_2 + NaNH_2 \quad \cdots \cdots \cdots \quad (9)$$
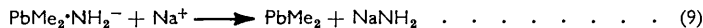
since the amides of sodium and lithium are insoluble in liquid ammonia at −78°. The dimethyl-lead may then remain until the temperature is raised to remove the last traces of solvent, then disproportionating:

$$2PbMe_2 \longrightarrow Pb + PbMe_4 \quad \cdots \cdots \cdots \quad (10)$$

and the tetramethyl-lead passes off as a volatile product, so that, as observed, the residual lead is only half that expected if solvolysis had been complete.
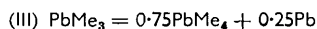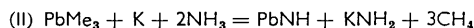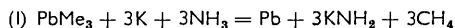
In the reactions of potassium with trimethyl-lead chloride (Table 2), the first step must be

$$Me_3PbCl + K \longrightarrow PbMe_3 + KCl \quad \cdots \cdots \cdots \quad (11)$$
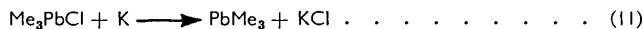
and it might then be expected that the next would be:

$$PbMe_3 + e^- \longrightarrow PbMe_3^- \quad \cdots \cdots \cdots \quad (12)$$

and that this would be followed by the solvolysis (5)—(8), so that methane would only appear after the solution became colourless, if excess of trimethyl-lead chloride were used. In fact, some methane, but no ethane, appears before this stage; the amount is rather variable, being greater if more potassium is present. To explain this, we may postulate that the $PbMe_3$ radical initially formed can react in three possible ways:

(I) $PbMe_3 + 3K + 3NH_3 = Pb + 3KNH_2 + 3CH_4$

(II) $PbMe_3 + K + 2NH_3 = PbNH + KNH_2 + 3CH_4$

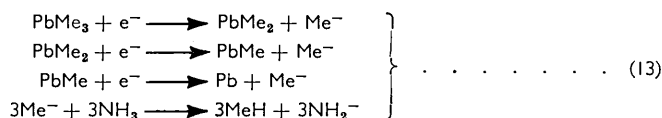(III) $PbMe_3 = 0{\cdot}75PbMe_4 + 0{\cdot}25Pb$

In equation (I), the methane is put equal to the initial methane found, and the equation used to calculate how much potassium is required and how much lead and amide are produced. The remaining potassium is now assumed to react as in equation (II), and used to calculate how much more lead (imide), amide, and methane are produced from it. Subtraction of the lead formed in (I) and (II) from that available as $PbMe_3$ originally gives a quantity of the latter to react as in equation (III), yielding more residual lead. From the three equations therefore, calculated amounts of residual lead, amide, and final methane (from II) can be compared with the amounts actually found; this is done in Table 3, for

TABLE 3.

Experiment	8	9	10	11	12
Final CH_4: calc.	0·69	0·21	0·30	0·93	0·12
found	0·69	0·18	0·29	0·93	0·14
Residual Pb: calc.	0·31	0·11	0·18	0·47	0·25
found	0·29	0·12	0·15	0·43	0·25
Residual NH_2^-: calc.	0·39	0·18	0·30	2·46	0·53
found	0·44	0·17	0·21	2·37	0·51

expts. 8—11. (In expt. 11, with excess of potassium, the observed amount of hydrogen is used to calculate potassium used and amide produced according to the equation $K + HN_3 = KNH_2 + \frac{1}{2}H_2$.) The Table indicates that it is reasonable to accept the equations; the mechanisms must then be considered. The methane of equation (I) must be attributed to removal of methyl *ions* by electron attack on trimethyl-lead, thus:

$$
\left.
\begin{aligned}
PbMe_3 + e^- &\longrightarrow PbMe_2 + Me^- \\
PbMe_2 + e^- &\longrightarrow PbMe + Me^- \\
PbMe + e^- &\longrightarrow Pb + Me^- \\
3Me^- + 3NH_3 &\longrightarrow 3MeH + 3NH_2^-
\end{aligned}
\right\} \qquad \cdots \cdots \cdots (13)
$$

This is clearly different from reaction (1) in which a methyl *radical* is formed; the total absence of ethane seems to preclude this reaction. The reason for the difference may lie in the different conditions; reaction (1) was operative where a small concentration of $PbMe_4$ was present, reacting slowly; here, a much larger concentration of $PbMe_3$ is reacting rapidly. Nevertheless, not all the $PbMe_3$ reacts as in (13); some must form the ion $PbMe_3^-$ by reaction (12), and this ion, in refluxing ammonia, undergoes complete solvolysis (5)—(8); hence the overall reaction given by equation (II). In the absence of excess of potassium, some $PbMe_3$ escapes attack by either of the above mechanisms, and finally disproportionates when the reaction products are heated to drive off solvent ammonia (equation III).

When lithium is used instead of potassium in the reaction with trimethyl-lead chloride (expts. 12 and 13), the relative amount of final methane is reduced. This is again attributed to cessation of solvolysis when reaction (5) is complete, the ion $PbMe_2 \cdot NH_2^-$ then reacting as in (9). Equation (II) now becomes $PbMe_3 + Li + NH_3 = PbMe_2 + KNH_2 + CH_4$ and calculated and experimental values can then be compared as before (expt. 12, Table 3).

The reaction mechanisms put forward in this paper are based upon stoicheiometric evidence only, and are therefore tentative. Kinetic measurements would be difficult but could test the validity of the reaction schemes proposed.