1233. *The Reaction of Vinyl-lead Compounds with Sodium in Liquid Ammonia*

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Previous studies[1] of the reaction of alkyl-lead compounds R_xPbCl_{4-x} ($x = 4,3$) with alkali metals in liquid ammonia at −78° showed that cleavage of alkyl groups can occur by reactions of the type

$$PbR_x + e^- + NH_3 \longrightarrow PbR_{x-1} + RH + NH_2^- \qquad (1)$$

which give finally metallic lead, and by ammonolytic reactions, *e.g.*,

$$PbR_2NH_2^- + NH_3 \longrightarrow PbR(NH_2)_2^- + RH \qquad (2)$$

giving finally lead amide or imide. In addition to the alkane RH formed by these reactions, some alkane R–R may also be formed by cleavage of alkyl groups as radicals. Reactions of type (2) are only important when the metal gives an amide soluble in liquid ammonia; otherwise, in the presence of excess metal, all lead–carbon bonds are cleaved. In the absence of excess metal, some PbR_x ($x < 4$) groups disproportionate to give, finally, PbR_4 and Pb. We report here a study of vinyl-lead compounds reduced by sodium in ammonia under similar conditions to those used previously.

Experimental.—Tetravinyl-lead was prepared by the published method,[2] and trivinyl-lead chloride and divinyl-lead dichloride by reaction of appropriate amounts of tetravinyl-lead

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[1] A. K. Holliday and G. Pass, *J.*, 1958, 3485.

[2] E. C. Juenge and S. E. Cook, *J. Amer. Chem. Soc.*, 1959, **81**, 3578.

and hydrogen chloride in n-hexane at −78° (monochloride) or at 20° (dichloride). Reactions were carried out as previously described [1] with recovery of all volatile products. Results of typical experiments are shown in the Table.

Reduction of vinyl-lead compounds by sodium in liquid ammonia at −78° (R = vinyl)

	Expt. no.:	1	2	3	4	5	6
x in R_xPbCl_{4-x}		4	4	3	3	2	2
R_xPbCl_{4-x} added (mmoles)		0·72	1·26	0·57	0·80	0·41	0·90
Na added (mmoles)		5·78	3·52	2·86	4·14	0·85	4·24
Reaction time		38 days	90 hr.	28 days	2 days	2 hr.	7·7 days
Volatile products (mmoles)	H_2	0·04	<0·02	0·02	—	—	0·02
	C_2H_4	2·73	1·93	1·66	1·98	<0·02	1·14
	R_4Pb	—	0·20	—	—	0·20	—
Hydrolysis products (mmoles)	H_2	1·32	<0·02	0·23	0·36	—	0·36
	C_2H_2	—	<0·02	—	—	—	<0·02
	C_2H_4	—	2·12	—	0·39	—	0·50
	NH_2^-	2·42	2·07	1·61	2·02	—	1·12
	Pb	0·66	0·89	0·50	0·79	0·20	0·79

Discussion.—The hydrogen appearing in the volatile products is due to the reaction $Na + NH_3 \longrightarrow NaNH_2 + \frac{1}{2}H_2$, and hydrogen on hydrolysis is formed when excess sodium remains. Where insufficient sodium was added to achieve cleavage of all vinyl groups, some tetravinyl-lead is found (expts. 2 and 5). The absence of C_4 hydrocarbons suggests that formation of any vinyl radicals must be followed by rapid uptake of an electron (and then the reaction $R^- + NH_3 \longrightarrow RH + NH_2^-$), so that radical–radical addition is prevented. All the lead in the residue appears as metal, and this fact and the amide-ion determination confirm that ammonolytic reactions are unimportant, as expected since sodium amide is insoluble in ammonia at −78°. Formation of ethylene must therefore be due to reactions of type (1), but, unless very long reaction times are used, all vinyl groups are not removed by these reactions, and more ethylene appears after hydrolysis of the solid residue. The data suggest that cleavage of vinyl groups by the sodium becomes difficult as x decreases to 1 in PbR_x, and this may be due to the formation of polyanionic species $(PbR_x)_n^{n-}$ similar to the polyplumbide ions (*e.g.*, Pb_9^{4-}) formed in the lead–sodium–ammonia system, which are known to resist attack by ammonia but are readily hydrolysed. The traces of acetylene found in two experiments after hydrolysis may come from small amounts of electron-rich poly(vinyl plumbide) anions. It is also worth noting that, although cleavage of vinyl groups from vinyltin compounds can be achieved more readily than cleavage of alkyl groups from alkyltin compounds, by reagents such as carboxylic acids,[3] complete removal of vinyl groups from tetravinyl-lead by such reagents is not achieved.

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[3] D. Seyforth, *J. Amer. Chem. Soc.*, 1957, **79**, 2133 S. D. Rosenberg and A. J. Gibbons, *ibid.*, p. 3218; A. Henderson and A. K. Holliday, *J. Organometallic Chem.*, in the press.