TABLE III

SOLUBILITY OF POLYMERIZED TRIMERIC PHOSPHONITRILIC ISOTHIOCYANATE IN HOT BENZENE

Temp. of polymn., °C.	Time of polymn., hr.	Wt. dissolved, %
145	1.75	62.2
145	2	21.9
145	6	19.50
145	12	14.96
145	24	14.92
210	10 min.	43.2
210	0.5	21.1
210	1	17.61
210	2	15.65
210	6	14.40
210	12	13.89
210	24	12.08

TABLE IV

SOLUBILITY OF POLYMERIZED TETRAMERIC PHOSPHONITRILIC ISOTHIOCYANATE IN HOT BENZENE

Temp. of polymn., °C.	Time of polymn., hr.	Wt. dissolved, %
180	2	94.0
180	6	16.20
180	12	11.76
180	24	11.71
210	1	45.7
210	2	16.76
210	6	14.49
210	24	9.43

The infrared absorption spectrum verifies the retention of the eight-membered phosphorus–nitrogen ring system and the presence of the isothiocyanate grouping.[1] The molecular weight was determined cryoscopically in benzene. Calcd. for $P_4N_4(NCS)_8$: mol. wt., 644. Found: mol. wt., 601, 606. The presence of reactive isothiocyanate groups was verified, as for I, by formation of adducts with amino, hydroxy and hydrazino compounds, for which pertinent data are given in Table II. Treatment of the octa-thioureido tetraphosphonitrile (ammonia adduct) in aqueous solution also results in the liberation of only one-half of the bound ammonia. Significantly different is the product obtained by reaction with *n*-butylamine. The octa-(N-butylthioureido) tetraphosphonitrile is soluble in ether, the reaction medium. If, however, the ether solution is refluxed a white precipitate, m.p. 155°, gradually separates. The composition and molecular weight of this product correspond to an adduct that can be represented by the empirical formula, $[PN(NCS)_2]_4 \cdot 6C_4H_9NH_2$.

Anal. Calcd. for $[PN(NCS)_2]_4 \cdot 6C_4H_9NH_2$: C, 35.6; H, 6.3; N, 25.2. Found: C, 36.1; H, 6.0; N, 22.9.

Polymerization of the Phosphonitrilic Isothiocyanates.—Heating *in vacuo* or in contact with the atmosphere at higher temperatures results in the gradual conversion of the liquefied isothiocyanates I and II into rubber-like gels. A solubility criterion was adopted to establish the extent of polymerization as a function of time and temperature. The polymerizate was extracted with benzene for 24 hours using glass extraction thimbles containing glass-wool filter pads. Typical results are given in Tables III and IV. For the most highly polymerized samples of both I and II, some 10 to 15% extractable material is still retained in the polymerizate. Up to 210° polymerization was not accompanied by appreciable weight losses; above this temperature the polymerizates became darker in color and more brittle. Weight losses of 27.8 and 16.6% were observed when samples of I were heated for 2 hr. at 300 and 260°, respectively.

Attempts also were made to effect homogeneous polymerization in solvents such as benzene, *n*-heptane, xylene, *o*-dichlorobenzene and nitrobenzene. No solid products were obtained with concentrations of I and of II as high as 20% and with temperatures at the boiling points of the solvents for reflux periods of 48 hr.

Preliminary X-ray diffraction studies of the polymeric phosphonitrilic isothiocyanates under various conditions of temperature and also under tension revealed that the transmission patterns of all samples are similar, consisting of two distinguishable halos corresponding to spacings of 3.5 and 9.5 Å. The possibly analogous phosphonitrilic chloride polymer gives three distinguishable halos (3.35, 6.15, 13.5 Å). These differences suggest a lesser initial order in the case of the polyphosphonitrilic isothiocyanate. X-Ray diffraction patterns of stretched fragments of the most extensible samples (maximum elongation, 200%) failed to show evidences for fiber patterns. If the structure of the polyphosphonitrilic isothiocyanate is imagined to be similar to that of the chloride polymer (*i.e.*, analogous repeating units, chain length and linearity), it is noteworthy that an approximate 400% elongation was required for crystallization in the case of the latter.[3]

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[3] K. H. Meyer, W. Lotmar and G. W. Pankow, *Helv. Chim. Acta*, **19**, 930 (1936).

URBANA, ILLINOIS

The Synthesis of Tetraethyllead by Reaction of Tetravalent Lead Salts with Triethylaluminum and Other Ethyl Metal Compounds[1]

BY FREDERICK W. FREY, JR., AND SHIRL E. COOK

RECEIVED JUNE 16, 1959

Lead metal was a by-product of reactions of a number of tetravalent lead salts with alkylmetal compounds. The corresponding reaction with phenylmetal compounds produced no lead metal. A reaction sequence, based on the instability of monoalkyllead salts, is proposed to explain the formation of lead metal as well as the range of organolead yields realized.

The reaction of lead dichloride with ethyl Grignard or ethyllithium represents the conventional laboratory method for the synthesis of tetraethyllead. The reaction of divalent lead salts, in general, with active ethylmetal compounds has been investigated thoroughly.[2] The reactions pro-

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[1] Presented at the 134th meeting of the American Chemical Society, Chicago, Ill., September 11, 1958.

[2] R. W. Leeper, L. Summers and H. Gilman, *Chem. Revs.*, **54**, 108 (1954).

ceed by the equation

$$2PbX_2 + 4EtM \longrightarrow Et_4Pb + 4MX + Pb \quad (1)$$

wherein half of the lead is reduced to lead metal. Very little attention has been given to investigation of the reaction of tetravalent lead salts[3,4] with alkylmetal compounds. This reaction is of interest because the tetravalent lead salt might be expected to be converted quantitatively to the desired tetraalkyllead compound without formation of any by-product lead metal

$$PbX_4 + 4EtM \longrightarrow Et_4Pb + 4MX \quad (2)$$

This investigation was undertaken initially to determine the reactivity of various tetravalent lead salts with triethylaluminum. However, when it became evident that lead metal is a by-product of all the reactions, the investigation was directed to a determination of the source of lead metal formation.

Experimental

Preparation of Reagents. (a) Alkylmetal Compounds. Ethyllithium,[5] **ethyl Grignard reagent,**[6] **ethylaluminum sesquibromide,**[7] **diethylcadmium,**[8] **diethylzinc,**[9] **diethylmercury,**[10] **phenyllithium**[11] **and triphenylaluminum**[12] were prepared by standard procedures reported in the literature. **Triethylaluminum** was obtained from Ethyl Corporation, Orangeburg, S. C. The triethylaluminum was found by infrared analysis to be better than 95% pure. The ether solutions of ethyllithium, phenyllithium and ethyl Grignard reagent were standardized by hydrolysis and titration with standard acid. No effort was made to determine the exact purity of the other materials since these reagents, with the exception of diethylmercury, were used in 100% excess. The purity of diethylmercury was not important as no tetraethyllead at all was produced in its reactions.

b. Tetravalent Lead Salts.—Lead tetraacetate was prepared by reaction of lead tetroxide in glacial acetic acid–acetic anhydride.[13] The **butyrate, benzoate** and **stearate** salts were prepared by reaction of lead tetraacetate with the appropriate acid and distillation of the acetic acid at reduced pressures.[14,15] The **complex hexachloroplumbates** were prepared by reaction of lead dioxide with cold concentrated hydrochloric acid and addition of a saturated aqueous solution of the appropriate ammonium or metal halide.[16]

All the lead salts were shown by analysis to have a minimum purity of 97%.

Reaction Procedure.—The reaction of the tetravalent lead salt with the alkylmetal compound was conducted in a 300-ml. 3-necked flask equipped with a Trubore stirrer, a reflux condenser and a dropping funnel equipped with a side arm for pressure equalization.

A typical reaction consisted in charging the lead salt (5–10 g.) into the flask and adding one-half the desired volume of solvent. The alkylmetal compound was weighed or pipetted into the dropping funnel and the remaining half of the solvent was added. The dropping funnel was charged in a nitrogen box. A rapid nitrogen purge was maintained during the reaction. The alkylmetal compound then was added dropwise to the stirred flask. After addition was completed, heat was applied and the reaction mixture was refluxed for 1/2 to 1 hour. After reaction was completed, the reaction mixture was quenched by dropwise addition of isopropyl alcohol and the evolved gas was collected. A sample of this gas was submitted for mass spectrometric analysis. After addition of alcohol, the reaction mixture was extracted with aqueous caustic solution to remove the by-product metal salt. The organic phase was then brought to volume in a volumetric flask. The organic lead content of the reaction mixture was determined spectrophotometrically by the dithizone method.[17] Two conditions assured the absence of any unreacted lead salt. The first was the use of a 100% or greater excess of metal alkyl to assure complete conversion to tetraethyllead. However, if any unreacted tetravalent lead salt remained, it was decomposed during the aqueous caustic extraction, since all the tetravalent lead salts are hydrolyzed by water.

The weight of lead metal produced in the potassium hexachloroplumbate–triethylaluminum experiments was determined by amalgamating the lead metal in the reaction solids with a pool of tared mercury under a hot 10% aqueous hydrochloric acid solution. After amalgamation was complete, the acid solution was decanted and the amalgam was washed with water and methanol and air dried. Lead weight was determined by difference. This method has been used extensively for the analysis of lead residues from the NaPb–EtCl reaction and has been found to be very accurate.

Discussion

Tetraethyllead yields from the reaction of tetravalent lead salts with the various ethylmetal compounds are given in Tables I and II. In all the reactions where organolead compounds were produced, lead metal came as a by-product except when arylmetal compounds were used, in which case no metallic lead was formed. Ethyl chloride also appeared as a reaction by-product when potassium hexachloroplumbate was the tetravalent lead salt employed.

TABLE I

HEXACHLOROPLUMBATES WITH ETHYLMETAL COMPOUNDS

Hexachloroplumbate (meq.)	Ethylmetal comp. (meq.)	Solvent	Tetraethyllead yield (%)
Ammonium (115.2)	Et_3Al (110.4)	Toluene	3.6, 4.0
Ammonium (115.2)	Et_3Al (110.4)	Hexane	3.2
Ammonium (115.2)	Et_3Al (110.4)	Diglyme[a]	2.3
Potassium (55.0)	Et_3Al (110.4)	Toluene	48.1, 50.3
Potassium (55.0)	Et_3Al (110.4)	Diglyme	50.2, 48.0
Potassium (64.8)	EtMgBr (65.0)	Toluene	0.8
Potassium (64.8)	EtMgBr (65.0)	DME[b]	68.3,68.8
Potassium (47.6)	Et_2Zn (95.4)	Toluene	56.1,53.7
Potassium (47.6)	Et_2Zn (95.4)	DME	50.0,49.6
Potassium (95.2)	Et_2Zn (95.4)	Toluene	47.3
Potassium (95.2)	Et_2Zn (95.4)	DME	48.1
Potassium (63.6)	EtLi (65.0)	DME	64.2
Potassium (48.6)	Et_2Cd (97.4)	DME	45.5
Potassium (102.4)	$E_3Al_2Br_3$ (253.5)	Toluene	None
Potassium (37.8)	Et_2Hg (37.8)	Diglyme	None

[a] Diglyme = dimethyl ether of diethylene glycol. [b] DME = dimethyl ether of ethylene glycol.

The range in yields, as well as the formation of metallic lead and ethyl chloride as by-products, can be explained by the reaction sequence

$$K_2PbCl_6 + 2EtM \longrightarrow 2KCl + 2EtPbCl_3 + 2MCl \quad (3)$$

$$2EtPbCl_3 \longrightarrow 2EtCl + 2PbCl_2 \quad (4)$$

$$2PbCl_2 + 4EtM \longrightarrow Et_4Pb + Pb + 4MCl \quad (5)$$

The tetraethyllead yields from reaction of ammonium hexachloroplumbate with triethylaluminum

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TABLE II

REACTION OF LEAD SALTS WITH ORGANOMETALLIC COMPOUNDS

			Normal addn.		Inverse addn. and excess Et_3Al	
Lead salt	RM	Solvent	R:Pb ratio	% Yield of R_4Pb	R:Pb ratio	% Yield of Et_4Pb
$PbCl_2$	EtMgBr	Et_2O–DME	2.0	44.9		
$PbCl_2$	EtMgBr	Et_2O–DME + EtCl	2.0	69.1		
K_2PbCl_6	Et_3Al	Toluene			11.0	64.0, 57.8
$Pb(OAc)_4$	Et_3Al	Toluene	2.5	57.6, 54.6, 55.5	5.0	64.0
$Pb(OBz)_4$	Et_3Al	Toluene	4.4	66.4, 64.6	11.0	90.1, 97.0
$Pb(OBu)_4$	Et_3Al	Toluene	4.4	57.2, 66.1	11.0	93.1, 85.8
$Pb(OSt)_4$[a]	Et_3Al	Toluene	2.0	50.2		
K_2PbCl_6	C_6H_5Li	Et_2O–DME	1.5	69.3[b]		
$Pb(OAc)_4$	$(C_6H_5)_3Al$	Toluene	1.4	95.8[c]		

[a] (OSt) designates stearate. [b] $(C_6H_5)_4Pb$ isolated as crystalline solid. [c] Yield based on solution analysis alone; no $(C_6H_5)_4Pb$ isolated.

tetraphenyllead yields of 69 and 96%, respectively. were poor because of loss of triethylaluminum by reaction of the labile hydrogens of the ammonium ion to evolve ethane. With potassium hexachloroplumbate–triethylaluminum, the yields reached a maximum of 50% and 44–46% of the lead values were converted to metallic lead. The formation of lead metal can be attributed to the alkylation of the lead dichloride which is produced *via* (4) on decomposition of the ethyllead trichloride formed as a first intermediate. Reaction 4 should be quite rapid, for the mono*alkyl*lead salts are very unstable and, with one exception,[18] attempts to synthesize such compounds have been unsuccessful. Furthermore, Criegee,[19] Demroth and Schempf have shown that the products resulting from the attempted synthesis of mono*alkyl*lead salts are always the divalent lead salts and the alkyl esters.

The best yields with potassium hexachloroplumbate were obtained using ethyl Grignard reagent and ethyllithium. Although the higher yields with these reagents can be explained by assuming the ethylation of the ethyllead trichloride, a more

$$EtPbCl_3 + \xrightarrow{Et_3Al} Et_2PbCl_2 \xrightarrow{Et_3Al} Et_4Pb \quad (6)$$

logical explanation is the direct ethylation of by-product metallic lead by ethyllithium or Grignard shown in equation 7.

$$2EtLi + Pb + 2EtCl \longrightarrow Et_4Pb + 2LiCl \quad (7)$$

The reaction depicted in equation 7 is believed to occur in the conventional laboratory synthesis of tetraethyllead where lead dichloride and ethyllithium react in the presence of ethyl iodide, the purpose of the ethyl iodide being to react with the metallic lead produced in the lead dichloride–ethyllithium reaction and quantitatively convert the lead values to tetraethyllead.

$$2PbCl_2 + 4EtLi \longrightarrow Et_4Pb + Pb + 4LiCl \quad (8)$$
$$Pb + 2EtLi + 2EtI \longrightarrow Et_4Pb + 2LiI$$

Furthermore, the ethylation of lead metal by ethyl halide and ethyllithium, ethyl Grignard or diethylzinc has been reported.[20] To demonstrate that the ethyl chloride evolved in (4) can react with lead metal before escaping from the reaction flask, lead dichloride was treated with ethyl Grignard reagent in the presence and absence of ethyl chloride. With no ethyl chloride present, the yield of tetraethyllead was less than 50%, as expected (Table II). However, when ethyl chloride was bubbled slowly into the solution during the reaction, the yield was increased to 69%. These data confirm the possibility of ethyl chloride reacting with metallic lead in an open system. With diethylzinc, the yields were slightly greater than 50%, while with diethylcadmium the yields approached those obtained with triethylaluminum. Both diethylzinc and diethylcadmium are only slightly reactive in the reaction shown in (7).

With our conditions, diethylmercury and ethylaluminum sesquibromide gave no tetraethyllead on reacting with potassium hexachloroplumbate. Instead the potassium hexachloroplumbate was reduced to lead dichloride *via* (3) and (4). This is not surprising since these two reagents are rather weak ethylating agents and, whereas they can react with covalent potassium hexachloroplumbate to produce ethyllead trichloride, they are not active enough to react with the more ionic lead dichloride obtained on decomposition of ethyllead trichloride.

Reaction of triethylaluminum with organic salts of tetravalent lead gave tetraethyllead in yields exceeding 50% (Table II). With these salts the higher yields cannot be attributed to a reaction similar to (7) since the ethyl esters of organic acids are not reactive. Instead the increase in yields over 50% must be attributed to the greater stability of the monoethyllead salt because of its more covalent character. This greater stability permits its further reaction with triethylaluminum to produce the very stable di- and triethyllead salts before it decomposes *via* (4). This is strikingly demonstrated by using a large excess of triethylaluminum, under which conditions the tetraethyllead yields were increased considerably and in some instances were nearly quantitative.

Finally, when the aryl metal compounds reacted with tetravalent lead salts, high yields of the aryllead compound were obtained without formation of any by-product metallic lead. This is consistent with the proposed reaction sequence for the alkylmetal compounds since the monoaryllead salts are stable and isolable.[21] Thus, reaction of phenyllithium with potassium hexachloroplumbate and triphenylaluminum with lead tetraacetate gave

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In conclusion, then, it is shown that high yields of tetraethyllead can be obtained by the reaction of tetravalent lead salts with the ethyl derivatives of the electropositive metals. The less reactive ethyl metal compounds, diethylmercury and ethylaluminum sesquibromide, do not produce tetraethyllead but simply reduce the tetravalent lead salt to the divalent lead salt. Metallic lead results in all reactions in which tetraethyllead is produced. The primary factor which determines the yield of tetraethyllead is the stability of the monoethyllead compound produced as the first intermediate. With potassium hexachloroplumbate a secondary reaction can occur to produce tetraethyllead. This reaction involves the ethylation of the by-product lead metal by the ethyl metal compound and the ethyl chloride which is formed on decomposition of the unstable ethyllead trichloride which forms as the first intermediate. Ethyllithium, ethyl Grignard reagent and diethylzinc are the only ethylmetal compounds found to be reactive in this secondary reaction.

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An Electromotive Force Investigation of the Product of the Solution of Antimony in Liquid Antimony Triiodide[1]

BY JOHN D. CORBETT AND FRANK C. ALBERS

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Formation of a lower iodide of antimony is strongly suggested by the transport of metal by gaseous SbI_3 and by the solution of the metal in liquid triiodide. The oxidation–reduction process relating the unknown solute and SbI_3 has been investigated at 251° by electromotive force measurements on the cell $C|Sb(N_M{}^0), SbI_3 \vdots Sb(N_M), SbI_3|C$ where the solution of mole fraction "dissolved" metal $N_M{}^0$ in equilibrium with solid metal serves as a reference electrode. Treatment of the results in terms of a general electrode reaction indicates that the solute is formed by a two electron reduction of SbI_3. The assumption that ions derived from the solvent carry the current within the cell is supported by similar results obtained for solutions containing 2 to 5 mole % added KI. The product of the reaction of antimony with liquid SbI_3 appears to be the catenated Sb_2I_4; the alternative, a diamagnetic, solvated SbI, is considered less likely.

Introduction

Although antimony triiodide is the only known iodide of antimony stable in the solid state, there is some evidence that significant amounts of reduction to a lower iodide may occur when the product can exist at low concentrations. The transport of the non-volatile antimony metal by gaseous SbI_3 at 300° is fairly unequivocal evidence for the formation of a subiodide, and the apparent solution of the metal in molten SbI_3, 1.69 mole % at 201° and 5.8% at 400°, also has been attributed to a similar reaction in the liquid state.[2]

In this particular case, application of the technique of acid-stabilization that has allowed the isolation of the lower oxidation states from other such systems[3] has not proved fruitful. The amount of reduction of SbI_3 is essentially unchanged by the addition of either AlI_3 or ZnI_2 to the melt, probably as a result of the small basicity of the molecular SbI_3 toward these acids.[4]

A study of the number of electrons involved in the oxidation–reduction process relating the lower halide (or metal) and the normal, solvent salt (as might be determined from concentration cell measurements) should be a particularly useful means of characterizing the solute in such solutions. This approach to the study of metal–metal halide solutions was pioneered by Karpachev and co-workers.[5-7] Using carbon as oxidation–reduction electrodes, they reported that the dependence of cell voltage on the concentration of "dissolved" metal indicated that molten solutions of $CdCl_2$, $PbCl_2$ and LiCl reacted with the respective metals to form Cd^0 [5] (or $Cd_2{}^{+2}$), Pb^{+} [7] and Li^0 or $Li_2{}^{+}$ [6] as solutes. In addition, the Ce–$CeCl_3$ system recently has been investigated, using a CeCl–Cl_2 reference electrode, by Senderoff and Mellors.[8] The present paper is concerned with a study of concentration cells with solutions of antimony in SbI_3 and the interpretation of the simple dependence of voltage on the amount of "dissolved" metal for this system.

Experimental

Somewhat different techniques than those previously reported[5] are necessary in the present system. The cell found most suitable for the concentration cell measurements is shown in Fig. 1. The electrodes consist of 1/2'' sections of 1/8'' spectroscopic electrodes (National #L3803) drilled 3/16'' deep from one end and then heated to 1000° *in vacuo* to remove the binder. These slip over 1/16'' tungsten wires which are sealed through the Pyrex cell with uranium glass. The diaphragm is a 10 mm., ultrafine, sintered glass disk; occasionally this was partially fused so as to decrease its area and porosity. Approximate amounts of metal (A. D. MacKay, 99.999%) were placed in the two compartments, with excess in the anode so that the so-called metal-satu-

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[1] Presented at the 135th meeting of the American Chemical Society, Boston, Mass., April 6, 1959. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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[6] S. Karpachev and E. Jordan, *ibid.*, **14**, 1495 (1940).

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