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VII *. REMOVAL OF ETHYLLEAD COMPOUNDS FROM AQUEOUS SOLUTION BY REACTION WITH ZINC

MARTIN H. HITCHEN, A. KENNETH HOLLIDAY and RICHARD J. PUDDEPHATT **
Donnan Laboratories, The University of Liverpool, Liverpool L69 3BX, U.K.

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Summary

Triethyllead chloride in aqueous solution reacts with zinc to give hexaethyllead as the major product. The reaction proceeds in two steps with the removal of soluble organolead species from solutio: being faster than the formation of hexaethyllead. Diethyllead dichloride also gives hexaethyllead on reaction with zinc, and triethyllead(IV) species were detected at intermediate stages of reaction. It is argued that hexaethyllead is not formed by reactions involving compounds with lead—zinc bonds but probably by dimerisation of $Et_3Pb^\cdot$ radicals. The reactions have application in the treatment of effluents from the manufacture of tetraethyllead.

Introduction

Treated effluents from the manufacture of tetramethyllead and tetraethyllead contain organolead species, principally trialkyllead(IV) and dialkyllead(IV) compounds, in the concentration range 10—100 ppm but the concentrations can be dramatically reduced further to less than 2 ppm by treatment of the aqueous effluent with zinc [2]. In Part VI, an investigation of the reaction of aqueous solutions of trimethyllead chloride and dimethyllead dichloride with zinc was reported [1]. It was shown that the final products were lead metal and methane and that the reaction occurred in two distinct steps, the first of which involved rapid removal of the organolead species from solution and the second of which involved slow breakdown of an uncharacterised intermediate to give the final products. It was suggested that complexes containing lead—zinc bonds such as Me_3PbZnX were formed, which underwent a 1,2-alkyl shift from lead

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* Part VI see ref. 1.

** Present address: Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7.

to zinc followed by hydrolysis of the resultant methylzinc compound [1]. In this paper a study of the reactions of triethyllead chloride and of diethyllead dichloride with zinc are reported.

Results

The reaction stoichiometry

Reaction of triethyllead chloride with zinc in 5% aqueous sodium chloride solution occurred to give a yellow oil, subsequently identified as hexaethyldilead. In addition a small quantity of gas was evolved and this was identified as very largely ethane with traces of ethylene, butane and tetraethyllead. This reaction appeared complete after 3—4 h at 40°C. After this the hexaethyldilead slowly reacted further to give ethane and lead metal, and no trace of tetraethyllead was found after 7 days. The yield of hexaethyldilead was later shown to be over 80% in most cases after 3—4 h reaction so that the stoichiometry could be described by eq. 1.

$$2\ Et_3PbCl + Zn \rightarrow Et_6Pb_2 + ZnCl_2 \qquad (1)$$

The rate of removal of triethyllead(IV) species from solution. Table 1 contains results from a study of the rate of removal of triethyllead(IV) species from solution by reaction with zinc. It can be seen that triethyllead chloride was removed more rapidly and completely when the reaction was conducted in an atmosphere of nitrogen than in air. In air, the reaction was accompanied by formation of large amounts of a white precipitate of zinc oxide which was formed by reaction of oxygen with the zinc metal. Triethyllead(IV) species were removed more efficiently when reactions were carried out in 5% aqueous sodium chloride solution than in water, and the rate was slightly higher at 40°C than at 18.5°C. Under optimum conditions, the removal of triethyllead(IV) species was over 60% complete in 5 min and over 90% complete in 15 min. The

TABLE 1

THE RATE OF REMOVAL OF TRIETHYLLEAD CHLORIDE FROM AQUEOUS SOLUTION UNDER VARIOUS CONDITIONS

Time/min	% removal [a]					
	A	B	C	D	E	F
1	17.2	17.3	31.5	32.6	31.2	23.6
3	34.8	27.2	40.1	62.7	42.1	32.0
5	57.3	35.8	68.8	66.5	64.0	51.9
10	81.6	51.4	87.6	85.5	69.6	71.2
15	88.2	56.7	93.9	93.4	74.0	85.1
30	96.3	70.0	98.8	98.8	86.5	95.0
60	97.2	84.7	99.0	99.2	89.8	98.7
180	96.4		100	100		100
1440	97.3	97.2			98.7	

[a] Conditions: A, 5% aqueous NaCl solution, 40°C, air atmosphere. B, aqueous solution, 40°C, air atmosphere. C and D, 5% aqueous NaCl solution, 40°C, N_2 atmosphere. E, aqueous solution, 40°C, N_2 atmosphere. F, 5% aqueous NaCl solution, 18.5°C, N_2 atmosphere. In each case, about 3×10^{-4} moles of Et_3PbCl were dissolved in 100 cm^3 solution and treated with zinc (5 g).

TABLE 2

YIELD OF HEXAETHYLDILEAD AS A FUNCTION OF TIME FROM THE REACTION OF Et_3PbCl WITH Zn [a]

		Time (h)														
		1	2	3	4	5	6	12	18	24	40	48	64	120	168	360
% Et_6Pb_2	A	71	76	82	84		77	71	68	55	32		24			22
	B	68	82			95				62		56		39	36	
	C											56			36	

[a] Initial concentration of Et_3PbCl was 6.05×10^{-4} mol/100 cm^3 solution. Conditions: A, 40°C, 5% aqueous NaCl solution. B, 30°C, 5% aqueous NaCl solution. C, 30°C, aqueous solution.

initial concentration of triethyllead chloride was varied over the range 7.5×10^{-5}—1.1×10^{-2} molar and the rate of removal was found to be essentially independent of the initial concentration within these limits.

In the reaction of triethyllead chloride with zinc in aqueous solution, it was shown that the concentration of chloride in solution did not change while the triethyllead(IV) species was completely removed. Similar results were previously reported in reactions of trimethyllead chloride with zinc [1].

The rate of formation of hexaethyldilead. Some results showing the rate of formation of hexaethyldilead are shown in Table 2. It can be seen that the rate was slower than the rate of removal of triethyllead(IV) species from solution, and hence that an intermediate must be formed on the zinc surface. For example, formation of Et_6Pb_2 was 60% complete in about 30 min, while removal of Et_3Pb^+ from solution was 60% complete in about 5 min under similar conditions (40°C, 5% NaCl solution). The rate of formation and total yield of hexaethyldilead appears to be almost independent of temperature and of the presence or absence of sodium chloride in solution. However, at the lower temperature the decomposition of hexaethyldilead was significantly slower. The yield of hexaethyldilead was essentially independent of the initial concentration of triethyllead chloride over a wide concentration range (Table 3), though there was a large scatter probably due to the heterogeneous nature of the reaction.

Decomposition of hexaethyldilead and tetraethyllead. In 5% aqueous sodium chloride solution hexaethyldilead decomposed slowly to give tetraethyllead and ethane roughly according to eq. 2.

$$Et_6Pb_2 + H_2O \rightarrow Et_4Pb + 2\,C_2H_6\ (+PbO) \qquad (2)$$

In the presence of zinc the decomposition was considerably faster especially during the first day (Table 4), and the composition of products was quite dif-

TABLE 3

THE EFFECT OF CONCENTRATION OF Et_3PbCl ON THE YIELD OF Et_6Pb_2 AFTER 24 h AT 40°C

$10^5[Et_3PbCl]$ mol/100 cm^3	151	121	90.8	60.5	30.3	15.1	7.6	3.0	1.5	0.76
% Et_6Pb_2	73	57	58	42	66	71	71	45	45	67

TABLE 4

THE RATE OF DECOMPOSITION OF HEXAETHYLDILEAD IN 5% AQUEOUS NaCl SOLUTION AT 40°C

Time (days)	% Et_6Pb_2	% Et_4Pb [a]	% C_2H_6 [b]
1 [c]	44.5	43.4	10.2
3 [c]	35.7	52.5	10.3
7 [c]	33.6	54.2	10.9
7 [d]	64.3	21.3	12.5

[a] Calculated using the stoichiometry $2\ Et_6Pb_2 \rightarrow 3\ Et_4Pb + Pb$. [b] Calculated using the stoichiometry $Et_6Pb_2 \rightarrow 6\ C_2H_6$. [c] In the presence of zinc (5 g). [d] In the absence of zinc. In all cases the initial concentration of Et_6Pb_2 was 4.76×10^{-4} mol/100 cm^3 solution.

ferent with more Et_4Pb and less ethane being formed. In addition, treatment of the residual zinc with hydrochloric acid led to the evolution of ethane, detected by GLC-mass spectrometry. These results indicate that the zinc plays a direct role in the decomposition of hexaethyldilead, though this cannot be proved conclusively by these experiments.

Tetraethyllead decomposed only very slowly in the presence of zinc, and the decomposition may occur by reaction with water (eq. 3).

$$Et_4Pb + H_2O \rightarrow Et_3Pb^+ aq + OH^- + C_2H_6 \qquad (3)$$

This would then be followed by further reaction of the triethyllead(IV) species with zinc as described above. Again treatment of the spent zinc with acid liberated more ethane.

It is known [3] that trimethyllead chloride reacts with hexamethyldilead according to the eq. 4.

$$2\ Me_3PbCl + Me_6Pb_2 \rightarrow 3\ Me_4Pb + PbCl_2 \qquad (4)$$

However, under our usual reaction conditions (but in the absence of zinc) we have shown that triethyllead chloride does not react with hexaethyldilead, and hence this type of reaction can be discounted.

Reactions in non-aqueous solvents. Triethyllead chloride did not react with zinc in dry benzene, pyridine, tetrahydrofuran or dimethylsulphoxide. How-

TABLE 5

THE RATE OF DECOMPOSITION OF TETRAETHYLLEAD IN 5% AQUEOUS NaCl SOLUTION AT 40°C IN THE PRESENCE OF ZINC [a]

	Time (days)	
	2	7
% Et_4Pb	93.4	90.7
% Et_3Pb^+	0.16	0.02
% C_2H_6 [b]	1.0	1.7

[a] Initial quantity of Et_4Pb was 15.33×10^{-4} mol/100 cm^3 solution. [b] Calculated according to the stoichiometry $Et_4Pb \rightarrow 4\ C_2H_6$.

TABLE 6

THE RATE OF REMOVAL OF DIETHYLLEAD DICHLORIDE FROM 5% AQUEOUS SODIUM CHLORIDE SOLUTION AT 40°C BY REACTION WITH ZINC AND THE RATE OF FORMATION OF Et_6Pb_2

Time (min)	% Et_2PbCl_2	% Et_3PbCl [a]	% Et_6Pb_2 [b]
1	68	7	
3	56	14	
5	31	19	
10	12	21	
30	1.2	24	
60	0.6	29	10
120	0	24	26
180	0	5	28
240			30
360			27
1440	0	2	22

[a] Calculated based on the stoichiometry 3 $Et_2PbCl_2 \rightarrow 2\ Et_3PbCl$. Initial concentration of Et_2PbCl_2 was 3.31×10^{-4} mol/100 cm^3 solution. [b] Calculated based on the stoichiometry 3 $Et_2PbCl_2 \rightarrow Et_6Pb_2$. Initial concentration of Et_2PbCl_2 was 3.35×10^{-4} mol/100 cm^3 solution.

ever, when the solvents were moistened with water reaction occurred to give mostly hexaethyldilead. Reaction of triethyllead chloride with zinc in dry methanol gave largely tetraethyllead.

Reactions with diethyllead dichloride

Diethyllead dichloride reacted with zinc in aqueous sodium chloride to give hexaethyldilead in moderate yield, in a reaction which was considerably slower than the analogous reaction of triethyllead chloride. At intermediate stages triethyllead(IV) species were formed in solution and reacted further with zinc. The results are given in Table 6 and again clearly show that the final products are formed more slowly than the rate at which diethyllead dichloride is removed from solution.

Reaction of Et_3PbCl/Me_3PbCl mixture with zinc

In this experiment an equimolar mixture of Et_3PbCl and Me_3PbCl in 5% aqueous sodium chloride was treated with zinc at 40° C. The chief product was hexaethyldilead (83% after 4 h) formed as a yellow oil. Methane and ethane (85 : 14 mixture, with about 1% butane and ethylene) together with tetramethyllead and tetraethyllead were detected in the gas phase. Remarkably, the rate of formation and yield of hexaethyldilead and of methane were essentially the same as if pure Et_3PbCl or Me_3PbCl respectively had been used as reagents, and no trace of mixed organoleads such as Me_3PbEt or Et_3PbMe could be found by GLC analysis.

Discussion

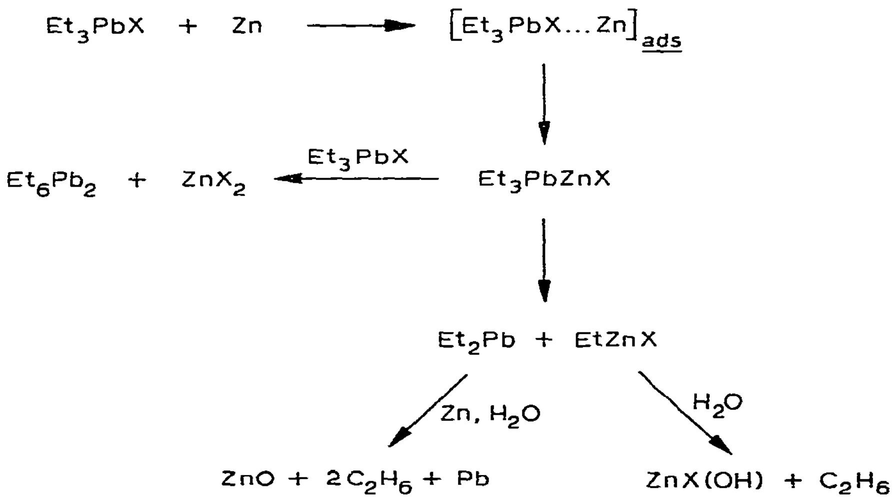
The reactions of triethyllead chloride and of diethyllead dichloride with zinc take place in two stages. The first stage involves the rapid removal of the soluble organolead species from aqueous solution to give uncharacterised species which are strongly bound to the zinc surface. This step is very similar and occurs at a similar rate to that observed in the analogous reactions of methyllead halides with zinc [1]. However, whereas the subsequent slow step in the reaction of trimethyllead chloride with zinc gave largely methane with a half-life of 13—15 h, with triethyllead chloride the chief product was hexaethyldilead and the half-life for its formation was ca. 20 min under similar conditions. In the reaction of trimethyllead chloride with zinc it was proposed that a reactive intermediate Me_3PbZnX was formed (X = Cl or OH) and that this underwent a 1,2-methyl shift reaction to give methylzinc species which were hydrolysed to methane [1]. It is possible to explain formation of hexaethyldilead in terms of an analogous lead—zinc bonded species as shown in Scheme 1.

It is possible to make two simple predictions from Scheme 1. Firstly, since the coupling to give hexaethyldilead occurs in competition with the 1,2-alkyl shift reaction, the yield of hexaethyldilead should increase with increasing initial concentration of triethyllead chloride. No such trend was observed using a wide range of concentrations of triethyllead chloride. Secondly, the coupling should occur equally efficiently with other trialkyllead halides. However the reaction using equimolar amounts of Me_3PbCl and Et_3PbCl failed to give any of the mixed species Et_3Pb—$PbMe_3$ or its expected decomposition products Et_3PbMe and Me_3PbEt [4]. In this reaction the triethyllead and trimethyllead(IV) species appeared to react quite independently. These results are not consistent with the species Et_3PbZnX being an intermediate in the formation of hexaethyldilead.

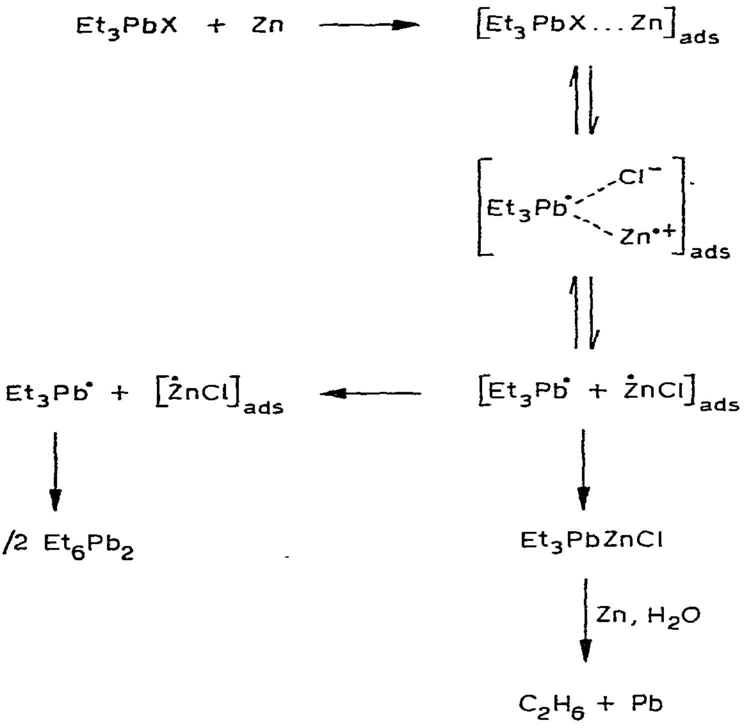
We suggest that the formation of hexaethyldilead is best explained by the mechanism of Scheme 2.

In this scheme, an electron transfer reaction occurs at the zinc surface to yield ultimately caged triethyllead radicals. These can then diffuse away and dimerise to give hexaethyldilead. Alternatively they may combine with the ZnCl radical at the surface to yield $Et_3PbZnCl$, which would then undergo the 1,2-alkyl shift reaction to give ethane after hydrolysis of intermediate ethylzinc

SCHEME 1



SCHEME 2



species. The mechanism is very similar to a mechanism proposed for formation of Grignard reagents from alkyl halides and magnesium [5]. The observation that the yield of hexaethyldilead is independent of the concentration of triethyllead chloride is fully consistent with this mechanism. In addition, if it is assumed that the formation of free $Me_3Pb^{\bullet}$ radicals is unfavorable in the (much slower) reaction of Me_3PbCl with zinc, then the absence of $Me_3Pb{-}PbEt_3$ or its decomposition products from the reaction of a mixture of Me_3PbCl and Et_3PbCl with zinc also follows naturally. It is known tnat $Me_3Pb^{\bullet}$ radicals are formed by reaction of Me_3PbCl with sodium at low temperature [6].

The reaction of diethyllead dichloride with zinc evidently occurs to give first an adsorbed species which then reacts to give a triethyllead(IV) species, and this in turn reacts with zinc to give hexaethyldilead. We would predict that the formation of hexaethyldilead, and particularly the fact that its further decomposition is slow, might cause problems in the treatment of effluents containing triethyllead(IV) species with zinc. In a flow process the droplets of hexaethyldilead might be expected to pass through the zinc column, but in a stirred system it should be easier to remove the hexaethyldilead by extraction into an organic solvent.

Experimental

Et_3PbCl was prepared by reaction of Et_4Pb with HCl in ether at −80°C. Et_2PbCl_2 was prepared by reaction of Et_4Pb with Cl_2 in ethyl acetate at −20°C. Et_6Pb_2 was prepared by reaction of Et_3PbCl with aluminum turnings [4,7].

Analytical methods

Concentrations of Et_3Pb^+ and Et_2Pb^{2+} species in aqueous solution were determined by the dithizone method described previously [1,8]. Zn^{2+} interfered and was removed by complexation with EDTA, and hexaethyldilead was removed from reaction mixtures before analysis by extraction with hexane. Full calibrations were carried out to check the validity of the procedure.

Analysis for hexaethyldilead was carried out either gravimetrically, by extraction into hexane and evaporation of the hexane under vacuum, or spectrophotometrically after extraction into hexane solution. The molar extinction coefficient for Et_6Pb_2 at 325 nm in hexane solution is 5.07×10^3 l mol^{-1} cm^{-1}. In some cases analysis by both methods was carried out and satisfactory agreement was found.

Chloride analyses were carried out by potentiometric titration with silver nitrate solution.

Tetraalkylleads were analysed by GLC using a 2 m column packed with 8% squalene, 2% silicone oil on chromosorb W operating at 126° C. Hydrocarbons were analysed by GLC using a squalene column operating at 43° C. Ethane was analysed quantitatively by normal vacuum line techniques.

Et_3PbCl with zinc

(a) Zinc metal (5 g) was added to a deoxygenated thermostatted solution of Et_3PbCl (3.3×10^{-4} mol) and NaCl (5 g) in distilled water (100 cm^3) under an atmosphere of nitrogen. The mixture was stirred magnetically and aliquots were removed for analysis of Et_3Pb^+ and Et_2Pb^{2+} at suitable intervals through a rubber septum cap using a syringe.

In another experiment in the absence of sodium chloride, the samples were analysed for both organolead species and chloride. Experiments with Et_2PbCl_2 and zinc were carried out in a similar way.

(b) A solution of Et_3PbCl (6.05×10^{-4} mol) and NaCl (5 g) in water (100 cm^3) in a round-bottomed flask fitted with a teflon tap was degassed by several freeze-pump-thaw cycles. Zinc (5 g) was added and the flask was sealed under vacuum. After shaking at 40°C for a predetermined time, the flask was cooled to −78° C and the volatile gases (very largely ethane) were introduced to the vacuum line and estimated quantitatively by volume and then identified by GLC. Hexane (20 cm^3) was added to the frozen solution which was then allowed to warm to room temperature. The hexane extract was then analysed by GLC and then quantitatively for Et_6Pb_2 by spectrophotometry or by gravimetric analysis.

Experiments on the rate of decomposition of hexaethyldilead and of tetraethyllead were carried out in a similar way.

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