Electrochemical synthesis of tetraethyl lead and tetraethyl tin via ethyl zinc intermediates

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Tetraethyl lead and tetraethyl tin were prepared by electrolysing DMF solutions of ethyliodide and ethylbromide in an undivided cell using a zinc cathode and a lead or tin anode. The process involves the cathodic production, probably by a catalytic mechanism, of ethyl zinc compounds which may then react at the anode to form the product. The most favourable feature of the process is the low electrical resistance of the cell, which allows the attainment of a high current density with a very low potential difference applied. The nature and concentration of the ethylhalide used are the main parameters which affect tetraethyl lead and tetraethyl tin formation.

1. Introduction

The reduction of alkyliodides and alkylbromides at sacrificial lead or tin cathodes is the most suitable cathodic process for the synthesis of some lead or tin tetralkylderivatives [1–4]. The electrode reaction involves the fission of carbon–halogen bonds, producing alkyl free radicals which attack and dissolve the cathode, forming organo-metallic derivatives. [5–7].

In principle this process is a desirable alternative to the traditional chemical method by which sodium–lead or sodium–tin alloys are used for providing the energy required for halide reduction.

In practice, the electrolytic process suffers from the limits imposed by the necessity to have an efficient separator between the anode and the cathode compartment. This fact complicates the electrolytic assembly and causes high dissipation of electric power. At tin cathodes, moreover, low yields of tin derivatives are generally obtained for alkylhalides other than methylhalide [6, 8, 9].

In these respects the anodic synthesis of lead or tin organoderivatives is more advantageous. Typical in this field can be considered the electrolysis of Grignard compounds at lead anodes in ethereal solvent for tetraethyl lead preparation, which has found industrial application [1–4]. This process is undoubtedly favoured by the utilization of cheap alkylating materials, the possibility of recycling some materials and the high yields of organolead. In this case too, the poor electrochemical features of the medium, the related fire risk and passivation phenomena for tin anodes [3], are limits not easy to overcome.

The synthesis described in this work may remove some of the problems mentioned above. This synthesis is realized by electrolysis of an alkylhalide in DMF solution between a zinc cathode and a tin anode in an undivided cell.

The process seems of wide utility for the preparation of lead or tin organoderivatives: $Pb(C_2H_5)_4$ and $Sn(C_2H_5)_4$ preparations are reported and discussed in the present paper.

2. Experimental

2.1. *Chemicals*

The reagents for the electrochemical synthesis and the standards for gas chromatographic analysis were all commercially available products and were generally used as supplied.

The electrolytic solvent, dimethylformamide, was stored over $CaCO_3$ and distilled before use. The background electrolytes, $NaClO_4$ and $ZnCl_2$ were dried in a vacuum oven for several hours before use.

Zn, Pb, Sn used for manufacturing the electrodes were of 99% purity.

2.2. *Apparatus and procedure*

A potentiostat (Amel model 557) was employed. Charge was measured with an electronic coulometer (Amel model 558).

Steady state potentiostatic experiments concerning alkyl halide reduction at Zn were performed in a divided cell. The working electrode was a zinc disc, area $\simeq 0.2$ cm^2, which was sealed into a teflon sheath, the secondary electrode was a platinum net and the two electrode compartments were separated by a coarse glass sinter (porosity 2). The reference electrode was an aqueous S.C.E. and was separated from the working electrode by a Luggin capillary and a tap.

Organolead and organotin compounds were prepared in an undivided cylindrical cell sealed at the top by a teflon plug, which was equipped with two glass tubes for degassing the solutions (by nitrogen) and two metallic wires for the electric connections.

The cathode was a cylindrical zinc sheet (dipping area $\simeq 18$ cm^2) surrounding a lead or tin anode (dipping area $\simeq 5$ cm^2).

The cell was generally charged with 25 ml solution (DMF/alkyl-halide/base electrolyte) which was electrolysed at a constant current. The total current ranged from 50 to 200 mA and the required potential was never higher than 3–4 V.

At the end of each run the weight loss of both the electrodes was determined, the organolead or organotin compounds were recovered from the electrolysed solution by extraction with n-hexane and analysis was made by g.l.c. (Perkin Elmer model 3920) on different columns using known standards.

3. Results

3.1. *Steady state experiments*

Steady state current–potential curves obtained at a zinc electrode for different concentrations of ethyliodide and ethylbromide in DMF at 25° C are reported in Figs. 1 and 2 respectively. No mechanism may be easily deduced from Tafel analysis of these curves owing to the large dis-
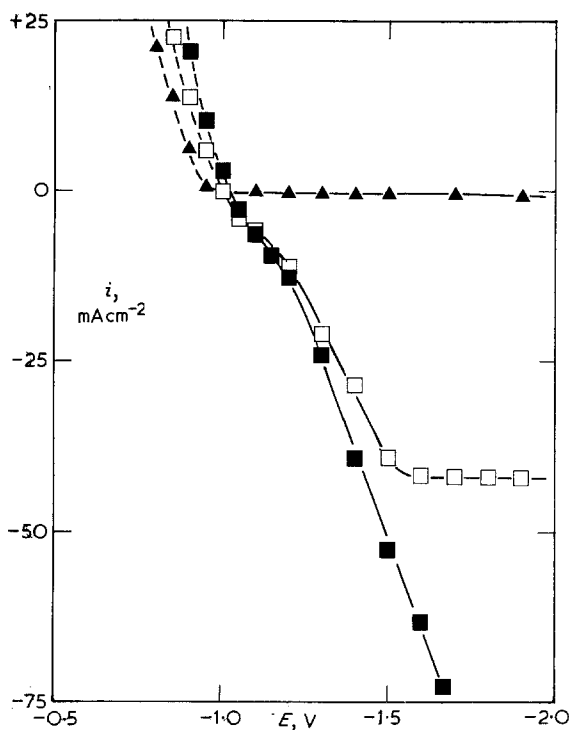

Fig. 1. Steady state current (i)-potential (E) curves for C_2H_5I at zinc electrode in DMF at 25° C. The dotted part of the curves is due to zinc oxidation. C_2H_5I equal to: ■ 0.62 mol l^{-1}; □ 0.31 mol l^{-1}; ▲ 0.00 mol l^{-1}.

solution of the zinc surface at the cathodic potentials. However one can qualitatively observe that:

(a) ethyliodide at zinc gives rise to a very easy cathodic process as is indicated by the large currents obtained at not very negative potentials;

(b) for higher ethyliodide concentrations the reduction process almost overlaps the process of zinc anodic dissolution;

(c) ethylbromide shows, for the same reduction conditions, a much slower reaction than ethyliodide.

3.2. *Preparative experiments*

When a DMF solution of the background electrolyte only (NaClO$_4$ 2%), was electrolysed between a zinc cathode and a lead (or tin) anode, negligible weight loss was observed for the electrodes after the passage of 400 C. On the other hand, when the electrolysis was performed in the presence of ethyliodide, a remarkable dissolution of both the cathode and the anode was observed and tetraethylderivatives of lead (or tin) were found as the main products of the process.
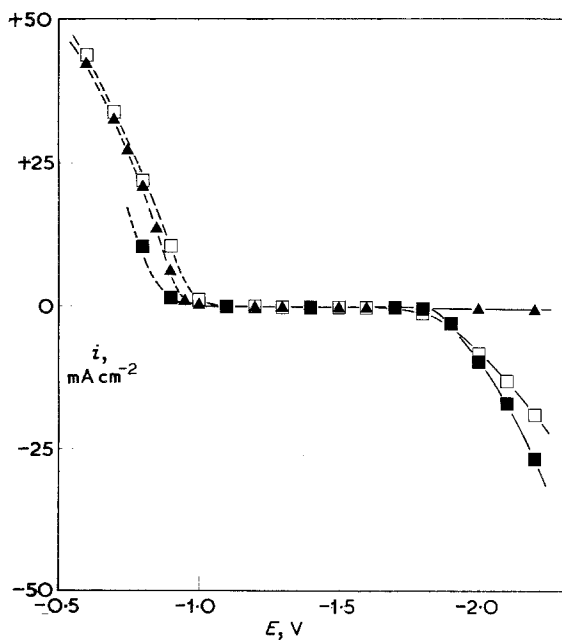
Fig. 2. Steady state i–E curves for C_2H_5Br at zinc electrode in DMF at 25° C. C_2H_5Br equal to: ■ 1·31; □ 0·75; ▲ 0·00 mol l⁻¹.

The synthesis of $Pb(C_2H_5)_4$ was studied as a function of the initial ethylhalide concentration and the quantity of electricity passed into the system. Table 1 gives the weight loss of the electrodes, the number of Faradays involved in lead dissolution and the yield of tetraethyl lead. This last result is given on the basis of both the loss in weight of the lead anode and the quantity of elec-

tricity passed. In this second case, we assumed that 4 moles of electrons were consumed for each mole of $Pb(C_2H_5)_4$ produced.

It is easy to observe that current yields in Table 1 do not substantially vary with the number of coulombs transferred to the system.

On the other hand, the yield of $Pb(C_2H_5)_4$ increases with the initial concentration of ethyliodide present in the system: this parameter determines also the extent of zinc cathode dissolution and seems to affect the number of Faradays involved for each mole of lead anodically dissolved (this number ranges between two and four).

When ethylbromide was used as the alkylating material, lower yields of $Pb(C_2H_5)_4$ were always obtained. In this case some yield improvement could be obtained by increasing the process temperature.

Table 2 illustrates the experimental conditions and the results thus obtained for the synthesis of $Sn(C_2H_5)_4$. The yields are here given on the basis of tin loss only: the current yields practically double these values as tin was constantly dissolved with a stoichiometry of $\simeq 2$ Faradays per mole.

The observations above for the data of Table 1 are substantially valid for the data of Table 2 also. As regards the relation existing between ethyliodide concentration and cathode dissolution, it can be noted further that the ratio (zinc loss/coulombs) tends to decrease with the quantity of electricity passed into the system.

Table 1. Synthesis of tetraethyl lead

Run no.	t (°C)	C_2H_5I (mol l⁻¹)	C_2H_5Br (mol l⁻¹)	Coulombs	Zn Loss (g)	Pb loss (g)	Electrons for Pb dissolution	$Pb(C_2H_5)_4$ Yield based on Pb loss %	$Pb(C_2H_5)_4$ Current yield %
1	20	0·745		270	0·275	0·305	1·90	17·7	37·4
2	30	1·240		150	0·929	0·162	1·98	81·3	164·3
3	30	1·240		240	1·000	0·268	1·93	46·4	95·8
4	30	1·240		400	1·995	0·432	1·98	95·5	193·0
5*	30	1·240		600	0·755	0·467	2·76	88·4	128·2
6	30	1·860		400	1·375	0·312	2·75	88·6	129·0
7	20	2·48		270	1·000	0·300	1·93	55·5	115·0
8	25		1·34	700	0·102	0·371	4·04	7·7	7·7
9	50		2·01	400	0·039	0·227	3·78	10·7	11·4
10	50		2·68	400	0·085	0·400	2·14	9·0	17·0
11,	60		1·34	400	0·077	0·421	2·04	8·0	15·8
12	60		2·01	400	0·185	0·407	2·11	14·4	27·3

Conditions: volume of the electrolysed solutions = 25 ml; total current intensity = 100 mA; support electrolyte = NaClO₄ 0·163 mol l⁻¹. * Current intensity = 50 mA.

Table 2. Synthesis of tetraethyl tin

Run no.	t (°C)	Support electrolyte (mol l⁻¹)	C_2H_5I (mol l⁻¹)	C_2H_5Br (mol l⁻¹)	Coulombs	Zn loss (g)	Sn loss (g)	$Sn(C_2H_5)_4$ Yield based on Sn loss %
13	0	NaClO₄ 0·163	1·240		360	0·561	0·227	19·0
14	20	ZnCl₂ 0·221	1·240		185	0·442	0·128	22·2
15	20	NaClO₄ 0·163	1·240		360	0·196	0·224	15·0
16	20	NaClO₄ 0·163	1·240		720	0·380	0·447	21·7
17	35	NaClO₄ 0·163	0·745		160	0·330	0·108	17·5
18	35	NaClO₄ 0·163	0·990		360	1·180	0·237	49·5
19	35	ZnCl₂ 0·221	1·240		360	1·120	0·231	80·5
20	35	NaClO₄ 0·163	1·490		360	1·950	0·226	74·5
21	35	NaClO₄ 0·163	2·480		360	2·760	0·221	87·0
22*	35	ZnCl₂ 0·21	2·480		650	2·100	0·406	87·5
23	25	NaClO₄ 0·163		1·34	330	0·039	0·204	3·9
24	25	NaClO₄ 0·163		2·01	400	0·054	0·248	4·0
25	25	NaClO₄ 0·163		2·68	400	0·117	0·245	7·8

Conditions: volume of the electrolysed solutions = 25 ml; total current intensity = 100 mA. * Current intensity = 200 mA.

4. Discussion

The results, especially when one considers the weight loss of the zinc cathode in relation to the organolead or organotin obtained, suggest that the synthetic process proposed here involves the production *in situ* of a zinc organoderivative, which may be converted at the anode into the lead or tin organoderivative.

The cathode and anode reactions will be discussed separately, below.

4.1. *Cathode reaction*

Zinc dust and simple alkyliodides may directly react under suitable conditions giving zinc organoderivatives [10], and the data of this work have shown that cathodic polarization increases the reaction rate. This fact may be emphasized at low temperature, for instance at 0° C, when the polarized sheet of run no. 13 (Table 2) lost 0·561 g after 1 h electrolysis, whereas under the same conditions no weight loss resulted from an unpolarized sheet.

It is easy to observe from the data of Tables 1 and 2 that the zinc loss, when compared with the quantity of electricity passed, exceeds that expected assuming the sacrificial cathodic reaction:

$$2 C_2H_5I + 2e + Zn \rightarrow Zn(C_2H_5)_2 + 2I^-. \quad (1)$$
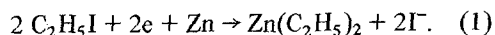
This fact suggests that at cathodically polarized

zinc large amounts of ethylzinc iodide may be formed by an autocatalytic mechanism, similar to that proposed for the reduction of alkyliodides at mercury [11] whereby a product of the reduction initiates a chain chemical process*. The sharpness of the cathodic curves of Fig. 1, which seem reversible for zinc oxidation, would thus be due to the reduction of catalytically formed $C_2H_5Zn^+$.

When the temperature is $\geqslant 10°$ C and at higher concentrations of ethyl iodide, ethylzinc iodide may also be produced by a spontaneous zinc corrosion reaction, which would give an apparent weight loss for the zinc cathode greater than that expected from the amount of charge passed.

Under the conditions above it is clear that zinc alkylation kinetics are more dependent on ethyl iodide concentration than on electrode charge transfer, and this fact explains the dependence of zinc loss on ethyl iodide concentration and its slowing down with the extent of the electrolysis (i.e. as ethyl iodide concentration decreases).

The sacrificial reaction 1 is likely to operate either at low ethyl iodide concentration or when ethylbromide is used as the alkylating material. In this second case, the high energy required for the

* This hypothesis is supported by some recent results which indicate the catalytic activity of the alkyl iodides during the cathodic ethylation of zinc by the electrolysis of ethyl sulphate (G. Mengoli and S. Daolio – *Chem. Comm.*, in press).
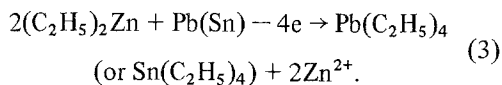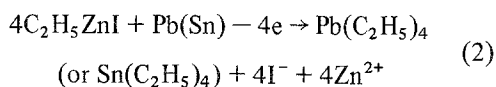
cleavage of the carbon–bromine bond shifts the reduction process of ethylbromide to very negative potentials (see Fig. 2), at which the alkyl radicals involved in metal–alkyl formation may be competitively reduced [1–4], with a consequent poorer production of zinc organoderivatives.

Since the cathodic production of zinc alkyls is here coupled to their utilization at the anode with consequent production of Zn^{2+} ions, these may be engaged in the cathode reaction as the electrolysis goes on. This fact has surely an unfavourable effect when ethylbromide is used, but with ethyliodide (which is mainly reduced catalytically), the cathode reaction may thus recycle some zinc without affecting its alkylation. An indication of this is given by runs no. 14, 19, 22 of Table 2 which were performed using $ZnCl_2$ as background electrolyte.

4.2. Anode reaction

$Pb(C_2H_5)_4$ and $Sn(C_2H_5)_4$ synthesis, realized in this work by electrolysis of organozinc compounds at lead and tin anodes, shows many similarities to the electrolytic process, mentioned in the introduction, which utilizes preformed organomagnesium compounds.

If the mechanism commonly adopted for the Grignard electrolytic process [1–4] is assumed, the possible anode reactions here could be:

$$4C_2H_5ZnI + Pb(Sn) - 4e \rightarrow Pb(C_2H_5)_4$$
$$(or\ Sn(C_2H_5)_4) + 4I^- + 4Zn^{2+} \quad (2)$$

$$2(C_2H_5)_2Zn + Pb(Sn) - 4e \rightarrow Pb(C_2H_5)_4$$
$$(or\ Sn(C_2H_5)_4) + 2Zn^{2+}. \quad (3)$$

However, the stoichiometry of the consumption of lead and particularly of tin is below 4 moles of electrons per mole of metal dissolved[†]. It therefore seems unlikely that at the anode organozinc compounds are directly oxidized to alkyl free radicals. More probably the halide ions freed at the cathode or the complex anions formed from ethyl zinc halides [3] catalyse the direct oxidation of the

[†] It has to be noted that in the electrolysis of Grignard compounds, less than 4 Faradays may be engaged for the sacrificial dissolution of lead [3].

anode, providing the required form of the recipient metal.

In any case, the process is complex since a two electron oxidation of the metal (tin was dissolved according to such stoichiometry in every case) should at best give a 50% yield of tetraethylderivative, and this value was often exceeded (see Tables 1 and 2). One may suggest the possible occurrence of parallel non-electrochemical routes to the alkylation of lead and tin [13].

5. Conclusion

The preparation of $Pb(C_2H_5)_4$ and $Sn(C_2H_5)_4$ proposed in the present paper offers an interesting comparison with the electrolytic synthesis using Grignard compounds.

Other than the production in situ of the reactive zinc alkyls, the favourable features of the method are due mainly to the utilization of a solvent particularly suitable for organozinc derivatives [10] and at the same time of good electrochemical properties. This fact allows the attainment of high current densities with very low voltage differences applied and without any passivation phenomena. Owing to the polarity of the media it is possible, moreover, to recover lead and tin organoderivatives by extraction with an hydrocarbon solvent.

At present, the utilization of an expensive alkylating material (the best results were obtained with ethyliodide) and the large dissolution of the zinc cathode are the most serious handicaps of the process. The first advantage could probably be eliminated by using a smaller amount of ethyliodide in the presence of an excess of ethylbromide (this procedure is possible in the chemical synthesis of zinc alkyls). A reduction of ethyliodide concentration would also reduce the second disadvantage, the excessive zinc dissolution.

It has to be noted, moreover, that zinc derivatives were always formed here in large excess of the stoichiometry necessary for the anode process. A suitable geometry of the electrolytic cell, with a smaller separation of the electrodes and an increase of the ratio electrode surface/volume of solution, would allow the use of more dilute solutions of ethylhalide and a strong reduction of zinc loss might be obtained without affecting the $Pb(C_2H_5)_4$ or $Sn(C_2H_5)_4$ yield.

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