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ANODIC ETHYLATION OF LEAD BY CATHODICALLY PRODUCED DIETHYLCADMIUM

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Summary

Tetraethyllead was prepared by electrolysing DMF or DMSO solutions of ethyl iodide and ethyl bromide in an undivided cell equipped with a cadmium cathode and a lead anode. Ethylcadmium intermediates are produced at the cathode, and react with the anode to form the product.

The yield of tetraethyllead synthesized this way is mainly determined by the cathodic formation of the ethylcadmium intermediates: when this reaction is favoured by either a high concentration of the ethyl halide or by use of a temperature of ca. 50° C, the yield of tetraethyllead is greatly increased.

It is known that diethylcadmium is employed as alkylation agent for the manufacture of tetraethyllead from lead acetate and triethylaluminium [1—3]. Only half of the lead present in lead acetate is utilized at the first stage of that process (eq. 1) but complete conversion of the residual metallic lead is achieved

$$4\,AlEt_3 + 6\,Pb(OAc)_2 \rightarrow 3\,Pb + 4\,Al(OAc)_3 + 3\,PbEt_4 \qquad (1)$$

$$Pb + 2\,EtI + CdEt_2 \rightarrow PbEt_4 + CdI_2 \qquad (2)$$

in the subsequent stage (eq. 2). The diethylcadmium required by this second stage is prepared by treatment of cadmium iodide with triethylaluminium. Alkylcadmiums may also be prepared electrochemically [4,5] by the sacrificial cathodic process (eq. 3).

$$RI + 2e \xrightarrow{Cd} CdR_2 + 2\,I^- \qquad (3)$$

Thus we have devised an electrolytic system whereby diethylcadmium synthesized in this way in an undivided cell is used for alkylating a lead anode. Such a system would bring about reaction 2 anodically, giving the advantage of an "in situ" production of the diethylcadmium intermediate.

We describe below the results obtained on electrolyzing ethyl iodide (or

TABLE I

SYNTHESIS OF TETRAETHYLLEAD

Conditions: Volume of the electrolysed solution 25 ml; support electrolytes NaI/TBAP

Run No.	Solvent	EtI (mol l^{-1})	EtBr (mol l^{-1})	T (°C)	Coulombs	Cd loss (g)	Pb loss (g)	Pb dissolved/Faraday (mol Faraday^{-1})	PbEt$_4$ % yield based on Pb loss
1	DMF	0.25	—	25	400	0.02	0.24	0.27	5.3
2	DMF	1.25	—	25	400	0.20	0.42	0.50	20.6
3	DMF	1.87	—	25	400	0.28	0.45	0.52	33.3
4	DMF	0.62	—	35	465	0.20	0.36	0.36	23.9
5	DMF	1.25	—	35	250	0.21	0.27	0.51	33.8
6	DMF	1.25	—	35	420	0.29	0.45	0.50	30.5
7	DMF	1.25	—	35	650	0.42	0.46	0.33	39.7
8	DMF	1.25	—	35	810	0.60	0.78	0.45	37.3
9	DMF	0.25	—	45	400	0.10	0.38	0.45	9.8
10	DMF	1.25	—	45	400	0.11	0.46	0.54	50.1
11	DMF	1.87	—	45	330	0.40	0.37	0.51	63.0
12	DMSO	1.25	—	25	350	0.19	0.36	0.50	22.3
13	DMSO	0.25	—	35	350	0.28	0.38	0.51	27.5
14	DMF	0.12	6.7	55	420	0.34	0.34	0.38	19.2
15	DMF	—	6.7	55	460	0.20	0.23	0.24	19.2
16	DMSO	—	6.7	55	440	0.34	0.38	0.41	29.1
17[a]	DMF	1.25	—	25	360	0.57	0.10	0.13	11.2

[a] With addition of ethylenediamine $\simeq 10^{-1}$ mol l^{-1}.

ethyl bromide) in an aprotic medium between a cadmium cathode and a lead anode.

Experimental

The preparative electrolyses were performed amperostatically with a current of 50 mA, using an electrolytic cell which consisted of a simple glass cylinder. The anode was a rolled lead sheet in the form of a cylinder (the immersed area facing the cathode was $\simeq$17 cm^2) surrounding the cathode which was a cadmium rod (the immersed area was $\simeq$8 cm^2): the distance between the electrodes was 0.5 cm.

The cell was usually charged with 25 ml of solution and the system was degassed by nitrogen.

The tetraalkyllead formed was determined by gas-chromatographic analysis after extraction from the electrolyzed solution with n-hexane.

Current potential curves (i/E) for the reduction of either ethyl iodide or cadmium ions were obtained potentiostatically in a divided cell [6] using a cadmium stationary microelectrode and a SCE reference electrode.

All the materials used were commercially available reagent grade chemicals.

Results and discussion

When 25 ml of a dimethyl formamide (DMF) or dimethylsulfoxide (DMSO) solution containing ethyl iodide (EtI) 10% and NaI 5%, or tetrabutylammonium perchlorate (TBAP) as background electrolyte were left for several hours in the cell described above, no weight loss for the anode and a negligible weight loss for the cathode were observed if no electric current was fed into the system. In contrast, when the same solution was electrolyzed at constant current (50 mA) substantial dissolution of the electrodes took place, and tetraethyllead was found as the main product.

The yield of tetraethyllead was studied as a function of the quantity of electricity passed, the temperature and the ethyl halide concentration. The results are reported in Table 1.

The production of tetraethyllead seems independent of the quantity of electricity within the electrolysis times of the runs reported in Table 1 (runs 5—8). The optimum yields are reached with high concentrations of EtI (runs 1—13) and temperatures slightly above ambient.

As there is initial deficiency of the cadmium derivative required by the reaction 2, the step controlling the yield of the whole process must be the cathodic one. Indeed both EtI and temperature may affect the ethylcadmium intermediate formation for the following reasons:

(a) The diethylcadmium produced at the cathode is subsequently engaged by reaction 2, wherein Cd^{2+} ions are freed. It is thus clear from Figs. 1 and 2 (which show the curves obtained for the reduction of EtI and Cd^{2+}, respectively) that under galvanostatic conditions Cd^{2+} ions rather than EtI may be reduced at the cathode: this trend may be reversed on increasing EtI and temperature.

(b) If diethylcadmium is produced only according to the stoichiometry of

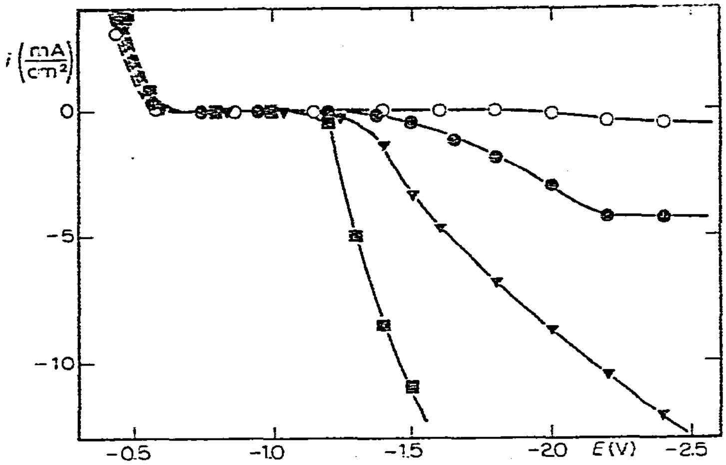

Fig. 1. Steady state current (i) potential (E) curves for EtI at cadmium electrode in DMF at 25°C with TBAP electrolyte. The dotted part of the curves is due to cadmium oxidation. EtI equal to: ■ 0.62 mol l^{-1}; ▼0.31 mol l^{-1}; ● 0.12 mol l^{-1}; ○ 0.00 mol l^{-1}.

reaction 3, not more than 0.5 moles of cadmium will dissolve for each mole of electrons passed. However, from the loss in weight of the cathode reported in Table 1 it can be deduced that this is not generally the case, the above stoichiometry often being exceeded. Indeed, if some Cd^{2+} ions were not been recycled by the cathode the weight loss would be higher.

Thus, chemical steps strongly dependent on concentration and temperature are possibly involved in the sacrificial formation of ethylcadmiums, as is the

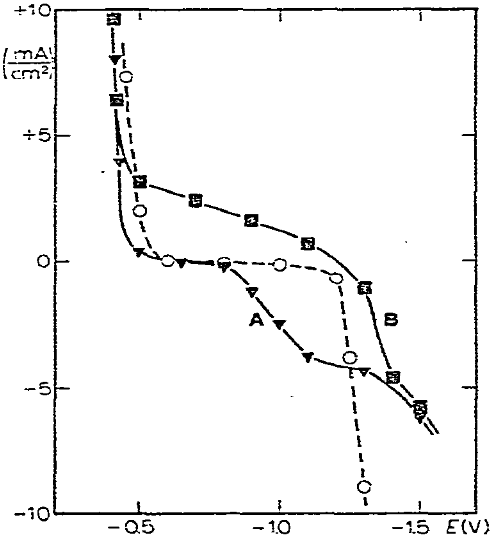

Fig. 2. Steady state current-potential curves for Cd^{2+} reduction at the cadmium electrode in DMF with TBAP base electrolyte. The dotted curve (○) shows the reduction of EtI (0.62 mol). Curve A (▼): Cd^{2+} = 6.5 × 10^{-2} mol l^{-1}; Curve B (■): Cd^{2+} = 6.5 × 10^{-2} mol l^{-1} in the presence of ethylenediamine 0.3 mol l^{-1}.

case in the reduction of either benzyl iodide at mercury [7] or simple alkyl iodides at zinc [8]. Use of very high concentrations of the alkylating agent and a temperature of 55° C enabled us to obtain significant yields of tetraethyllead even from ethyl bromide (runs 14—16), although EtBr is much more resistant to electrochemical reduction than EtI.

With regard to the alkylation of the lead anode, we must consider at least two routes for reaction 2:

(a) heterogeneous reaction. This involves the direct oxidation of ethylcadmium at lead with production of ethyl free radicals, which in turn react with the anode: lead derivatives at a lower alkylation stage are thus produced, and on dissolution undergo further alkylation by EtI.

(b) homogeneous reaction. This takes place between diethylcadmium and some oxidized form of lead (e.g. Pb^{2+}) directly provided by the anode.

The data on loss in weight of the lead reported in Table 1 show a dissolution stoichiometry ranging from 0.25 to 0.5 moles dissolved for each mole of electrons passed, indicating the operation of more than one process.

The results show although alkylcadmiums are less effective than alkylmagnesiums [6,9,10] and alkylzincs [11] for electrochemical synthesis of tetraalkyllead, cathodically produced diethylcadmium may satisfactorily alkylate a lead anode above room temperature. In principle if Cd^{2+} ions freed by reaction 2 should be partially inhibited from cathodic reduction by a suitable complexing agent (see Fig. 2 curve b), either milder reaction conditions or cheaper alkylating agents (EtBr) might be utilized satisfactorily. However, the weight loss of the electrodes in the explorative run 17 of Table 1, shows that in the presence of 0.1 *M* ethylenediamine the cathodic formation of diethylcadmium at 25° C is apparently increased but the extent of alkylation of the lead anode is not increased.

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