Use of Diethyl Sulphate for the Anodic Synthesis of Tetraethyltin *via* Alkylzinc Intermediates

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Summary Tetraethyltin was prepared by electrolysing diethyl sulphate between a zinc cathode and a tin anode.

THE alkylzinc sulphates[1] are useful alkylating agents which may be prepared either by a two-stage process *via* alkylzinc iodides,[2] or by direct reaction of zinc dust with dialkyl sulphates at $\geqslant$ 100 °C in the presence of small amounts of dialkylzinc or alkyl iodide.[2] The reaction between a metal and an organic compound (RX) very often involves the reduction of the R–X bond with formation of alkyl radicals which may attack the metal and produce organometallic compounds. When the metal is zinc, galvanic catalysts (*e.g.* the zinc–copper couple[3]) are generally used; however, we now report that the reaction may also be promoted by cathodic polarization.

When a zinc sheet was used as a cathode in a divided cell containing diethyl sulphate and tetrabutylammonium perchlorate as support electrolyte (the presence of an electrolytic solvent is not necessary), sacrificial dissolution of the metal was observed, which increased on addition of catalytic amounts of ethyl iodide. This cathodic process was further coupled to an anodic process which can use the reactivity of the zinc alkyls produced at the cathode.

A set of experiments was performed by electrolysing under various conditions diethyl sulphate in an undivided cell between a zinc cathode and a tin anode (distance of the electrodes $\leqslant$0·5 cm). Thus tetraethyltin was synthesised by a single process using a cheap starting material. Low yields generally resulted when diethyl sulphate without any additive was used; *e.g.* after the passage of 400 coulombs into 25 ml of $EtSO_4$ at 80—90 °C, the current yield of $SnEt_4$ formation was not higher than 12%. (The current yields were computed by assuming the formal utilization of 4 electrons for each $SnEt_4$ molecule produced).[4] When catalytic amounts of ethyl iodide were added to the system, tetraethyltin formation was strongly favoured. Using the above conditions, the presence of 0·062 mol l^{-1} EtI increased the yields to 52%; this fact was only in part due to the ethylzinc iodides in the anode reaction as the yields did not increase on varying EtI from 0·062 to 0·248 mol l^{-1}.

In the absence of EtI, the production of $SnEt_4$ at the anode is limited by a poor production of zinc alkyls at the cathode: a low steady-state current was in fact recorded for the Et_2SO_4–TBAP system at a zinc microelectrode. When EtI is present, the easy reduction of the R–I bond shifts the cathode process to more positive potentials and causes a strong increase to the steady-state current; under these conditions Et_2SO_4 takes part in the formation of zinc alkyls mainly by a catalytic mechanism of the type shown in equations (1)—(3).[5]

$$EtI + e + Zn \rightarrow EtZn^{\cdot} + I^- \tag{1}$$

$$EtZn^{\cdot} + Et_2SO_4 \rightarrow EtZn^+ + EtSO_4^- + Et^{\cdot} \tag{2}$$

$$Et^{\cdot} + Zn \rightarrow EtZn^{\cdot} \tag{3}$$

A positive indication of the occurrence of these radical-exchange processes was obtained from experiments using propyl iodide as catalyst. Even if Pr^nI is primarily reduced at the cathode, mixed ethyl–propyl tin compounds were always obtained.

When Pr^nI was in higher concentrations (0·51 mol l^{-1}) mainly tetrapropyltin was formed. (The current yields were: 29% for $SnPr^n_4$; 32·2% for mixed compounds; 2·5% for $SnEt_4$). When conversely Pr^nI was in lower concentrations (0·102 mol l^{-1}) mainly tetraethyltin was formed. (The yields were: 4·1% for $SnPr^n_4$; 51% for mixed compounds; 32·6% for $SnEt_4$).

It is expected that the process described here for tetraethyltin may be extended to the preparation of other alkyltin derivatives (symmetrical or not), by using different sulphates and varying alkyl iodides.

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