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Short communication

ANODIC SYNTHESIS OF TETRAMETHYLTIN AND HEXAMETHYLDITIN VIA METHYLZINC INTERMEDIATES

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It is known that zinc and simple alkyl iodides react very easily forming alkyl zinc iodides and dialkyl zinc [1]. The use of galvanic couples for catalyzing this reaction [2,3] suggests that some electrochemical step is initially involved.

Evidence that the process can be electrochemically promoted was obtained in this work by the following experiments:

(1) A zinc microelectrode was potentiostatically polarized in DMF solutions containing $NaClO_4$ as background electrolyte and varying amounts of CH_3I. The resulting steady state curves *i—E* reported in Fig. 1 emphasize the easy reduction of CH_3I at zinc.

(2) Two similar zinc sheets (weight 10 g) were dipped under nitrogen in two cells thermostatted at 0°C, containing a DMF solution 10% of CH_3I and 2% of $NaClO_4$. Only one sheet was cathodically polarized allowing 100 mA constant current to pass through the cell. After 1 h this sheet had lost 1.120 g and zinc alkyl was formed, whereas the weight of the unpolarized sheet remained practically unchanged.

The shape of the cathanodic system of Fig. 1, as well as the dissolution of the polarized zinc, which largely exceeds what is provided by the sacrificial cathodic formation of organocompounds suggest that:

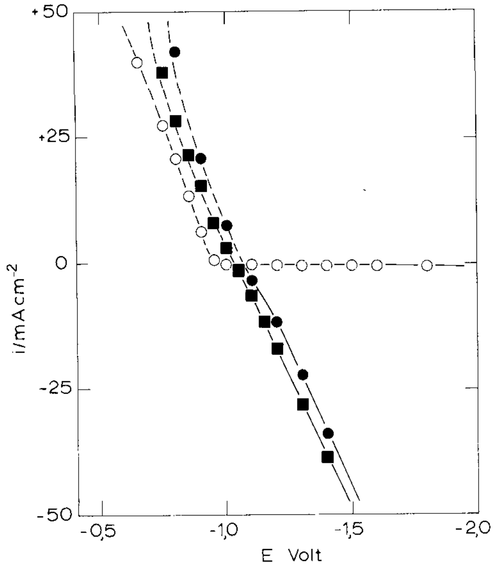
(a) the cathodic currents of Fig. 1 are at least in part due to the reduction of chemically pre-formed methyl zinc iodides;

(b) these methyl zinc iodides are probably produced by a mechanism which is catalysed by zinc cathodic polarization.

The mechanism might be similar to one of those suggested for explaining similar effects during the reduction of organic iodides at mercury: that is either an autocatalytic process whereby a product of the reduction facilitates further chemical steps [4], or the simpler mechanism proposed by Brown et al. [5].

At cathodically polarized zinc it is possible that zinc alkyls are also formed by the electrochemical process:

$$2CH_3I + 2e + Zn \rightarrow Zn(CH_3)_2 + 2I^- \qquad (1)$$



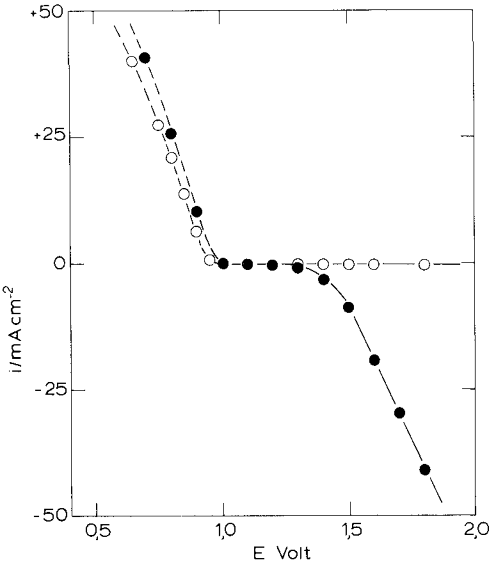


Fig. 1. Steady state current (*i*) potential (*E*) curves for CH_3I at zinc electrode in DMF at 25° C. The dotted part of the curves is related to zinc oxidation. [CH_3I] equal to: (■) 0.650 mol l^{-1}; (●) 0.325 mol l^{-1}; (○) 0.000 mol l^{-1}.

Fig. 2. Steady state *i*—*E* curve for (●) [CH_3Br] = 1.35 mol l^{-1} at zinc in DMF at 25° C; (○) $NaClO_4$ (2%) in DMF.

as in the reduction of some RX compounds at sacrificial cathodes of lead and tin [6—9]. This seems to be the case when the strength of alkyl—halogen bond is increased and halide reduction at zinc becomes far less easy, as for CH_3Br (see Fig. 2). Methyl zinc compounds are formed by macroscale reduction in this case too: the stoichiometry of their production is mainly in agreement with reaction (1) and no autocatalysis seems to be operating.

Following these results, the object of this work was to couple the cathodic formation (electrocatalysis and electrosynthesis) of zinc alkyls to an anodic process which may lead to the synthesis of other organometallic compounds by using the zinc derivatives as alkylating material. The process would have some similarities with the electrolytic tetralkyl lead industrial synthesis which uses Grignard compounds as alkylating material at lead anodes in ethereal solutions [6—9]. To this purpose CH_3I and CH_3Br solutions in DMF were amperostatically electrolyzed between a zinc cathode (a rolled sheet) and a tin anode (a rod) inside the cathode at the average distance of 0.5 cm.

The different conditions of the runs and the results thus obtained are reported in Table 1. Tin organo derivatives were extracted by *n*-hexane at the end of each run, and were determined by v.p.c. analysis.

High yields of tetramethyltin and not negligible amounts of hexamethylditin were generally obtained. The yields are given on the basis of the loss in weight of the tin anode; for tetramethyltin the current yields, based on the

TABLE 1

Anodic synthesis of tin organoderivatives

Conditions: Volume of the electrolyzed solutions 25 ml; total current intensity 100 mA; t 25° C; base electrolyte $NaClO_4$ 2%.

Run	Coulombs	$[CH_3X]$ /mol l^{-1}	Zn loss /g	Sn loss /g	$Sn(CH_3)_4$		$Sn_2(CH_3)_6$ Yield based on Sn loss/%
					Current yield /%	Yield based on Sn loss/%	
1	360	0.405(CH_3I)	0.325	0.224	99.1	49.0	2.2
2	360	0.810(CH_3I)	0.676	0.223	186.3	92.4	5.7
3	360	1.620(CH_3I)	1.641	0.224	166.2	82.1	11.3
4	360	2.580(CH_3I)	3.112	0.215	187.6	92.7	5.5
5	185	1.620(CH_3I)	1.270	0.118	187.8	90.5	7.6
6	250	1.620(CH_3I)	1.350	0.162	185.0	87.9	5.2
7	660	1.620(CH_3I)	1.920	0.399	136.1	69.1	4.8
8 [a]	690	1.620(CH_3I)	1.750	0.379	103.4	57.9	4.8
9	300	1.050(CH_3Br)	0.070	0.200	47.1	21.7	—
10	540	0.510(CH_3Br)	0.155	0.301	36.9	19.3	—

[a] Base electrolyte $ZnCl_2$ 3%.

formal stoichiometry:

$$4CH_3ZnI - 4e + Sn \rightarrow Sn(CH_3)_4 + 4Zn^{2+} + 4I^- \qquad (2)$$

are given too.

Current yields are generally twice those based on tin loss as this one does not agree with the stoichiometry of reaction (2), but needs two electrons only for tin atom dissolved: this fact leads us to think that the anode reaction provides the required oxidation form of the recipient metal more than a direct oxidation of zinc organo derivatives.

However, the anode process is in some manner related to the products of cathode reaction since no decrease of the anode weight was verified when electrolyzing the system DMF/$NaClO_4$ alone.

It must be noted that as the electrolysis goes on the cathode reaction provides also some recovery of Zn^{2+} formed by reaction (2).

Preliminary experiments have shown that the process described here may be used for the synthesis of other organotin or organolead compounds.

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