Electrochimica Acta, 1973, Vol. 18, pp. 369–372. Pergamon Press. Printed in Great Britain

CATHODIC SYNTHESES OF TIN ALKYLS—II. REDUCTION OF SIMPLE ALKYL HALIDES

O. R. BROWN, E. R. GONZALEZ and A. R. WRIGHT
Electrochemistry Research Laboratory, School of Chemistry, University, Newcastle-on-Tyne, England

(*Received* 26 *October* 1972)

Abstract—In ethanolic solution methyl iodide reduces on tin cathodes to tetramethyltin but ethyl halides do not yield the corresponding tin ethyls except in insignificant yields. Increases in alkyl halide concentrations improve the yields of tin alkyls and also increase the passivation of the surface towards the reduction. The distribution of gaseous products from ethyl iodide reduction indicates the formation of small concentrations of free ethyl radicals at less negative potentials. Electrodes directly immersed in the catholyte are inactive and require cathodic polarisation in the background medium to improve activity.

INTRODUCTION

Although the reduction of alkyl halides in various solvent systems has been used successfully to synthesis alkyls of lead[1–3] and mercury[4, 5] from cathodes of those metals there is little information on analogous reactions at tin cathodes. Ulery[1] made brief mention of the reduction of methyl bromide to tetramethyltin in acetonitrile solutions and Vance[6] noted the attack of tin cathodes during the reduction of methyl iodide in *dmf* solutions. Neither of these authors reported the efficient preparation of higher tin alkyls by the cathodic reduction of halides. The present study was undertaken to find if the method could be extended beyond the methyl halides.

EXPERIMENTAL

Ethanol was chosen as solvent principally because it dissolves tetraethyltin, tetramethyltin, sodium iodide, tetrabutyl-ammonium iodide and ethyl iodide without reaction and is an adequate proton source for any carbanions which form. It was obtained as the constant boiling fraction on distilling absolute alcohol (James Burroughs Co.). Ethyl iodide, ethyl bromide, methyl iodide were used directly as received from B.D.H. Tin cathodes used in preparative and kinetic studies are described in part one[7]. All potentials were measured and are quoted here with respect to a calomel/saturated KCl aq. reference electrode separated from the Luggin capillary by a liquid junction in a closed tap. In all experiments 3-compartment cells were used, the anolyte and catholyte (volume 10^2 cm^3) being separated by a fine porosity glass frit.

Analysis of tetramethyltin and tetraethyltin were carried out by comparison with standard materials (B.D.H.) using G.L.C. An F and M 810 instrument was employed with a 6 mm × 1·3 m column of Apiezon L (25%) on Chromosorb W (60/30) and a 6 mm × 2 m column of 10% GESE 52.

Gas analysis was performed by adjusting the nitrogen flow rate through the catholyte to a fixed value measured on a soap bubble flowmeter at the exit point. Then, at 10 min intervals, during a run the gas was sampled and analysed by G.L.C. Also the solution was analysed by G.L.C. before an electrolysis and at its end. By integrating the gas analysis data graphically for each component and adding the solution contribution it was possible to determine the total amounts of butane, ethane and ethylene produced during an electrolysis.

Potentiostats and other electrochemical instruments used in this study were designed and constructed in these laboratories.

RESULTS

When 0·1 M solution of ethyl iodide in 0·5 M sodium iodide was electrolysed at −1·9 V currents were much lower than the expected value of the diffusion limiting current but appreciably higher than the background current. When a charge had been passed, equivalent to one faraday per mole of ethyl iodide initially present in the catholyte, currents were still more than half the maximum value which had been reached during the electrolysis. No perceptible attack of the tin cathode surface had occurred and tetraethyltin was undetectable. Analysis of gas evolved from the cathode during electrolysis showed butane, ethane and ethylene to be present.

0·1 M solutions of ethyl iodide were also electrolysed using 0·3 M TBAI or a mixture (0·5 M NaOH/0·5 M NaI) as electrolytes. In both cases no metal alkyls were formed, the three hydrocarbons being

the only products. Similarly when a 0·1 M solution of ethyl bromide in 0·5 M sodium iodide was reduced no measurable ($>10^{-4}$g) weight loss was incurred by the cathode after the passage of 330 C. However when ethyl iodide was itself used as solvent with 0·16 M TBAI electrolyte, 180 C caused a weight loss of 3·8 mg from the tin cathode corresponding to a current yield of 7 % for tetraethyltin, a fact that was confirmed by G.L.C. analysis of the catholyte. In this run currents were lower even than those observed in ethanolic solutions and, in order to carry out the experiment in a reasonable time, a potential of −2·1 V was applied.

By contrast, when methyl iodide (0·1 M in 0·5 M NaI in ethanol) was reduced a 25 % current yield of tetramethyltin was obtained. This figure is based on weight loss from the cathode and an assumption of the nature of the product. G.L.C. analysis of the gas stream showed methane and ethane both to be present. A dark grey film formed on the cathode surface. Once again currents were so low that −2·1 V was used for the reduction. This was also the case when, in a subsequent run, the methyl iodide concentration was 5·0 M. Then a 73 % current yield of tetramethyltin was established both by weight loss and by G.L.C. analysis of the catholyte.

Three preparative experiments were carried out to detemine the effects of electrode potential and ethyl iodide concentration on the yields of the gaseous reduction products in that system when 0·5 M NaI was used as electrolyte. The results are given in Table 1.

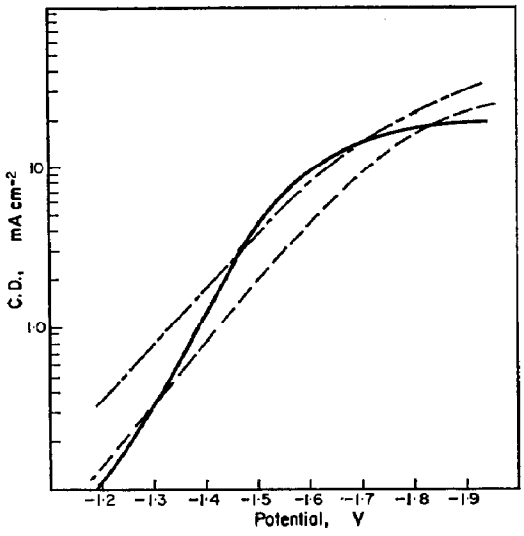


Fig. 1. Polarisation curves for solutions of ethyl iodide in 0·5 M sodium iodide, measured at a disc rotation speed of 75 rad/s and scan rate of 30mV/s.
—— 0·1 M EtI, — · — · 1·0 M EtI (first scan); - - - - 1·0 M EtI (repeat scan).

in an EtI reduction current density of 1·6 mA cm^{-2} at −1·8 V. This current did not rise with time. For subsequent kinetic measurements electrodes were fully activated by pre-electrolysis for two h.

Such an activated electrode was used to record polarization curves between −1·2 V and −1·9 V after the solution had been made 0·1 M in ethyl iodide. Then without opening the cell the reactant concentration was increased to 1·0 M and the scan repeated. After a few minutes the scan was again repeated and the currents were seen to have decreased with time (Fig. 1).

Table 1

Electrode V	EtI concentration M	Charge passed C	Amount of butane μmol	Amount of ethane μmol	Amount of ethylene μmol
−1·5	0·1	95	145	276	33
−1·8	0·1	220	608	471	41
−1·8	1·0	79	354	80	36

In the kinetic experiments it was noticed that the activity of the tin cathode towards ethyl iodide reduction in NaI solution was conditioned by the time spent in pre-electrolysis at cathodic potentials in the background electrolyte. This observation accounted for apparently irreproducible behaviour in early preparative runs. Pre-electrolysis in the background solution for 2 h at −1·9 V enabled subsequent currents at −1·8 V, after the addition of ethyl iodide to a concentration 0·1 M whilst holding the electrode at −1·4 V, to reach quickly a limiting value of 50 mA cm^{-2} at a rotation speed of 37 rad/s. When shorter pre-electrolysis times were chosen the currents subsequent to ethyl iodide addition were lower and took much longer to rise whereas pre-electrolysis for only one minute resulted

In order to test whether electrode activation was caused by the incorporation of sodium cations into the tin lattice[8], the activation programme was repeated with a freshly polished tin electrode, using 0·5 M TBAI in place of sodium iodide. However in this case only 10 min at −1·9 V were sufficient to cause the subsequent current after the addition of ethyl iodide (0·1 M) to reach almost its diffusion controlled limit at −1·9 V.

Finally using 0·5 M TBAI electrolyte the reaction order was explored by making gradual additions

of ethyl iodide so that solutions of strengths 10^{-2}, 3×10^{-2} and 10^{-1} M were examined. Sweeps were commenced at −1·9 V and carried out in an anodic direction. Results are given in Fig. 2. At low current levels rotation speed changes were without effect In the dilute solutions limiting currents were shown, by their rotation speed dependence, concentration dependance and magnitude, to be diffusion controlled.

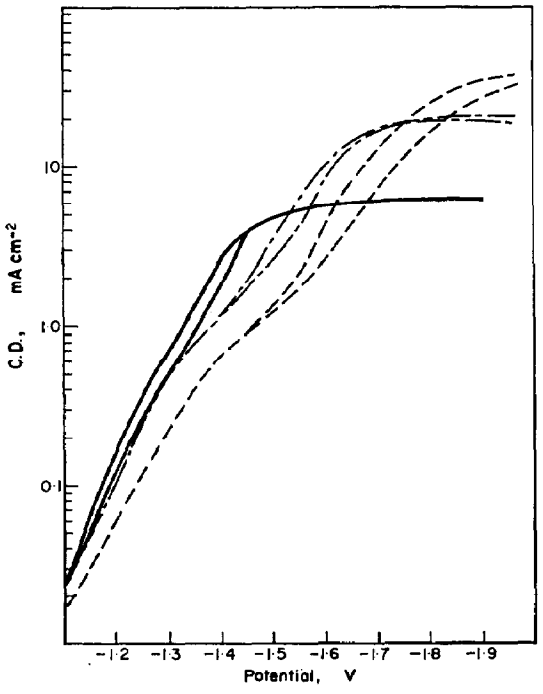


Fig. 2. Polarisation curves for solutions of ethyl iodide in 0·5 M tetrabutylammonium iodide, measured at a disc rotation speed of 50 rad s^{-1} and a scan rate of 30 mV s^{-1}.
—— 0·01 M EtI, — - — 0·03M EtI, - - - - 0·1 M EtI

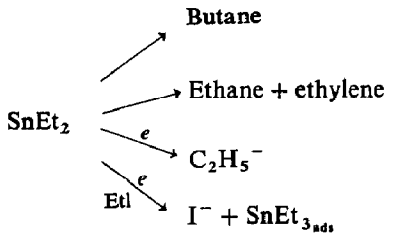
DISCUSSION

Tetramethyltin can be formed in the reduction of methyl halides at tin cathodes in ethanol as in acetonitrile[1] and *dmf* [6]. However tetraethyltin is formed in poor yields which contrast with the almost quantitative analogous reaction on lead [1, 2, 3]. In seeking to explain these differences it is necessary to distinguish whether adsorbed ethyl radicals cannot be formed easily on tin or whether, once formed, they predominently give rise to products other than tin alkyls.

Outstanding features of the reductions of methyl and ethyl bromides and iodides on tin cathodes are the low potential dependance of the currents, the low values of the currents particularly in the more concentrated solutions of the alkyl halide and the sensitivity of the electrochemical kinetics towards pretreatment of the electrode. The first electron transfer is clearly irreversible and the behaviour is consistent with a mechanism in which the first step requires the availability of free sites. The number of these can be decreased by the presence of oxidised films on the surface, removable by pre-electrolysis, or by the adsorption of some reaction products. The reaction order in ethyl iodide is particularly informative. In dilute solutions of the reactant there is, as expected, first order behaviour in the limiting current region. However in the neighbourhood of −1·5 V the reaction order was invariably found to be negative. Data shown in Figs. 1 and 2 are not true steady state currents; with time the currents fell, particularly in concentrated solutions of the alkyl halide. This fall can be associated with the negative reaction order phenomenon. It was evident that inhibition of the total current was caused by polarisation of the electrode whilst it was in contact with a high concentration of ethyl iodide. Therefore the inhibitor formation must have a high order in ethyl iodide. The production of tin alkyls is also favoured by a high concentration of the alkyl halide. Yet tetraalkyltin cannot be the inhibitor; it is soluble in the medium and, unlike radicals, is not chemisorbed.

Although the heats of adsorption of alkyl radicals on tin and lead are not available it is reasonable to suppose that they will be in the same sequence as the mean bond energies of the alkyl-metal bonds in the tetraalkylmetal compounds. The mean dissociation energies are given by Long[9] for the metal tetramethyls. The Sn–Me bond (53·3 kcal) is considerably stronger than the Pb–Me bond (35·9 kcal). Therefore it is probable that tin permits the adsorption of alkyl radicals at suitable surface sites such as kink sites. However the rate of reduction of alkyl halides will depend upon the number of such sites which are available; this in turn depends upon the rate of removal of the adsorbed alkyl groups in following steps. All following steps are expected to be slower on tin than on lead owing to the greater stability of the alkyl radical on tin. The higher sublimation heat of tin (71·9 kcal) relative to lead (46·3 kcal) ensures that attack of the cathode surface will also be slower on tin. Thus a higher coverage of sites by adsorbed organic species is expected to occur on tin and this must lead to lower measured currents. It would be an oversimplification of the situation which exists on the tin surface to suggest that the adsorbed species are simple alkyl radicals chemisorbed at one type of surface site There must exist a distribution of heats of adsorption across the heterogeneous solid tin surface. Moreover the number of alkyl groups associated with a surface tin atom can vary between unity in a simple adsorbed alkyl radical and two or possibly three when steric factors are favourable. If the inhibiting species is $SnEt_{3ads}$ then the effect of ethyl iodide concentration on the rate of inhibition is under-

standable; an intermediate $Sn\,Et_{2ads}$ can decompose in several possible ways:



The importance of the effect of the concentration of ethyl iodide adjacent to the surface on the inhibition could be demonstrated using the rotating tin disc electrode in 0·1 M EtI in 0·5 M TBAI solution at 1·9 V. Then at low rotation speeds (20 rad/s) the current approached the diffusion limiting value and remained steady but on increasing the speed to 300 rad/s it fell steadily and irrecoverably within a few seconds to less than half the original value.

It is necessary now to consider why hydrocarbon products should be favoured in ethyl halide reduction. Firstly we examine the results of Table 1 and consider the intermediates which lead to these products. They might arise either from radical or carbanion intermediates.

Perhaps the most surprising feature is that the ratio of butane:ethane increases as the potential is changed from −1·5 to −1·8 V. This result suggests that ethane is derived from a radical rather than a carbanion. However ethane formed according to the above scheme would be expected to be accompanied by an equal amount of ethylene; this is not found experimentally. The analyses appear fairly reliable, the total amounts of ethane and butane corresponding within 12 % to the coulombs passed on the basis of 2e/mole. We conclude that the predominant hydrogen abstraction reaction by the ethyl radical in this system does not produce ethylene; for example hydrogen abstraction from the solvent may occur. It is difficult to conceive of chemisorbed ethyl radicals participating in hydrogen abstraction reactions. It would appear therefore that at −1·5 V ethyl iodide is reduced mainly to free radicals which undergo first order decomposition. The increase in the butane:ethane ratio promoted by negative potentials and high ethyl iodide concentrations can be explained either as the dimerisation of free radicals when they are present in higher concentrations or the formation of ethyl carbanions, or possibly concerted reactions of the type;

$$C_2H_5I + C_2H_{5ads} + e \longrightarrow C_4H_{10}$$

In ethyl iodide reduction it appears that favourable sites on the cathode surface become covered with ethyl radicals or other ethyltin radicals derived from them. These are removed only with difficulty. Consequently currents are low and correspond to the slow formation of free ethyl radicals.

If the low yields of tetraethyltin and the low currents observed in the reduction of ethyl halides are to be attributed to the strong adsorption and difficult removal of ethyl radicals, then it is necessary to explain the successful cathodic syntheses of tetramethyltin from methyl iodide and of tetracyanoethyltin from acrylonitrile[7, 10]. We have stated previously[6] that loss of a tin atom from a kink site in the surface cannot be achieved by the formation of a single tin-alkyl bond. Instead fission of the tin-tin bond is expected to occur only when several alkyl groups are associated with the central tin atom. Clearly steric considerations may be paramount. In the reduction of methyl halides it is possible for a tin atom at a kink site already bonded to two methyl groups, to act as a nucleophilic reagent towards a third methyl halide molecule. This step is expected to be vastly more difficult when each methyl group is replaced by ethyl. Although the cyanoethyl radical is even more bulky than ethyl the steric situation in the reduction of acrylonitrile is more favourable than that of ethyl iodide in regard to tin alkyl formation. The nitrile groups of those cyanoethyl radicals initially bonded to the central tin atom do not cause a problem because they are well separated from the active centre There are no awkward groups on thc β-carbon atom of acrylonitrile to prevent it achieving a position adjacent to the $Sn\,(CH_2\,CH_2\,CN)_{ads}$ species to form the transition state of the final electron transfer reaction.

β-iodopropionitrile behaves similarly to iodoethane, giving metal alkyl products when reduced on cathodes of mercury, lead or thalliim but not on tin [5]. Use of β-chloro-propionitrile instead of the iodo-compound did lead to hexacyanoethylditin but only in a current yield of 12 %. The smaller chlorine atom must alleviate the steric hindrance experienced by the iodide.

Acknowledgement—This work has been supported by the Science Research Council.

REFERENCES

1. H. E. Ulery, *J. electrochem. Soc.* **116,** 1201 (1968).
2. R. Galli, *J. electroanal. Chem.* **22,** 75 (1969).
3. M. Fleischmann, D. Pletcher and C. Vance, *J. electroanal. Chem.* **29,** 325 (1971).
4. O. R. Brown, H. R. Thirsk and B. Thornton, *Electrochim. Acta.* **16,** 495 (1971).
5. A. P. Tomilov, Yu. D. Smirnov and S. L. Varshavskii *Zh. obshch. Khim.* **35,** 391 (1965).
6. C. Vance, Ph. D. thesis, University of Southampton, (1972).
7. O. R. Brown, E. R. Gonzalez and A. R. Wright, *Electrochim. Acta.* to be published.
8. B. N. Kabanov, I. I. Astakhov and I. G. Kiseleva, *Russ. chem. Rev.* **34,** 775 (1965).
9. L. H. Long, *Pure appl. Chem.* **2,** 61 (1960).
10. A. P. Tomilov, *Zh. obshch. Khim.* **38,** 214 (1968).