# THE REDUCTION OF SIMPLE ALKYL IODIDES AT TIN CATHODES IN DIMETHYLFORMAMIDE

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Abstract—The reduction of methyl, ethyl, n-propyl and n-butyl iodides has been studied at a tin cathode in dimethylformamide. The major product from the reduction of methyl iodide is tetramethyl tin but from ethyl, propyl and butyl iodides it is butane, hexane and oxtane respectively. Also as the size of the alkyl group increases the yield of tin alkyl decreases and yield of monomer hydrocarbon (i.e. ethane, propane and butane respectively) becomes more important. Steady state, cyclic voltammetric and pulse experiments have been used to study these reductions.

The factors which determine the change in the products with changes in the electrode material and the structure of the alkyl iodide are discussed.

The mechanism for the cathodic cleavage of carbonhalogen bonds has been the subject of an extended controversy. Thus there has been dispute as to whether the overall process involves one or two electrons and whether the two electron process occurs in a single step or in two distinct stages; a wide range of evidence including preparative studies, coulometry, polarography, stereochemical studies and plots of Taft polar and steric constants vs half wave potentials have been produced to support the various mechanisms[1-7].

Recent studies have shown that the mechanism depends both on the structure of the halide and the electrolysis conditions eg solvent, pH, electrode material; thus the formation of lead alkyls during the reduction of alkyl halides at a lead cathode in aprotic solvents[8-10] is clearly a one electron process while the reduction of halides to the corresponding hydrocarbon[1,2,6] and the cathodic coupling of alkyl halides to activated olefins[11] all proceed via an overall two electron reduction. A further complexity arises in these electrode reactions where organometallic species are intermediates even though they are not amongst the final products. This situation has been postulated during the reduction at mercury [12-14], although the products isolated can arise by an overall two electron process the organometallic intermediate may itself be reduced.

In this paper we report a detailed study of simple alkyl halides at a tin electrode in dimethylformamide. Some preliminary results for these systems were reported by Ulery[9]; he found that only methyl iodide gave a well formed reduction wave and was reduced to tin tetramethyl. It should be mentioned that a number of other tin alkyls have been prepared electrochemically, for example, by the oxidation of organoaluminium compounds[15] and the reduction of acrylonitrile and 3-chloro-propionitrile[16,17].

# EXPERIMENTAL

# Chemicals

Dimethylformamide was B.D.H. Ltd. reagent grade and was purified by two vacuum distillations. On the first occasion it was distilled from anhydrous sodium carbonate in order to remove acid impurities.

Tetra-n-butylammonium perchlorate was prepared by double decomposition from aqueous solutions of tetra-n-butylammonium hydrogen sulphate (AB Biotec Labtjanst, Sweden) and Analar perchloric acid and the precipitated product was recrystallised from ethanol/ water and dried in a vacuum oven at 60°C. Sodium perchlorate was prepared by the reaction of Analar sodium carbonate with Analar perchloric acid, crystallised from water and dried in vacuo at 100°C. Sodium iodide was Analar grade and was dried at  $150^{\circ}$ C in a vacuum oven. The alkyl iodides were B.D.H. reagent grade and were used without purification. The tin electrodes were made from B.D.H. Ltd tin foil or tin sticks. Before preparing the electrode, the tin was converted to rod form; in the case of the tin sticks this was carried out simply by turning on a lathe and when tin was bought in the form of foil, the tin was melted, poured into a mould and finally turned on a lathe after it had solidified.

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# Apparatus

A Chemical Electronics valve potentiostat and pulse generator type R.B.1. together with an X-Y recorder were used in all experiments. The *i*-t transients were stored in a Hi-Tek Instruments type AA1 Signal Averager. The transients were plotted from the store onto an X-Y recorder.

Throughout the investigation three compartment cells were used. In kinetic experiments the working electrode was a tin disc, area 0.085 cm<sup>2</sup>, which was sealed into a teflon sheath while for preparative electrolyses the working electrode was a tin rod, area 8  $\text{cm}^2$ . The reference electrode which was a Radiometer aqueous sce. was separated from the working electrode by a Luggin capillary and a tap and the working electrode and platinum secondary electrode were separated by a No. 2 glass sinter. The volumes of the solution in the cathode compartment were approximately 10 cm<sup>3</sup> and 30-40 cm<sup>3</sup> for kinetic and preparative experiments respectively. All preparative experiments were carried out in a darkened cell to prevent photochemical decomposition of electrolysis products. Prior to non-steady state experiments, the tin disc electrode was polished with fine emery paper. The experiments were all carried out with unstirred solutions.

### Analysis

All analysis was carried out by V.P.C. using a Pye 104 vapour phase chromatograph; qualitative and quantitative analysis of electrolysis products were performed by comparison of retention times (on two columns) and peak areas with those for solutions of known standards. The analysis conditions were

(a) for Sn(CH<sub>3</sub>)<sub>4</sub>; a 2 m column packed with celite + 10% silicone oil at 50°C. Nitrogen flow rate 60 cm<sup>3</sup> mm<sup>-1</sup>

(b) for  $Sn(C_2H_5)_4$ ; a 2 m column packed with celite + 10% polyethylene-glycol adipate + 1% phosphoric acid at 80°C. Nitrogen flow rate 60 cm<sup>3</sup> min<sup>-1</sup>

(c) for alkanes; a 3 m column -5% silicone oil on

chromosorb W.A\_80 $\pm$ 100 mesh—room temperature— Nitrogen flow rate 20 cm<sup>3</sup> min<sup>-1</sup>

(d) for alkyl iodides; the 10% silicone oil at 50°C or the 10% polyethylene-glycol adipate + 1% phosphoric acid at 80°C were used. Nitrogen flow rate 60 cm<sup>3</sup> min<sup>-1</sup>

#### RESULTS

#### Steady state experiments

Steady state *i*-*E* curves were obtained for 0.1M solutions of four simple alkyl iodides at a tin cathode in dimethylformamide to which various supporting electrolytes had been added and the data taken from these curves are summarised in Table 1. It can be seen that the limiting currents depend on the cation of the inert electrolyte and are considerably lower than those expected for a diffusion controlled process. Furthermore the Tafel slopes indicate a complex reaction mechanism. The *i*-*E* curves for solutions containing a sodium salt as the inert electrolyte showed abrupt changes at -2.4V probably due to sodium deposition on the cathode.

In the cases of methyl iodide and ethyl iodide, steady state *i*-*E* curves were also run for a series of concentrations of the alkyl iodides in dimethylformamide containing tetrabutylammonium perchlorate (0.25M). In the concentration range  $2.5-50.0 \times 10^{-2}$ M, the currents for the reduction of both iodides showed a first order dependence on their concentrations for potentials in the limiting current region; in the Tafel region, the reaction orders were considerably less than one. At higher concentrations of these alkyl iodides (1M), the *i*-*E* curves showed a second larger wave at more cathodic potentials ( $E_{1/2}$  approximately -2.5V). This second process was not investigated further in this work.

# Preparative studies

Controlled potential electrolyses were carried out at several cathode potentials for dimethylformamide solutions of methyl iodide containing either sodium or

Alkyl iodide	Base electrolyte	$E_1$ V*	Tafel slope mV <sup>-1</sup>	Limiting current mA cm <sup>-2</sup>
	$0.25M(n-C_4H_9)_4NClO_4$	- 1.98	1/230	8.0
	0.25M NaClO	-1.85	1/330	2.3
	0.25M NaI	-2.02	1/300	3.5
C <sub>2</sub> H <sub>5</sub> I	$0.25M(n-C_4H_9)_4NClO_4$	-2.04	1/230	6.1
	0.25M NaČIO	- 1.95	1/210	2.0
	0.25M NaI	-2.08	1/225	1.0
n-C <sub>3</sub> H <sub>7</sub> I	0.25M(n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NClO <sub>4</sub>	-2.06	1/300	5-3
n-C <sub>4</sub> H <sub>9</sub> I	$0.25M(n-C_4H_9)_4NCIO_4$	-2.15	1/240	5.0

Table 1

Data taken from steady state i-E curves for the reduction of alkyl iodides (01M) at a tin cathode in dimethylformamide. Potentials are quoted vs the aqueous sce.

\* Potential at which the current is 1mA/cm<sup>2</sup>

Concentration of methyl iodide	Base electrolyte	Potential V*	$C ml^{-1}$ <sup>†</sup> of catholyte	Current yield§ of SnMe₄
0.5M	NaClO <sub>4</sub>	<u> </u>	14.0	62%
0·33M	NaClO	-1.95	15.2	54%
0·50M	$(C_4H_9)_4NClO_4$	-1-92	10.3	67%
0·33M	(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NClO <sub>4</sub>	-2.10	10.3	64%
0·50M	$(C_4H_9)_4NClO_4$	-2.30	14.0	58%

Table 2

Yield of tin tetramethyl from the reduction of methyl iodide at tin in D.M.F.

† Number of coulombs passed/ml catholyte when electrolysis was ended and the solution analysed.

§ Yield determined by V.P.C. analysis of the catholyte.

\* Potentials quoted vs aqueous sce.

tetrabutylammonium perchlorate. In all electrolyses the major product was tetramethyl tin; the current yields for this product are summarised in Table 2. During the electrolysis some gas evolution was observed and V.P.C. analysis of this gas showed that it was essentially ethane. No methane could be detected even at the most negative potential at which an electrolysis was carried out.

Similar experiments with ethyl iodide as the electroactive species were considerably less successful in preparing an organo-tin product. Indeed, the current yield of tin tetraethyl was in the range 3-10 percent in a series of electrolyses where the cathode potential was varied between -1.95V and -2.45V and the electrolyte was either sodium or tetrabutylammonium perchlorate. The major product was butane which was formed in current yields above 40 percent. Some ethane was also identified but its yield was substantially below that of butane.

Single electrolyses were performed with *n*-propyl iodide and *n*-butyl iodide as the electroactive compounds. The electrolyses were carried out at a potential just prior to the limiting current plateau but in neither case could any\_organo-tin compound be identified amongst the products. From *n*-propyl iodide the major product was hexane, current yield 40 percent, together with propane, 30 percent, while with *n*-butyl iodide the electrolysis led to octane, 44 percent, and butane, 36 percent.

With all the alkyl iodides some tin was lost from the cathode in excess of that isolated as the metal alkyl; this tin was found as metal powder in the base of the cell. The quantity of this excess tin was large when the cathode was manufactured from foil by melting and moulding into rod form but only very small when the cathode was made from commerical tin rod. Since the loss of tin was dependent on the preparation of the cathode, it was felt likely to be a physical effect rather than an indication that the mechanism of formation of tin tetraalkyl involved disproportionation of a tin (II) organometallic intermediate (compare lead[8,9,10]).

### Coulometry

Controlled potential coulometry was carried out on solutions of all four alkyl iodides at a tin cathode in dimethylformamide. In view of the time required for an exhaustive electrolysis, the *n*-values reported in Table 3 were-calculated from the quantity of the electroactive species removed during the electrolysis; at the termination of the electrolysis the unreacted alkyl iodide was determined by V.P.C. analysis.

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Alkyl iodide	Initial concentration	Electrolyte	Cathode potential*	C ml <sup>-1</sup> of catholyte <sup>†</sup>	n-value
CH <sub>3</sub> I	0·33M	NaClO <sub>4</sub>	- 1.95	15-2	0.92
CH <sub>3</sub> I	0-33M	(C <sub>4</sub> H <sub>9</sub> ) NClO <sub>4</sub>	-2.10	10-1	1.10
C <sub>2</sub> H <sub>5</sub> I	0·48M	NaClO <sub>4</sub>	-1.95	19.4	1.15
C <sub>2</sub> H <sub>4</sub> I	0·25M	(C <sub>4</sub> H <sub>0</sub> ) <sub>4</sub> NClO <sub>4</sub>	-2.25	15.2	1.07
C,H,I	0·25M	(C.H.) NCIO	-2.45	19.4	1.45
n-C <sub>4</sub> H <sub>7</sub> I	0·20M	(C.H.) NCIO	-2.25	16.3	1.22
n-C₄H <sub>9</sub> I	0·22M	(C4H9)4NClO4	-2.30	19.3	1.35

Coulometric data for the reduction of alkyl iodides at tin in dimethylformamide. \* Potentials quoted vs aqueous sce

† Number of coulombs passed/ml of catholyte when the electrolysis was terminated for analysis.

It may be noted that for the reductions in dimethylformamide containing tetrabutylammonium perchlorate, the *n*-values for methyl and ethyl iodide are close to one when the electrolysis is carried out at a potential just prior to the limiting current plateau. With the higher homologues, at a similar potential just prior to the plateau, the *n*-value shows a tendency to increase, the *n*-value being 1.22 and 1.35 for propyl and butyl iodide respectively.

## Non-steady state experiments

Cyclic voltammograms were run at a tin electrode for solutions of methyl and ethyl iodide in dimethylformamide containing sodium or tetrabutylammonium perchlorate (the potential sweep range was generally -1.2V to -2.7V). These showed single cathodic peaks which were irreversible; indeed, no anodic peaks were observed before tin dissolution occurred. The cyclic voltammograms did, however, show hysteresis of the type shown in Fig. 1 of Ref. [10], ie at certain potentials around the foot of the peak, there is more cathodic current on the reverse sweep than on the sweep towards negative potentials.

Potential step experiments, where the potential was pulsed from -1.5V to potentials where reduction of methyl and ethyl iodide took place led to rising i-t transients. In a typical experiment with the tin electrode in a solution of methyl iodide (0.66M) in dimethylformamide containing tetrabutylammonium perchlorate, the cathode potential was stepped from -1.5Vto -1.95V and the resulting, rising *i-t* transient had a timescale of approximately one second. The timescale of the transient was, in fact, independent of the potential in the range -1.90V to -2.40V. The transients were, however, more difficult to characterise than those previously reported at lead cathodes [10] and hence they were not studied in depth.

### DISCUSSION

Previous papers on the reduction of simple alkyl iodides in dimethylformamide have reported that when the cathode is lead, the electrode process occurs via the transfer of a single electron per molecule of alkyl iodide and results in the formation of a lead tetraalkyl; with methyl and ethyl iodides the current yields of the lead alkyls are over 80 percent[10] and even with propyl and butyl iodide the current yields exceed 50 percent[18]. On the other hand, when the electrode is

4 RI + 4e 
$$\xrightarrow{\text{Pb cathode}}$$
 PbR<sub>4</sub> + 4I<sup>-</sup>

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mercury, a two electron reduction occurs and the product is the monomer alkane. The current yield is again high[2,12]. The mechanism of this reaction is still

RI + 2e 
$$\xrightarrow{\text{Hg cathode}}$$
 I<sup>-</sup> + R<sup>-</sup>  $\xrightarrow{\text{H}^+ \text{ abstraction from}}$  RH.

under discussion but in recent papers there has been a trend towards postulating the involvement of organometallic intermediates[12,13,14].

The results in this paper show that the behaviour at a tin cathode is again different. With all four alkyl halides. the controlled potential coulometry and the identified electrolysis products show that the major electrode reaction is a process which involves the overall transfer of a single electron. Although a high yield of tin alkyl is obtained only when the electroactive species is methyl iodide, the minor product from the reduction of methyl iodide and the major product from the reduction of ethyl iodide is, however, also indicative of a mechanism involving a radical intermediate or an intermediate containing a tin-carbon bond.

$$RI + e \xrightarrow{Sn \text{ cathode}} Sn - R \xrightarrow{3e+3RI} SnR_4$$

The dimer hydrocarbon could also arise through a carbanionic intermediate

$$RI + 2e \longrightarrow I^- + R^- \xrightarrow{RI} R - R + I^-$$

a mechanism which also results in the transfer of only one electron per alkyl iodide molecule, but this mechanism seems unlikely since no dimer has been reported at mercury cathodes and the carbanion would probably be free in solution and hence its reactions would be independent of the electrode material. Furthermore, the yield of the monomer hydrocarbon is much lower than would be expected if this mechanism were operative.

The close similarity in the results from steady state, cyclic voltammetric and potential step experiments with solutions of methyl iodide and ethyl iodide would also seem to suggest that the two alkyl halides are reduced with similar mechanisms. In particular it would suggest that the formation of tin tetramethyl from methyl iodide and of butane from ethyl iodide have a common rate determining step. The results at a tin electrode also closely resemble those at lead; a published study [10] of the reduction of alkyl iodides at lead concluded that the hysteresis on the cyclic voltammograms and the rising *i-t* transients could be explained in terms of the mechanism

$$M + RI + e \xrightarrow{k_6} M - R + I^-$$
 (1)

(M is metal atom and M - R is a surface species involving a metal-carbon bond) followed by the competing sequences

$$MR + RI \xrightarrow{k_{\tau}} Product \qquad (2)$$

and

$$MR + RI \xrightarrow[k_2]{k_1} MR_2I \qquad (3)$$

$$MR_2I + e \xrightarrow{k_3} MR_2 + I^-$$
 (4)

$$MR_2 + RI + e \xrightarrow{k_4} MR_3 + I^-$$
 (5a)

$$2MR_3 + M \xrightarrow{\kappa_5} MR_4 + 2MR$$
 (6)

ie a mechanism which involves the slow formation of a surface species which can catalyse the formation of metal tetraalkyl. A detailed explanation of the data required the competing reaction, reaction (2), although the high yields of lead alkyl and the form of the *i*-t transients require that the catalytic cycle, steps (3)-(6)must be faster than reaction (2). The resemblance in results between those at lead and tin suggest that a similar mechanism may be operative at tin. Indeed to explain the products at tin one further reaction is required, for example

$$MR_2 + RI + e \xrightarrow{k_4} MR + R_2 + I^-$$
(5b)

in competition with reaction (5a). The ratio of metal alkyl to dimer will then be dependent on the ratio of rate constants  $k_4/k'_4$  and since both reactions follow the rate determining step, step (3) or step (4), depending on the electrode potential, a change in this ratio will not affect the observed *i*-*E* or *i*-*t* curves. Further the differences between the reaction at lead and tin cathodes and between methyl iodide and ethyl iodide on tin may be qualitatively understood in terms of the relative sizes of a tin and a lead atom and a methyl and an ethyl group.

The products from the reduction of propyl and butyl iodide may also be understood in these terms. With increasing size of the alkyl group, not only does the ratio  $k_4/k'_4$  decrease further, but also the strength of the carbon-tin bond decreases. Hence there is a greater tendency for this bond to be reductively cleaved and a carbanion formed. Thus the yield of monomer hydrocarbon increases.

Hence we conclude the products from the reduction of alkyl iodides at various metals will depend on three key factors:

(i) The degree to which radical intermediates are stabilised by interaction with the electrode material *ie* the strength of the metal-carbon bond. This factor will depend both on the metal of the electrode and the size and structure of the alkyl group and is largely indicated by the half wave potential for the alkyl halide; strong interaction between the radical and the electrode metal will result in the reduction occurring at less negative potentials.

(ii) The extent to which the organometallic inter-

mediate can undergo further reduction to give carbanionic species. This reaction will, of course, depend on potential.

(iii) The relative rates of chemical reactions in the complex sequence of events following the initial formation of the alkylated metal surface. It is clear from the nature of the overall process which results in the formation of a molecule with four carbon chains around a single metal atom that the reaction sequence must be complex and that the relative rates of the reactions will be susceptible to subtle changes in the size of the metal atom and the alkyl group. When these chemical processes follow the rate determining step, changes in their relative rates may not affect simple electrochemical experiments.

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