

# Direct production of butyltin chlorides from a paired electro-organic synthesis

P. PARSONS-WINGERTER\*, R. F. SAVINELL

*Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106, USA*

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Butyltin chlorides were produced directly from butyl chloride and a tin cathode in several undivided cell reactors with tetraethylammonium chloride and acetonitrile solvent. The complex reaction chemistry was investigated primarily in a small batch cell with a 1 cm<sup>2</sup> planar cathode. Current densities from cathodic linear potential sweeps at 1 mV s<sup>-1</sup> were correlated successfully with current densities and butyltin products from potentiostatic experiments. Potential windows on product formation and other major limiting reactions were thereby identified. Product yield was shown to be strongly dependent on electrolyte gas conditions, with yield decreasing as the reactor is increasingly deaerated. Use of the initial open circuit potential (i.o.c.p.) as an indicator of reaction gas conditions proved to be a convenient and reproducible technique. Under favourably oxidized conditions, current densities in the product formation potential region ranged from 66 mA cm<sup>-2</sup> at -2.74 V vs SCE to 250 mA cm<sup>-2</sup> at -2.98 V vs SCE which are considerably higher than previously reported current densities for this synthesis. Surprisingly, the aeration history of butyl chloride prior to synthesis may be an important factor in subsequent product yield.

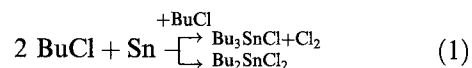
## 1. Introduction

Butyltin chlorides command the largest share of the industrial organotin market [1]. The butyltin products targeted for the direct and paired electro-organic synthesis reported here are dibutyltin dichloride ((CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub> or Bu<sub>2</sub>SnCl<sub>2</sub>) and tributyltin chloride ((CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>)<sub>3</sub>SnCl or Bu<sub>3</sub>SnCl). Both compounds are starting materials for many commercial organics, and in general are derivatized by nucleophilic substitutions at the tin-halogen bond [2–5]. Dibutyltins are used primarily as plastic stabilizers against photochemical effects. Tributyltins function selectively as non-mammalian biocides, and therefore are used as additives in agricultural pesticides and antifouling agents in marine paints.

We have studied the potentially direct and paired synthesis of butyltin chlorides in several undivided cell reactors. In a 'paired' electrolysis, intermediate products formed at the anode and cathode react to form the final synthetic product. Although research in organic electrochemistry has focused recently on the potential process benefits of paired syntheses, few commercially paired processes have been developed to date [6]. Much effort has been invested in the development of direct syntheses of alkyl metal halides [2], in which the metallic and organic starting materials react with each other to form the organo-metallic product, rather than by an indirect mechanism requiring an energetic metallic intermediate such as the Grignard reagent R<sub>2</sub>MgX (R an organic species, and X, a halide). However, the

commercialization of a direct synthesis of alkyltin halides has been difficult for four reasons [7]: (i) the low reactivity of alkyl chloride reactants, against (ii) the high cost of the more reactive alkyl halides such as the alkyl bromides and iodides; (iii) the high temperature of the direct reaction combined with the low boiling point of an alkyl halide reactant, requiring the use of high-pressure reaction vessels; and (iv) competing byproduct dehydrohalogenation reactions which occur at high reaction temperatures. An electrochemical process which directly energizes the alkyl halide reduction sidesteps all of these commercialization problems: the electrochemical reaction proceeds successfully with less expensive alkyl chlorides, and because of low electrochemical process temperatures, avoids competing dehydrohalogenation reactions, as well as the need for high-pressure vessels.

In the 1970s, Utery reacted butyl chloride (BuCl) at a tin cathode in divided and undivided cells [1, 8–11]. In an undivided reactor, the overall cell reactions resulting in the products of interest are



Through various reaction pathways, numerous products or competing byproducts may result, including Bu<sub>4</sub>Sn, the white precipitate Bu<sub>2</sub>SnO, alkyltin polymer (Bu<sub>2</sub>Sn)<sub>x</sub>, chlorostannate salt complexes, and alkane offgases [1]. The similarity by which carbon and tin form their bonds was noted by Kekulé; both tetrahedral elements polymerize and

\* Present address: Department of Chemical Engineering, John Hopkins University, Baltimore, MD 21218, USA

cyclize, although carbon polymerizes more easily [4, 12]. Product selectivity is therefore important for the development of a successful process.

Here we report progress in the reproducibility, selectivity and tin conversion of the butyltin synthesis pioneered by Ulery. To achieve these objectives, we incorporated experimental methods used by various investigators to standardize and optimize sacrificial organometallic reduction electrolyses. These techniques include initial open-circuit potential determinations (i.o.c.p.) used by Galli and Olivani in the reaction of ethyl bromide at a lead cathode [13,14]; pre-electrolyses [15–17], which were determined by Brown and coworkers to be especially important for tin reactions, and steady-state potentiostatic polarization measurements [13, 14]. We demonstrate that linear potential sweeps, when shown to correlate with the results of potentiostatic experiments, can be used to perform initial investigations of the complex butyltin chloride synthetic chemistry quickly and easily.

## 2. Experimental details

### 2.1. Synthesis

BuCl (Aldrich, >99.5%) was reacted in concentrations of 2.0 to 3.0 M at tin cathodes in undivided cells with graphite anodes, MeCN solvent ( $\text{CH}_3\text{CN}$ ; Fisher and Aldrich HPLC or ACS grade, less than 0.01%  $\text{H}_2\text{O}$ ), 0.05 to 0.50 M TEAC supporting electrolyte ( $(\text{CH}_3\text{CH}_2)_4\text{NCl}$ ; Kodak 98%), and 0.50 M  $\text{H}_2\text{O}$  inhibitor (at first doubly ( $5 \text{ M}\Omega \text{ cm}^{-1}$ ), and then triply ( $18 \text{ M}\Omega \text{ cm}^{-1}$ ) distilled; the two purities of water resulted in no apparent synthetic differences). Tin for the planar cathodes was provided by Pitt Metals, McDonald, PA; purity by atomic adsorption was determined to be 98%.

As preliminary work, the solubilities and conductivities of various reactant/solvent/tetraalkylammonium chloride salt solutions (BuCl/MeCN/TAAC) were studied at room temperature [18]. Water content of the TEAC salt (stored under vacuum desiccation) was routinely measured with a Mettler DL18 Karl Fischer titrator and methanol solvent. TEAC and water concentrations were adjusted accordingly; TEAC water content was generally around 6–8%. Use of TEAC dried to 1%  $\text{H}_2\text{O}$  content in a vacuum oven resulted in no apparent synthetic differences. Reaction solutions were prepared immediately before each experiment. Reaction temperatures ranged from 22 to 35°C. Lower onium salt concentrations such as 0.25 M of tetraethyl or tetrabutylammonium halide were found by Ulery to decrease cathodic sludging, with small amounts of water (such as 0.5 M) judged to be the most effective 'hydroxylic tin sludge suppressor', although such inhibitors may be unnecessary in an undivided cell [8]. Undivided cells produce less tin polymer byproducts [1].

### 2.2. Batch cell experiments

A cylindrical glass vessel of 30 ml capacity served as the apparatus. The tin cathode ( $1.0 \text{ cm}^2$  working face, insulated on all other sides) was separated by 1 cm from the graphite anode (2.5 cm high  $\times$  1.5 cm wide  $\times$  0.8 cm thick). A PTFE capillary tube, attached at one end directly to the upper cathode surface, and at the other to a reference reservoir, served as a Luggin probe. The reference electrode (SCE, porous ceramic junction) was housed in an electrode reservoir bottle which was connected by a PTFE capillary line (0.8 mm) to the cell. The cell was not gas-tight, but was operated under a positive pressure. A bevelled rubber stopper sealed the cell, but did not contact the solution. The stopper was equipped with ports for the electrode lead wires, a syringe injection port for GC/MS analysis, a glass thermistor probe, gas inlet (glass capillary sparger), and gas outlet tubing (with adjustable clamp closure). The cell contained a PTFE magnetic stirbar, and was mounted above a stirrer/hot plate for mixing and temperature control. A top view schematic of the cell is shown in Fig. 1.

**2.2.1. Electrode preparation:** A copper lead wire was soldered to the tin cathode. The cathode was prepared according to the method of Gileadi and coworkers [19] in a four or five stage polishing procedure. The working tin surface was sanded with 320 (if necessary) and then 600 grade sandpaper, and next polished with felt-type cloth containing 30 and  $6 \mu\text{m}$  diamond polished compounds (Buehler, manmade). Silicone rubber insulation was then applied on all sides except the working face (General Electric, RTV 108, translucent). Since contaminants were found by GC/MS analysis to leach from the silicone rubber insulation, the cathode assembly was cured in stirred warm MeCN/BuCl solution for several hours. GC/MS analysis of electrolytes confirmed no further release of contaminants from the 'cured' cathode. Immediately prior to the experiment, the cathode surface was polished with  $0.3 \mu\text{m}$  alumina powder (Buehler), sonicated in  $\text{H}_2\text{O}$  and then MeCN for 2 min, and finally rinsed in MeCN. The graphite anode was washed with  $\text{H}_2\text{O}$ , sanded, and sonicated in  $\text{H}_2\text{O}$  and then MeCN for 2 min each, and rinsed in MeCN.

**2.2.2. Initial open circuit potential:** After the addition of reaction solution to the cell and reference electrode reservoir, the beginning initial open circuit potential (of cathode with respect to SCE) was measured, and allowed to stabilize for two minutes. Gas (high-purity air or nitrogen) was then sparged to the cell to achieve the desired i.o.c.p. The gas flow was adjusted to maintain a stable i.o.c.p. value for a period of 10–12 min, after which the desired pre-electrolysis, or initial reaction potential, was applied (while maintaining a constant gas flow rate).

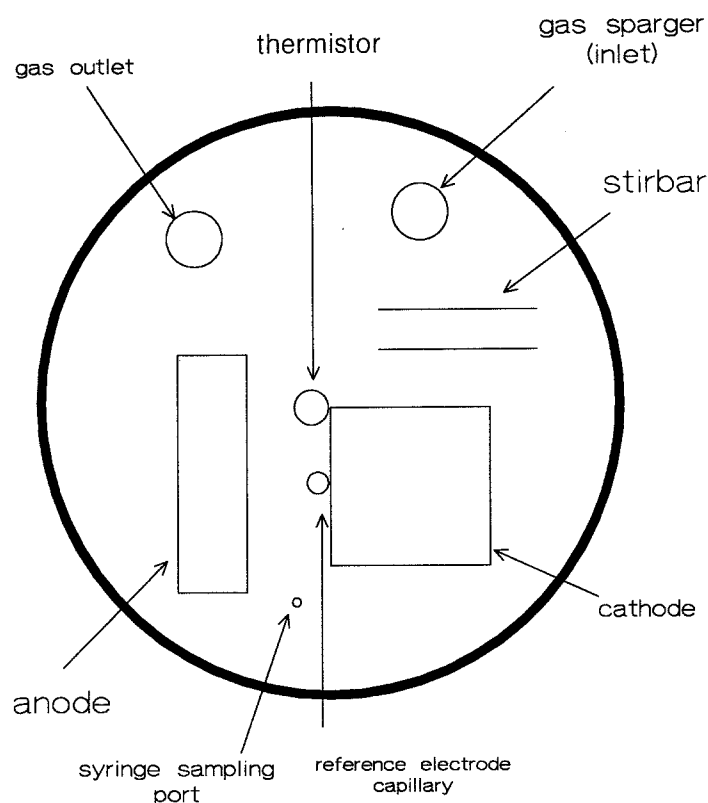


Fig. 1. Top view schematic of experimental batch cell.

In the batch cell, low gas flow rates were measured as 28–30 bubbles per min through a capillary sparger. Medium and high flow rates were adjusted according to a flowmeter, but flow rates are not reported, since mixing in the cell was undefined, and gas conditions were essentially monitored by i.o.c.p. values.

**2.2.3. Linear potential sweep experiments:** Following establishment of the i.o.c.p., the potential was stepped to an initial value of  $-0.82\text{ V}$  vs SCE, and thereafter scanned at a rate of  $-1\text{ mVs}^{-1}$ . The slow sweep from  $-0.82\text{ V}$  acted as a preelectrolysis, since only low-level corrosion reactions occurred until approximately  $-1.6\text{ V}$ . Quaternary ammonium salt reaction solutions and tin cathodes are effectively preelectrolysed by low voltage applications in 10 min [15, 20]. Final potentials were generally  $-3.04\text{ V}$ , especially in the presence of BuCl reactant, since reactions at more negative potentials appeared to scavenge liquid butyltin products.

**2.2.4. Potentiostatic experiments:** Following establishment of the i.o.c.p., a preelectrolysis was applied prior to potentiostatic (product determination) experiments. In general preelectrolysis consisted of the application of a low cathodic potential, such as  $-1.8$  or  $-2.2\text{ V}$ , for 20 min. Thereafter the potential was stepped to the desired value for 60 min. Directed GC/MS sampling through the syringe port was performed before i.o.c.p. determination, before electrolysis, immediately before the potential was applied, and then at 30 and 60 min after potential

application. Cathode weight, as well as cell and reservoir volumes, were measured before and after each potentiostatic experiment.

**2.2.5. Treatment of BuCl reactant:** We found that exposure of BuCl to air prior to synthesis appears to affect its reactivity significantly. No special precautions were noted by previous researchers on the storage of alkyl halide reactants, except for unstable tert-butyl halides [8]. The BuCl behaviour observed by us is documented more fully elsewhere [18], but described here briefly as background for the present work. In initial experiments, storage of commercially obtained BuCl stock bottles under ambient (aerated) conditions resulted in decreasing reactivity over one month of 20–25% of initial values (as determined by current response during the reactions). In subsequent experiments, freshly opened stock reactant of the same highly reactive lot was maintained under nitrogen until use, and showed excellent reproducibility. Several different lots of BuCl exhibited low reactivity when freshly opened, and were presumably already unfavourably aerated. As analyzed by GC/MS, no significant contamination was found in the various lots of BuCl. BuCl stored under nitrogen required reaeration immediately prior to the reaction, to attain high and reproducible current densities. Air was bubbled with a pasteur pipet through the BuCl for about 30 s, and a short burst of air introduced into the reaction solution prior to both aerated and deaerated i.o.c.p. procedures.

Table 1. Results with initial conditions for linear potential sweep experiments. All experiments were run with 0.5 M H<sub>2</sub>O and MeCN for gas-bubbled initial open circuit potential (IOCP) times of 12–14 min. then scanned from –0.82 V to –3.04, –3.10 or –3.16 V.

Experiment Number	Concentration (M)		Gas flow	IOCP (–V <sub>c</sub> )	i <sub>c</sub> at –2.98 V <sub>c</sub>	Soluble Product <sup>a</sup>	Observations of Solution Behaviour <sup>b</sup>
	BuCl	TEAC					
1–3	2	0.25	low air	0.52–0.62	240–250	yes	murky brown solution with black precipitate to clear, light yellow solution
4–5	2	0.25	low N <sub>2</sub>	0.75	160–180	yes	murky brown solution to clear, light yellow solution
6	2	0.25	med N <sub>2</sub>	0.79	130	yes	murky brown solution to clear, light yellow solution
7–8	0	0.25	low air	0.61	44–52	no	clear, amber solution with black precipitate
9–10	0	0.25	high N <sub>2</sub>	0.79	63–65	no	clear, colourless solution with black precipitate
11–13	0	0	low air	0.49–0.55	6–11	no	clear, grey solution with dark grey precipitate
14–15	0	0	high N <sub>2</sub>	0.62	2–3	no	clear, dark gold solution

<sup>a</sup>Bu<sub>4</sub>Sn, Bu<sub>3</sub>SnCl and/or Bu<sub>2</sub>SnCl<sub>2</sub> as detected by GC/MS. No BuSnCl<sub>3</sub> was detected.

<sup>b</sup>After the scans, butyl chloride reaction solutions underwent dramatic colour changes when removed from reactor atmosphere to ambient atmosphere. Reaction solutions without butyl chloride did not change appearance when removed from the reactor to ambient atmosphere.

### 2.3. Flow cell experiments

The apparatus, of 400 to 600 ml capacity, contained an undivided cell with a 20 cm<sup>2</sup> tin cathode and graphite anode, separated by a 1 cm-wide flow channel. After *in situ* sparging of the liquid reagents, reactions were run under closed N<sub>2</sub> atmosphere at 3 M BuCl, 0.5 or 0.05 M TEAC, 0.5 M H<sub>2</sub>O, MeCN, 100 mA cm<sup>–2</sup> current density, 2.1 cms<sup>–1</sup> electrolyte velocity, and 35°C. Two types of reaction samples were taken through a septum: ‘direct’ samples with a 1 or 5 μl gas-tight syringe, which were immediately injected into the GC/MS; and ‘indirect’ samples with a 2 ml syringe, which were saved under ambient atmosphere for later analysis. The indirect samples reacted quickly with the ambient (oxygenated) atmosphere, turning from a deep-gold or brown colour to a clear, pale-yellow solution containing a white precipitate. Redistribution reactions of the

Table 2. Experimental conditions for product determination reactions. All experiments were run potentiostatically for 60 min. at concentrations of 2M BuCl, 0.25 M TEAC, 0.5 M H<sub>2</sub>O, 14.9 M MeCN (except Exp. P2, at 0M BuCl, 0.25 M TEAC, 0.5 M H<sub>2</sub>O, 18.8 M MeCN)

Reaction Conditions				
Exp. No.	Remarks	Gas Flow	IOCP (–V <sub>c</sub> )	Applied Potential (–V <sub>c</sub> )
P1		medium N <sub>2</sub>	0.79	1.50
P2	OM BuCl	high N <sub>2</sub>	0.85	2.20
P3		high N <sub>2</sub>	0.82	2.75
P4		medium N <sub>2</sub>	0.79	2.75
P5		low N <sub>2</sub>	0.73	2.90
P6		low N <sub>2</sub>	0.73	2.97

butyltin chloride products were often observed in indirect samples after some hours or several days.

### 2.4. Analysis

For calculation of tin faradaic efficiencies and material balances, the primary product reaction at the cathode was assumed to occur according to the mechanism in Equation 4, in which two electrons are transferred per tin atom dissolved. Qualitative and quantitative GC/MS analysis of liquid compounds were performed on a Hewlett–Packard GC 5890 A/MSD 5970 with 99.5% helium gas carrier, a packed column insert and two Hewlett–Packard–1 glass capillary columns, identical except for length (25 and 50 m × 0.32 mm × 0.52 μm film thickness, crosslinked methyl silicone gum). Standards were purchased from Aldrich. Dried weight analysis, by which the sample is simply dried to a constant solid weight, was used to measure the solid contents of liquid samples, and some precipitated solid samples.

## 3. Results of discussion

### 3.1. Initial open circuit potential (IOCP)

During early batch cell experimentation, it was noticed that not only the i.o.c.p., but also the current density (and thus perhaps the product formation rate), are direct and strong functions of cell gas conditions. Thereafter the i.o.c.p. was used as an indicator of consistent initial gas conditions. Gas flow rates of ‘low’, ‘medium’, or ‘high’ were adjusted to achieve a desired i.o.c.p., and then left at that same flow rate during subsequent electrolysis. The i.o.c.p. values for the potential sweep and potentiostatic experiments

Table 3. Product determination experimental results

Exp. No.	$i_c$ Range (mA/cm <sup>2</sup> ) <sup>a</sup>	Weight of Cathode Loss (g)	Faradaic Efficiency <sup>b</sup>		Major Soluble Product <sup>c</sup> (g)	Aerated Ppt (g)	Reaction Solution Appearance Change <sup>d</sup>	Product Conversion from Tin (%)
			Electrons Transferred (e <sup>-</sup> /Sn atom)	Current Efficiency (%)				
P1	0.13 → 0.05	0.009	0.0358	—	none	none	Clear, light gold	0
P2	0.56 → 0.63	-0.001	infinite	—	none	none	Clear, light gold	0
P3	13.6 → 12.0	0.033	1.68	119.2	Bu <sub>3</sub> SnCl	none	Murky, gold-brown solution to clear, light gold solution	—
P4	23 → 20	0.062	1.67	122.0	Bu <sub>2</sub> SnCl <sub>2</sub> , Bu <sub>3</sub> SnCl, Bu <sub>4</sub> Sn	none	Murky, brown solution to clear, gold solution	—
P5	170 → 70	0.208	2.91	69	Bu <sub>4</sub> Sn (0.031)	0.052 (white)	Murky, black-brown solution, w/black precipitate to clear, light-gold solution	17
P6	200 → 90	0.228	2.79	72	Bu <sub>3</sub> SnCl (0.056)	0.095 (white)	—	29

<sup>a</sup> Cathodic current density range during potentiostatic reaction from 5 to 60 min.

<sup>b</sup> Faradaic efficiencies calculated according to cathode weight loss basis. Current efficiencies = %  $\left(\frac{\text{actual tin loss}}{\text{theoretical tin loss}}\right)$

<sup>c</sup> Soluble butyltin products detected by GC/MS immediately following removal of sample from reactor by syringe and direct injection into the GC at 30 and 60 min reaction time. Product yields were quantified for runs no. P5 and P6.

<sup>d</sup> Butyl chloride solutions at applied potentials within the product formation region underwent dramatic colour changes when removed from reactor atmosphere to ambient atmosphere. Reaction solutions under conditions not forming product did not change appearance when removed from the reactor to ambient atmosphere.

under various reaction conditions are shown in Tables 1 and 2. Effects of cell gas conditions, as indicated by i.o.c.p., can be seen in Tables 1 and 3, and Figs 2 and 4.

For this solution-cathode system, there appeared to be an initial unstable gas transition region from approximately -0.69 to -0.73 V, in which the potential fluctuated, and for which the introduction of small amounts of air or nitrogen pushed the potential to its respective aerated (more positive) or deaerated (more negative) potential. Thus the i.o.c.p. aeration range was approximately -0.52 to -0.69 V; the

i.o.c.p. deaeration range, -0.73 to -0.85 V. An i.o.c.p. of -0.85 V was attained only by application of very high nitrogen flow, accompanied by eventual evaporation of the solution. The effect of aeration or deaeration on the i.o.c.p. was reversible. Galli [13] reported that i.o.c.p. values for ethyl bromide polycarbonate solutions with tetraethyl or tetrabutylammonium bromide at a lead cathode increased about +0.1 V when oxygen was bubbled to the solution.

The aeration and deaeration effects on subsequent current densities are different in character, as

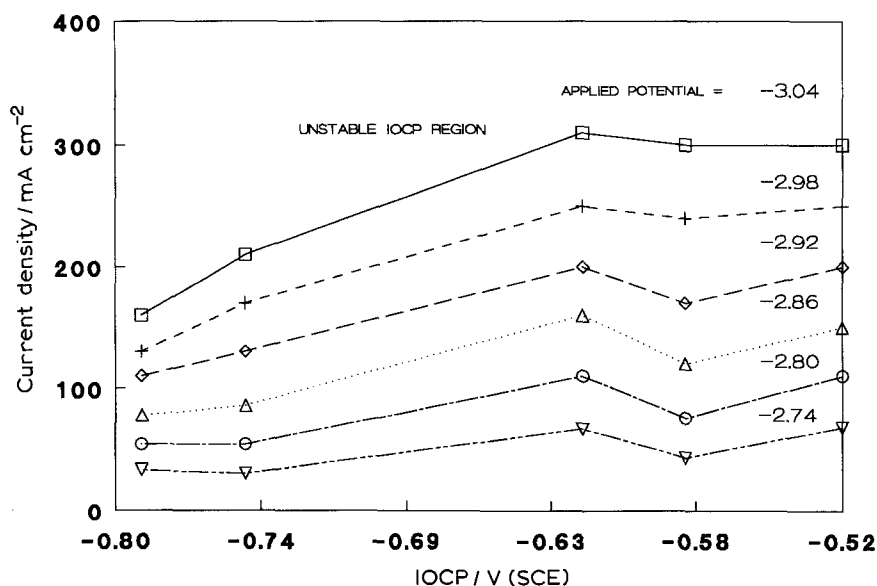


Fig. 2. Current density as a function of initial open circuit potential at various applied potentials. All solutions are 2 M BuCl, 0.25 M TEAC, and 0.5 M H<sub>2</sub>O in MeCN.

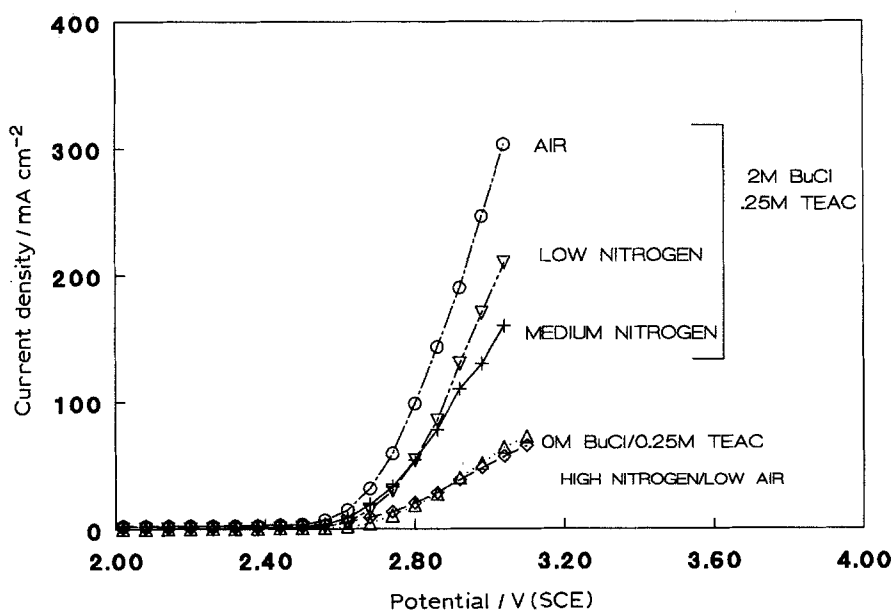


Fig. 3. Current density as a function of applied potential for various solution and gas conditions. All solutions are 0.25 M TEAC and 0.5 M  $H_2O$  in MeCN; as indicated, those with BuCl are 2 M BuCl. The overlapping results at 0 M BuCl and 0.25 M TEAC are from experiments with and without air (i.e. with nitrogen). Results for air and BuCl represent the mean values of three experiments, in which the average of the standard deviations divided by their mean values from  $-1.6$  to  $-3.04$  V (after low-level corrosion reactions) was 0.16. Results after initial low-level corrosion reactions for low nitrogen and BuCl, for air and no BuCl, and for nitrogen and no BuCl represent the mean values of two experiments apiece, for which the average of the standard deviations divided by their mean values was 0.09 ( $-2.56$  to  $-3.04$  V), 0.07 ( $-1.66$  to  $-3.04$  V), and 0.13 ( $-2.56$  to  $-3.04$  V), respectively. Only one experiment was performed for medium nitrogen and BuCl.

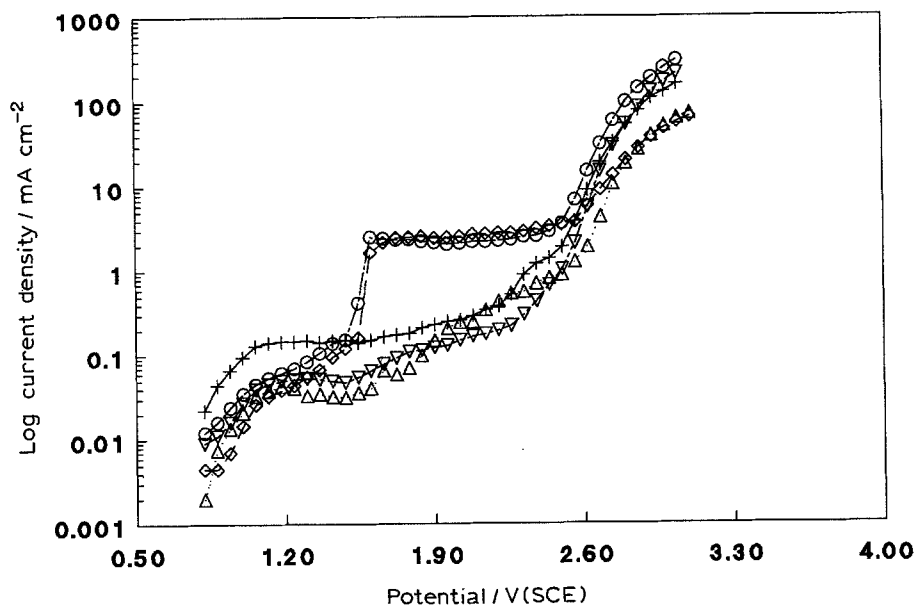


Fig. 4. Current density on a log scale as a function of applied potential for various solution and gas conditions. All solutions are 0.25 M TEAC and 0.5 M  $H_2O$  in MeCN; as indicated, those with BuCl are 2 M BuCl. Symbols and experiments are identical to those in Fig. 3.

illustrated in Fig. 2. Current densities in the aerated electrolyte region appear to be independent of the i.o.c.p. Therefore results reported in Table 1, and Figs 3 and 4 represent the combined data from experiments with aerated electrolyte. At higher negative applied potentials, however, current densities in the deaerated i.o.c.p. region decrease with increasing nitrogen flow. Therefore results are reported as functions of single i.o.c.p. values, sometimes averaged for duplicate experiments.

### 3.2. Linear potential sweep

Polarization conditions and results for reaction

variables and competing reactions are given in Table 1 and Figs 3 and 4. Under various degrees of reaction aeration, cathodic potential sweeps were performed with MeCN solvent and 0.50 M  $H_2O$  for two solution compositions: 2 M BuCl/0.25 M TEAC and 0 M BuCl/0.25 M TEAC. The divergence of these two cases at higher negative potentials is apparent in Figs 3 and 4. Three potential ranges of distinctly different current response characteristics for solutions with BuCl reactant are clearly visible on a log scale plot in Fig. 4. These ranges were correlated with potentiostatic (product determination) results to define a potential window for butyltin chloride product formation.

In the low potential region from approximately

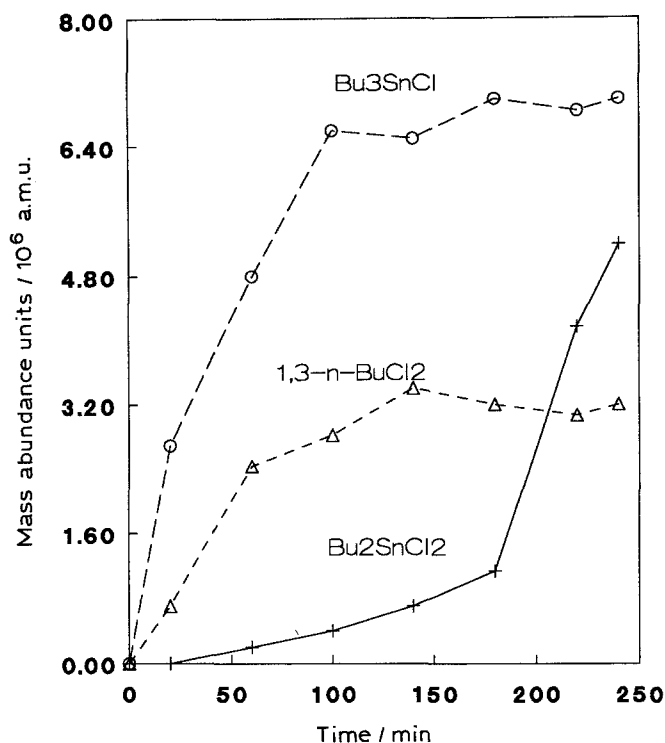


Fig. 5. Product yield as a function of reaction time for the flow cell experiment. Reaction conditions: 3 M BuCl, 0.05 M TEAC, 0.5 M H<sub>2</sub>O, and MeCN with 100 mA cm<sup>-2</sup> current density under closed nitrogen atmosphere at 35°C.

-1.0 to -1.5 V, there appeared to be low-level corrosion-reduction reactions common to all cases (Fig. 4). In the second potential region (about -1.6 to -2.5 V), current was enhanced for all aerated solutions, apparently due to oxygen reduction or oxygen-mediated reactions. Within this potential region, a gold-coloured film always developed on the cathode surface.

At about -2.5 V, the currents begin to show strong dependence on total solution composition (Figs 3 and 4). At potentials more negative than -2.5 V, the presence of BuCl greatly increased the current density. Furthermore, aeration of the BuCl/TEAC solution resulted in even greater current density. In 2 M BuCl/0.25 M TEAC, at potentials more negative than -2.6 V, gold-brown streams of liquid issued from the cathode. These streams progressively darkened in response to increasingly negative potential until about -2.98 V. At potentials more cathodic than -2.98 V, the evolution of black precipitate from the cathode became visible, although the solutions were often almost opaque at this point. These dark fines, which are probably butyltin polymer and/or butyltin-TEAC complexes, generally turned white upon exposure to air. Aeration during the potential sweeps delayed somewhat the onset of solution murkiness and opacity.

Thus from -2.5 to -3.0 V, butyltin products are associated with a brown-coloured sacrificial reaction, for which the rate of product formation perhaps increases with increasing solution aeration (Fig. 3). This possibility is supported by the fact that aeration does not increase current density in solutions without BuCl (Fig. 3). Because of various experimental observations, Ulery speculated that

oxygen and chlorine together in an undivided cell may interact to generate radicals independently of cathodic electron transfer [1].

### 3.3. Steady-state potentiostatic experiments

Conditions and results of the potentiostatic batch cell experiments are presented in Tables 2 and 3. Current densities are reported from 5–60 min reaction time, since (stepped) initial currents were high. All experiments, except one at the applied potential of -2.20 V, were run at 2 M BuCl, 0.25 M TEAC, and 0.5 M H<sub>2</sub>O with MeCN.

The experiments at applied potentials of -1.50 and -2.20 V showed the presence of clear, gold films on the cathode surface, accompanied by low currents, no measurable change in cathode weights, and no detectable products or precipitates as analysed by GC/MS. The solutions changed in appearance from clear and colourless, to clear and light gold. At -1.50 V the cathode surface remained smooth, but changed from shiny to dull. At -2.20 V and 0 M BuCl, the cathode remained shiny, the reaction solution turned clear gold in colour, and the current density increased slightly after 60 min. Recorded currents at -2.20 V with no BuCl showed the same pronouncedly noisy behaviour characteristic of this potential region as in the linear potential sweep experiments.

Potentiostatic experiments at -2.75 V targeted the lower limit of the potential window on product formation. At high and medium nitrogen flow, current densities at 5.0 min reaction time in the presence of BuCl were 13.6 and 23 mA cm<sup>-2</sup>, res-

pectively, and remained quite constant throughout the experiments. These current densities are comparable to current densities at  $-2.75$  V in the linear potential sweep experiments at medium and low nitrogen flow of 33 and 29–31  $\text{mA cm}^{-2}$ , respectively. As expected, reaction conditions resulted in no production of solid  $\text{Bu}_2\text{SnO}$  or other solids. Butyltin products were readily detected by GC/MS, but the low concentrations of these compounds could not be quantified. Faradaic efficiency calculations show less than two electrons transferred per tin atom in both experiments.

Potentiostatic experiments with  $\text{BuCl}$  at  $-2.90$  and  $-2.97$  V and low nitrogen flow tested the upper limit of the potential window on product formation. Current densities decreased by over 50% after 60 min. Significant amounts of liquid butyltin products (detected by GC/MS) and apparent white  $\text{Bu}_2\text{SnO}$  precipitate (following product solution exposure to air) were used to calculate product conversions. The low tin conversions reported are probably due in part to inefficient recovery techniques for these small-scale experiments. Potentiostatic current densities at low nitrogen flow after 5.0 min reaction time of 170 and 200  $\text{mA cm}^{-2}$  are comparable to linear potential sweep results at low nitrogen flow of 160–180  $\text{mA cm}^{-2}$ . Faradaic efficiency calculations show almost three electrons transferred per tin atom in both experiments.

Current densities resulting in butyltin product formation obtained in both the potential sweep and potentiostatic experiments are often substantially higher (34 to 250  $\text{mA cm}^{-2}$ , depending on gas and potential conditions) than current densities of 17 to 100  $\text{mA cm}^{-2}$  reported by Ulery [1, 9–11].

### 3.4 Flow cell experiments

The results of one four-hour experiment are described here, although a number of experiments were performed. At 0.05 M TEAC, the calculated faradaic efficiency was 2.68 electrons transferred per Sn atom, or 74.5% current efficiency, for 5.94 g of tin dissolved. Under nitrogen atmosphere, the solution colour changed from colourless and clear to an olive brown after several minutes of reaction, and darkened increasingly with time. After approximately 30 min, noticeable outgassing from the reaction solution indicated presumably the production of chlorine and/or alkanes. Both reaction samples and the product solution, however, quickly turned clear and light yellow after exposure to ambient atmosphere. The solutions also showed formation of a white precipitate, probably  $\text{Bu}_2\text{SnO}$ , and not salt complexes, since solids were not present prior to ambient air–solution contacting.

Product accumulation in the sumps of the flow cell was studied by direct sampling and analysis by GC/MS, and the results are shown in Fig. 5. Two low molecular weight  $\text{BuCl}$  side-products, 1,3-*n* $\text{BuCl}_2$  and 1,4-*n* $\text{BuCl}_2$ , were found in all butyltin syntheses,

including the batch cell experiments. For this flow cell experiment,  $\text{Bu}_3\text{SnCl}$  appeared to reach a steady-state value at three hours, while  $\text{Bu}_2\text{SnCl}_2$  was still increasing rapidly at four hours. Conversely, in the tetraalkylammonium bromide-catalysed production of butyltin bromides, dibutyltin dibromide concentration first reached a steady-state value, but tributyltin bromide concentration continued to increase rapidly [21].

Butyltin product redistribution [5] has been observed in many product solutions throughout this research. Because the synthesis reported here apparently contains excess chlorine at the conclusion of the reaction, redistribution always resulted in increasing chlorination of the butyltin compounds. Thus, in the flow cell experiment, direct sampling showed the majority of the liquid product to be  $\text{Bu}_3\text{SnCl}$ , with a significant amount of  $\text{Bu}_2\text{SnCl}_2$ , and a small amount of  $\text{Bu}_4\text{Sn}$  (not shown). An indirect (aerated) sample, analyzed after several days, showed the relative amounts of  $\text{Bu}_3\text{SnCl}$  and  $\text{Bu}_2\text{SnCl}_2$  to be almost reversed.

In another set of experiments, the cell was packed with tin particles of 600–850  $\mu\text{m}$  diameter, and a microporous separator used to separate the cathode compartment from the anode compartment. This cell arrangement resulted in high butyltin polymer yields, accompanied by low product yields. The results may be attributed to poor hydrodynamic and/or current density distribution characteristics of the packed bed. The pyrophoric behaviour of butyltin polymer noted by Ulery [1] was observed in several of the packed bed experiments.

### 3.5. Quaternary onium salt: mechanistic considerations

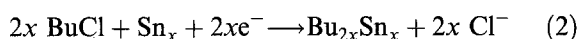
An important factor in the butyltin synthesis reported here is the quaternary onium salt. It obviously serves as the current-carrier; its possible role as reaction catalyst, promoter or 'phase-transfer agent' is appreciated, but less understood. Quaternary onium salts have been used as reaction promoters in both electrolytic and nonelectrolytic alkylmetallic syntheses. In the reduction of ethyl bromide at a lead cathode for the production of tetraethyllead, Galli and Olivani found that tetraethyllead formation was significant in the presence of tetraethyl and tetrabutylammonium bromides, but insignificant for various inorganic salts such as  $\text{LiClO}_4$  [13, 14]. Brown and coworkers reacted ethyl iodide at tin and lead cathodes in DMF or ethanol with both quaternary ammonium halide and inorganic salts; substantial ethyl iodide conversion resulted only with onium salts in DMF [15, 20]. In contrast, Fleischmann, Mengoli and Pletcher reported that onium salts had low promoting effect compared with inorganic salts such as  $\text{NaI}$  in alkyl halide reductions at a tin cathode [22]. It was suggested that these results may be due to insufficient cathode preparation [15, 19].

Onium salts have been used in catalytic amounts for direct nonelectrolytic reactions, such as the synthesis of butyltin bromides from butyl bromide and tin,

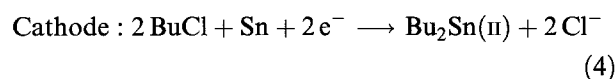
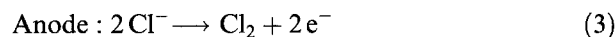


from tin tetraiodide or dibutyltin polymer from butyl chloride [21, 23]. Holland achieved high and selective tin conversion to trialkyltin halides using stoichiometric amounts of quaternary ammonium salts at 120°C [7]. However, Ugo, Chiesa and Fusi found that a catalyst system consisting of crown ether/KI/DMF and no onium salts resulted in high, selective tin conversion to dialkyltin chlorides and bromides at 100°C [24].

Various mechanisms have been proposed and discussed for the direct production of alkyl metal halides, including alkyltin halides [1, 3, 7, 8, 13, 14, 23, 25–27]. For the reduction of BuCl at a tin cathode resulting in predominantly dialkylation products, with electrical efficiencies of two electrons consumed per tin atom dissolved, Ulery suggested that BuCl reacts with tin as [1]



The value for  $x$  depends on whether dibutyltin leaves the cathode as a monomer ( $x = 1$ ), or a tin–tin associated (tin-polymer) species. When primarily monomeric butyltin products are formed, it is hypothesized that the dominating cathodic reaction produces a short-lived, active intermediate, dibutyltin ( $\text{Bu}_2\text{Sn(II)}$ ). Whether alkyltin(II) compounds can exist as monomers is somewhat controversial; such species may actually be small tin cyclics and oligomers, susceptible to the same reactions proposed for other tin(II) compounds [4, 28, 29]. Assuming a dibutyltin monomer, however, the direct heterogeneous process may be summarized as



The overall mechanism in Equation 2 could be interpreted as a two-step sequence of one-electron RX reductions, consistent with either one of two mechanisms considered by Ulery for one-electron RX reduction [8]. Both mechanisms assume that, in the cathode-directed alignment of the polar RX molecule, the electropositive R group faces the cathode, directing away the electronegative X atom. According to the first reduction mechanism (Elving's postulate of a general nucleophilic substitution), charge is transferred from the cathode to the halogen in an intermediate transition step [8, 30]. The alkyl group then binds to the metal, releasing the halide anion.

In the second reduction mechanism, RX bond rupture at the cathode results in R' and X<sup>-</sup> without new bond formation. Such a mechanism requires an additional chemical reaction to form the carbon–metal bond, which Ulery suggests may be analogous to Paneth's classic metal scavenging reaction [8, 31]. This mechanism is identical to that proposed by Galli and Olivani for the reduction of ethyl bromide at a lead cathode to ethyllead in the presence of an onium salt, which competes successfully against a two-electron transfer reaction resulting in alkane offgases

[13, 14]. Such one-electron reduction is analogous to that proposed for the well-known Monsanto process of acrylonitrile reduction to adiponitrile, in which adsorption of onium salts at the electrode apparently eliminates a competing two-electron process [13, 14].

From polarographic studies of alkyl halides at a lead cathode [8], Ulery concluded that the Elving mechanism dominates in electrosyntheses resulting in alkyl metal products, but that the second mechanism is present to a greater or lesser extent, depending on various reaction conditions. Unlike some suggested mechanisms, the reaction schemes postulated in Equations 2 and 4 accommodate the formation of butyltin polymers, as well as  $\text{Bu}_4\text{Sn}$  and butyltin chloride products.  $\text{Bu}_4\text{Sn}$ ,  $\text{Bu}_3\text{SnCl}$  and  $\text{Bu}_2\text{SnCl}_2$  are probably formed from BuCl and anodically produced  $\text{Cl}_2$  by oxidative addition to  $\text{BuSn(II)}$  in monomer, tin cyclic or polymer form. Oxidative addition is an established mechanism for these reactions [28].

Many of the mechanisms for the direct, non-electrolytic production of alkyltin halides in the presence of a quaternary ammonium salt have been reviewed by Holland [7], who himself proposed a corrosion mechanism with anodic and cathodic charge balances for the direct production of triorganotin halides with stoichiometric amounts of onium salt (Scheme 5 in above reference). According to Holland's mechanism, onium salt-generated halide ions and tin react to form the nucleophile  $\text{SnX}_3^-$  (X a halide), which successively adds alkyl halide by mono-addition, followed by either di or tri-addition, while regenerating the  $\text{SnBr}_3^-$  nucleophile. When small amounts of halide ion are available, the diorganotin dihalide is formed; with large amounts of halide ion present, the triorganotin halide.

In the flow cell experiment (Fig. 5), Ulery's mechanism [1] could explain the steady state concentration of  $\text{Bu}_3\text{SnCl}$  after three hours, in contrast to the initially smaller, but constantly increasing concentration of  $\text{Bu}_2\text{SnCl}_2$ , since increasing amounts of anodically produced chlorine would favour production of  $\text{Bu}_2\text{SnCl}_2$ . Holland's mechanism [7], according to which decreasing amounts of TEAC favour production of  $\text{Bu}_2\text{SnCl}_2$ , could also account for the observed production formation. However, the small amount of TEAC initially present in our reaction would not appear to support Holland's mechanism. As suggested by Ulery, it seems likely that different mechanisms for the production of alkyltin halides dominate according to controlling reaction conditions. In the potentiostatic experiments, for example, 1.7 electrons transferred at  $-2.75 \text{ V}$  increased to 2.9 and 2.8 electrons at  $-2.90$  and  $-2.97 \text{ V}$ , respectively (Table 3).

### 3.6. Aeration of BuCl

The effect of prior air exposure on BuCl reactivity is presently not understood by us. Because BuCl stored under nitrogen required reaeration prior to the

reaction to attain high and reproducible current densities, it is possible that BuCl aeration produces reaction intermediates for butyltin electrosynthesis which are favourable in the short-term, but unfavourable in the long-term. Or the apparent importance of BuCl aeration for this synthesis may be simply an impurity effect. For whatever reason, the state of BuCl reactant appears to be an important variable.

#### 4. Conclusion

Two important findings of this research on butyltin electrosynthesis can be identified. (i) From correlation of linear potential sweeps with potentiostatic batch cell experiments, four major reaction regions were established as functions of decreasing potential, including a proposed potential window on butyltin product formation. Current densities resulting in butyltin product formation are significantly higher than those reported by others in previous work. (ii) Process gas conditions are fundamental to both reproducibility and high product yield. Gas conditions for ensuing electrolytic reactions were established according to measured i.o.c.p's; increased current densities due to butyltin product formation resulted from aerated solutions. Even the aeration of the BuCl reactant prior to synthesis appears to be an important process variable.

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