

Electrocatalytic reduction of alkyl iodides in tetrahydrofuran at silver electrodes

Christopher A. Paddon,¹ Farrah L. Bhatti,² Timothy J. Donohoe² and Richard G. Compton^{1*}

¹Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK

²Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, UK

Received 18 September 2006; revised 24 October 2006; accepted 25 October 2006

ABSTRACT: Recent interest in the electrocatalytic activity of silver towards the reduction of alkyl iodides has led us to investigate whether the effect is observed in tetrahydrofuran (THF) at room temperature. Using platinum electrodes in THF for the reduction of alkyl halides at 298 K has been hampered by the solvent window, which ‘obscures’ the voltammetric signals of interest. In order to overcome these problems, voltammetry has been performed at low temperature and was shown to extend the voltammetric window, leading to accurate electrochemical analyses and even novel changes in mechanism(s) of the reactive species following electron-transfer (ET). Herein, it is shown that for a primary and tertiary alkyl iodide in THF, electroreduction at silver leads to a significant shift in the reduction potential to more positive values compared to platinum. In addition, following reduction, a characteristic series of oxidation peaks are observed and are shown to be due to the specific activity of iodide ions towards silver following reductive cleavage of the parent alkyl iodide. This characteristic feature is not observed with other halide ions: bromide and chloride. Preparative electrolyses at controlled-potential have suggested that the reduction of the above alkyl iodides is a one-electron concerted process. The ‘free’ iodide ions act as a monitor of reaction progression, and the carbon-centred radical either dimerises and/or abstracts a hydrogen atom from the electrolyte/solvent; 1-iodoadamantane giving percentage yields of 58% adamantane and 39% 1,1'-biadamantane, the primary alkyl iodide, prepared in-house, giving 67% R-H and 25% R-R. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: electrocatalysis; alkyl iodides; silver electrode; tetrahydrofuran (THF); adsorption

INTRODUCTION

The electrocatalytic reduction of organic halides has received much attention in the last few decades.^{1–3} Silver as an electrode material has been found to possess extraordinary electrocatalytic properties^{4,5} which have been utilized in synthetic^{6–9} and environmental applications.^{10–12} The reduction of carbon–halogen bonds has also attracted much interest as a model process for the investigation of dissociative electron transfers (DETs) which occur at ‘inert’ electrodes (for example at platinum and glassy carbon (GC)).^{13–15} A catalytic surface such as silver has been shown to modify the reaction scheme possibly through the formation of a more favourable activated complex(es) and/or interaction of the metal with the organic halide and its reduction intermediate(s) and product(s)¹⁶ and it has been reported that the electron transfer and dissociation are concerted yielding directly a radical and anion. In addition, it has been noted that the

molecular structure of the organic halide,^{17,18} the type of halogen atom,¹⁷ the surface morphology of the electrode,¹⁹ and adsorption of the reagents and their reduction products especially halide ions,^{20–22} all play a role in the catalytic process. More recently, the effect of the solvent used in the electrocatalytic reduction of organic bromides on silver has been investigated.²³

Herein, we report on the electrocatalytic reduction of two organic iodides in tetrahydrofuran (THF); a ‘model’ tertiary alkyl halide: 1-iodoadamantane, **I** and a primary alkyl halide, **II**, prepared in-house, as shown in Fig. 1. Compound **II**, being a primary alkyl iodide, provided us with an inert electrochemical backbone which acted as a molecular ‘tag’ following ET, thus allowing spectroscopic detection and chromatographic separation following bulk-electrochemical procedures not seen with straight chain alkyl halides such as 1-iodopentane. THF is used as the solvent of choice as it is used frequently in synthetic single electron transfer (SET) reductions as a ‘neutral solvent’ that is, electrophilic attack of intermediates is much lowered in this solvent. The results of voltammetric analyses using silver electrodes in THF at 298 K were surprising, showing not only a significant shift

*Correspondence to: R. G. Compton, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK.

E-mail: Richard.Compton@chem.ox.ac.uk

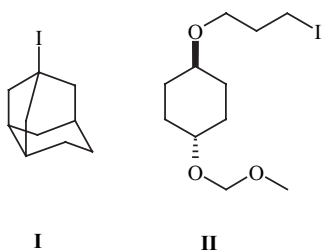


Figure 1. Structures of 1-iodoadamantane, **I**, and *trans*-1-(3-iodopropoxy)-4-(methoxymethoxy)cyclohexane, **II**

of the reduction potential to more positive values as described by other workers, but also a unique and characteristic pattern of oxidative iodine-electrochemistry following reductive cleavage of the alkyl iodide. In particular, we observed a specific adsorption of iodide ions^{24,25} not seen at 'inert' electrodes such as platinum. These are shown to be due to the activity of iodide (I^-), tri-iodide (I_3^-) and iodine (I_2) towards the silver surface. Adsorption has important implications in many fields, such as corrosion, galvanic deposition, electrosynthesis and of course, electrocatalysis.²⁵ These features were observed only when using silver electrodes and appeared regardless of the type of alkyl iodide used. In addition, this characteristic feature of iodide ions was not observed with other halide anions such as bromide and chloride. To the best of our knowledge, this follow-up electrochemistry in THF has not been reported thus far, in contrast to the extensive investigations of iodide/tri-iodide and iodine electrochemistry at platinum electrodes in organic solvents^{26–30} and in aqueous solutions.^{31–33} In fact, in previous reports using aprotic solvents such as acetonitrile, *N,N*-dimethylformamide, dimethylsulfoxide, acetone, and propylene carbonate, no mention has been given as to whether or not any follow-up electrochemistry occurs within the full potential window.²³

Finally, controlled-potential, bulk electrolyses are used to determine the number of electrons, n , involved in the reduction process at silver and also identify additional products that are formed and not being electroactive within the potential window. The 'free' iodide ions act as a monitor of reaction progression, and the carbon-centred radical either dimerises and/or abstracts a hydrogen atom from the electrolyte/solvent; **I** giving percentage yields of 58% adamantane and 39% 1,1'-biadamantane, and **II** giving 67% R-H and 25% R-R.

EXPERIMENTAL

Reagents

1-Iodoadamantane, **I** (Fig. 1) (Aldrich, 98%), tetra-*n*-butylammonium perchlorate (TBAP), tetra-*n*-butylammonium iodide (TBAI), tetra-*n*-butylammonium bromide

(TBABr), and tetra-*n*-butylammonium chloride (TBACl) (Fluka), were used as received without any further purification. Anhydrous tetrahydrofuran was purified by filtration through two columns of activated alumina (grade DD-2) as supplied by Alcoa, employing the method of Grubbs *et al.*³⁴ *Trans*-1-(3-iodopropoxy)-4-(methoxymethoxy)cyclohexane, **II** (Fig. 1) was prepared in-house and a brief description of its synthesis is given below:

Potassium carbonate (560 mg, 4.10 mmol) and sodium iodide (2.53 g, 16.9 mmol) were added to a solution of the mesylate: 3-[[*trans*-4-(methoxymethoxy)cyclohexyl]oxy] propyl methanesulfonate, (1.00 g, 3.40 mmol) in acetone (30 ml) and stirred at 40 °C for 6 h. The reaction was concentrated *in vacuo* and extracted from saturated aqueous sodium thiosulfate (50 ml) with diethyl ether (2 × 50 ml). The combined organic extracts were dried and evaporated under reduced pressure to give **II** (980 mg, 88 %) as a colourless oil.

***Trans*-1-(3-iodopropoxy)-4-(methoxymethoxy)cyclohexane.** 1H NMR δ_H (400 MHz, $CDCl_3$) 4.67 (2H, s, OCH_2OCH_3), 3.54 (3H, m, cyclohexane CH and OCH_2), 3.37 (3H, s, OCH_2OCH_3), 3.29 (3H, m, cyclohexane CH and CH_2I), 2.02 (6H, m, cyclohexane CH_2 and OCH_2CH_2), 1.36 (4H, m, cyclohexane CH_2); ^{13}C NMR δ_C (100MHz, $CDCl_3$) 94.7, 76.7, 74.4, 67.4, 55.2, 33.6, 29.7, 29.3, 4.0; **MS** m/z (CI+) 346 (100%, $[M+NH_4]^+$); **HRMS** $C_{11}H_{22}O_3I$ (MH) requires 329.0614, MH^+ found 329.0607 (−2.1 ppm); **IR** ν_{max} (film)/ cm^{-1} 2936, 1454, 1376, 1107, 1043.

Cyclic voltammetry (CV)

Voltammetric measurements were carried out on an Autolab PGSTAT20 (Eco-Chemie, Utrecht, Netherlands) potentiostat. A three-electrode arrangement was used in an air-tight, three-necked electrochemical cell. The cell with solid electrolyte, was dried *in vacuo* overnight before solvent addition and electrochemical experiments. The working electrodes employed were a 1.71 mm (diameter) silver electrode (housed in a TeflonTM insulating case), and a 1 mm (radius) platinum electrode (Cypress Systems, Inc., KS) with a large area, shiny platinum wire (Goodfellow Cambridge Ltd, Cambridge) as the counter electrode. The silver electrode was carefully polished before use on a clean polishing pad (Kemet, UK) using 3 μm and 1 μm diamond spray (Kemet, UK). The platinum electrode was polished using 1.0 μm and 0.3 μm aqueous-alumina slurries (Beuhler, Lake Buff, IL). All working electrodes were then rinsed in de-ionised and doubly filtered water of resistivity no greater than 18 $M\Omega$ cm, taken from an Elgastat filter system (Vivendi, Bucks, UK) and carefully dried prior to use. A $Fc/Fc^+PF_6^-$

reference electrode was developed for use in THF and at low temperatures.³⁵ The temperature was monitored and controlled by an external system (Julabo FT902, JULABO Labor Technik GmbH, D-77960 Seelbach/Germany) and in all reactions was kept constant at 295 K \pm 1 K. Typically, the solutions were degassed vigorously for 5 min using impurity-free argon (BOC gases, Guildford, Surrey, UK) to remove any trace oxygen and an inert atmosphere was maintained throughout all analyses. All solutions were prepared under an atmosphere of argon using oven-dried glassware such as syringes and needles used for the transfer of moisture-sensitive reagents. All voltammetric measurements were performed inside a faraday cage in order to minimise any background noise.

Preparative electrolysis

Controlled-potential, bulk electrolyses were carried out in a two-compartment cell, the catholyte and anolyte being separated by a sintered glass frit. The cathode was a rectangular silver plate (area = 6.25 cm²) (Goodfellow, UK), and the anode, a platinum mesh housed within the separate compartment with 0.1 M TBAP in THF. A Fc/Fc⁺PF₆⁻ reference electrode was used and a shiny silver wire (250 μ m, diameter) (Goodfellow) served as an 'in-situ' monitor of the reaction progression. All electrolyses were vigorously stirred using a magnetic stirrer bar and the temperature maintained at 295 K \pm 1 K using an external system (Julabo FT902, JULABO Labor Technik GmbH, D-77960 Seelbach/Germany).

Saturated aqueous ammonium chloride (2 ml) followed by water (10 ml) was added to the electrolysed solution upon reaction completion. Diethyl ether (20 ml) was then added and the two fractions separated. The organic fraction was then washed with aqueous hydrochloric acid (1 M 6 \times 10 ml), saturated aqueous sodium thiosulfate¹ (10 ml), saturated sodium bicarbonate (10 ml), and saturated aqueous sodium chloride (10 ml). The organic layer was dried over magnesium sulphate and then carefully evaporated under reduced pressure especially in the case of 1-iodoadamantane electrolyses where adamantane as a product, is known to sublime in the rotary evaporator.

The products were identified by a combination of ¹H NMR, ¹³C NMR (Bruker AV400 (400 MHz) spectrometer), gas chromatography (GC), thin-layer chromatography (TLC), flash chromatography (acetone/petrol gradient elution) and mass spectrometry in which mass spectra (*m/z*) were recorded in electrospray ionisation (ESI) mode on a Fisons Platform II. Accurate mass (HRMS) were recorded under conditions of ESI on a

¹Saturated aqueous sodium thiosulfate was added to remove the iodine which was observed to accumulate significantly in the organic layer during extractions.

micromass LCT (resolution = 5000 FWHM) using a lock-spray source.

RESULTS AND DISCUSSION

Cyclic voltammetry of 1-iodoadamantane **I** and *trans*-1-(3-iodopropoxy)-4-(methoxymethoxy)cyclohexane **II**

First, a blank voltammogram was obtained to determine the potential window in THF (0.1 M TBAP) at a silver electrode. It was observed that the cathodic window extended from < -0.1 V to *ca.* -3.5 V relative to Fc/Fc⁺PF₆⁻. Following this, the voltammetric response of **I** and **II** were recorded in separate experiments and the voltammograms are shown in Figs 2 and 3 respectively. Cyclic voltammetry is consistent with an *n* = 1 electron process with values of the transfer coefficient, α in the range: 0.5 to 0.3. This is in good agreement with previous literature reports of α values where the breaking of a carbon-halogen bond is concerted with the electron transfer process.^{16,23} As a function of scan rate, **I** was additionally analysed and the voltammograms are shown in Fig. 4. The reduction of both substrates (peak A) was observed to occur at more positive cathodic potentials in comparison to platinum being used as the electrode material. In the case of substrate **II**, Fig. 3 shows a small *pre-peak* which may be due to the adsorption of the parent iodide to the electrode surface.¹⁶ Upon reversing the potential i.e., anodically scanning, a series of oxidation peaks was seen and are shown again by Figs 2 and 3. Indeed, this characteristic series of peaks is seen in both cases regardless of whether **I** or **II** is analysed. It was hypothesised that these were due to iodide ions formed

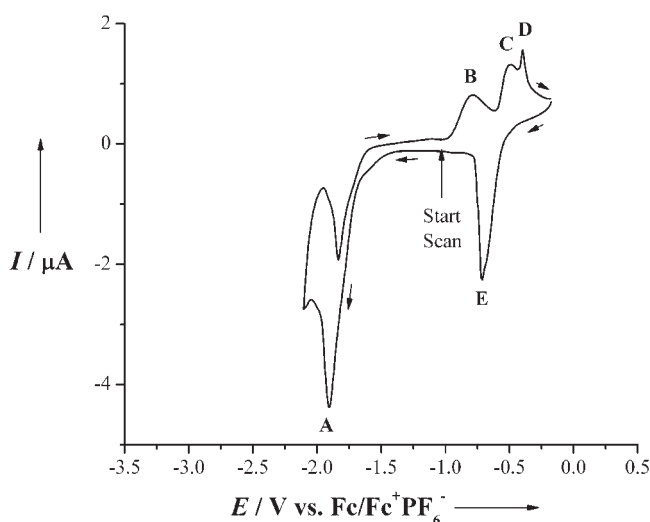


Figure 2. Voltammetric response of 1-iodoadamantane, **I**, (6.7 mM) in THF (0.1 M TBAP) using a silver electrode (1.71 mm (diam.)), recorded at a scan rate of 75 mV s⁻¹ at 295 K. Start scan: -1.0 V, first reverse: -2.2 V and second reverse: -0.1 V versus Fc/Fc⁺PF₆⁻

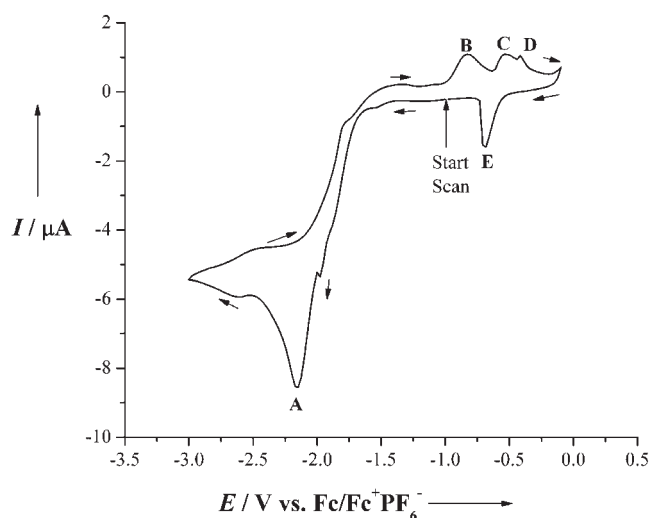


Figure 3. Voltammetric response of *trans*-1-(3-iodopropoxy)-4-(methoxymethoxy)cyclohexane, **II**, (3 mM) in THF (0.1 M TBAP) using a 1.71 mm (diam.) silver electrode, recorded at a scan rate of 50 mV s^{-1} at 295 K. Start scan: -1.0 V , first reverse: -3.0 V and second reverse: 0 V versus $\text{Fc}/\text{Fc}^+\text{PF}_6^-$

following the reductive cleavage of the alkyl iodide. In order to characterise these, a source of iodide ions was used.

Cyclic voltammetry of tetra *n*-butylammonium iodide (TBAI) at silver

In order to provide evidence for iodide electroactivity following the reductive cleavage of the alkyl iodide, tetra

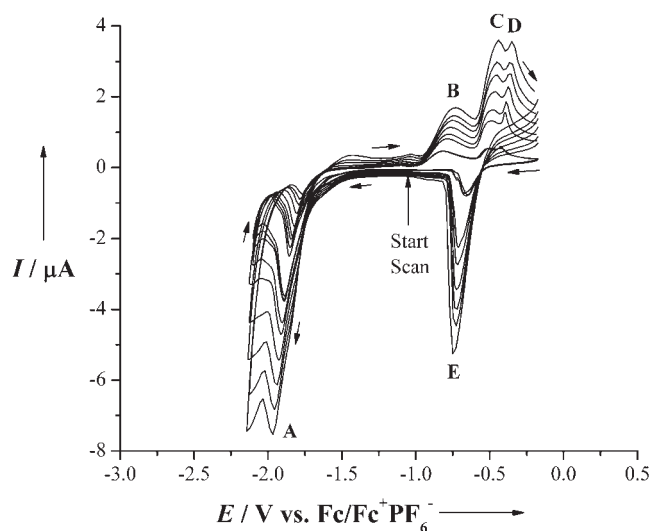


Figure 4. Voltammetric response of 1-iodoadamantane, **I**, (6.7 mM) in THF (0.1 M TBAP) using a silver electrode (1.71 mm (diam.)), recorded at various scan rates: 30, 40, 50, 75, 100, 150, 200, 250 and 300 mV s^{-1} at 295 K. Start scan: -1.0 V , first reverse: -2.2 V and second reverse: -0.1 V versus $\text{Fc}/\text{Fc}^+\text{PF}_6^-$

n-butylammonium iodide (TBAI) was used as a source of iodide ions. In addition, it was also of interest to investigate further the report that the addition of iodide ions negatively 'shifts' the reduction peak potential of a 'probe' organic halide molecule, induced by progressive additions of halide ions.^{20,36} The voltammograms following sequential additions of iodide ions are shown in Fig. 5. It can be seen that no 'shift' occurs in the reduction peak potential (peak **A**) of the alkyl iodide, **II**. However, the oxidation peaks observed previously now increase with successive additions of iodide ions (peaks **B**, **C**, **D**). In addition, the cathodic scans show not only a sharp stripping peak (peak **E**), but the emergence of an additional peak, **F**. From these analyses, a complex pattern of reactivity can be deduced and so in an attempt to 'simplify' the voltammetry, we used an 'inert' electrode material, platinum, in order to remove the specific interactions of silver with halide ions.

Cyclic voltammetry of tetra *n*-butylammonium iodide (TBAI) at platinum

The voltammetric response of a solution of TBAI in THF using a platinum electrode is shown in Fig. 6. It can be seen that only two anodic peaks are seen within the potential window (peaks **W** and **X**). These peaks correspond well to those seen at silver i.e., peaks **B** and **C** and also to previous literature reports on iodide

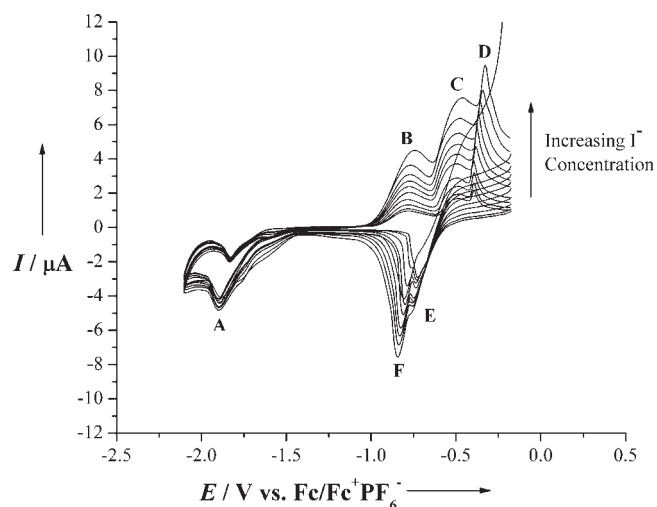


Figure 5. Characterisation of iodide ions: Voltammetric response of 1-iodoadamantane, **I**, (6.7 mM) in THF (0.1 M TBAP) using a silver electrode (1.71 mm (diam.)), recorded at a scan rate of 75 mV s^{-1} at 295 K. Start scan: -1.0 V , first reverse: -2.2 V and second reverse: -0.1 V versus $\text{Fc}/\text{Fc}^+\text{PF}_6^-$. Tetra *n*-butylammonium iodide (TBAI) was added sequentially and the voltammetric response recorded. TBAI concentrations: (i) 0.14 mM, (ii) 2.83 mM, (iii) 5.67 mM, (iv) 1.13 mM, (v) 1.58 mM, (vi) 2.11 mM, (vii) 2.59 mM, (viii) 3.16 mM, (ix) 3.71 mM and (x) 4.75 mM

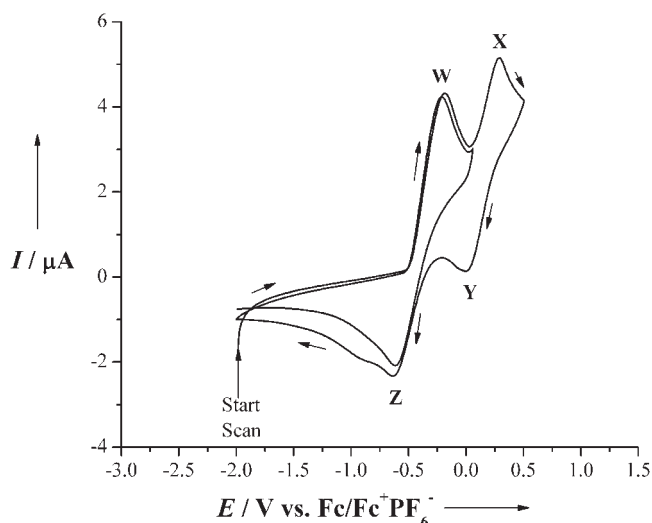
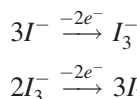


Figure 6. Voltammetric response of iodide ions (8.5 mM TBAI) using a platinum electrode (1 mm (diam.)) in THF (0.1 M TBAP) at 295 K. Scan rate: 100 mV s^{-1} . Start scan -2.0 V , first reverse: 0.2 V , second reverse: 0.5 V versus $\text{Fc}/\text{Fc}^+\text{PF}_6^-$

activity at platinum in non-aqueous solvents^{26–29} and also bromide activity in room temperature ionic liquids (RTILs).^{37,38} However, no peak **D** was observed, even at lower temperatures, where the anodic potential window was extended relative to $\text{Fc}/\text{Fc}^+\text{PF}_6^-$. The two voltammetric peaks for the oxidation of iodide ions are shown below:



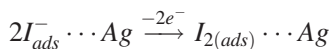
Therefore peaks **B** and **C** are consistent with those observed using platinum electrodes. Peak **D** however, must be specific to silver. Analysis of the area under peak **D** for TBAI at silver using selected scan rates was performed and the data are summarised in Table 1. The values for surface coverage and molecules per cm^2 are not inconsistent with monolayer coverage. Therefore, it is likely that due to silver having a high affinity for iodide ions, these are stabilized sufficiently so that the reduction

Table 1. Analysis of peak **D** at various scan rates following reduction of TBAI only, in THF (0.1 M TBAP) at 298 K

Scan rate (mV s^{-1})	A.U.P D ^a (μC)	Surface coverage (mol cm^{-2})	Molecules (cm^{-2})
5	9.2	2.1×10^{-9}	1.3×10^{15}
10	5.6	1.3×10^{-9}	0.8×10^{15}
50	1.5	3.3×10^{-10}	0.2×10^{15}
75	1.3	2.9×10^{-10}	0.1×10^{15}

^a Area under peak **D**.

of specifically adsorbed iodide is not observed until much more positive potentials:



The origin of peak **E** is likely due to adsorption of iodine by the silver or indeed the substrate iodide being specifically adsorbed as reported by other workers.^{20–22} With increasing iodide concentrations, peak **F** is observed which is most likely due to the increased concentrations of I_2 being generated which can be reduced to I_3^- and then reduced to I^- . This latter step now competing with the former.²²

Cyclic voltammetry of tetra *n*-butylammonium-bromide and chloride at silver

To provide further support to the specific affinity of silver toward iodide ions salts of the bromide and chloride were analysed voltammetrically at a silver cathode. The cyclic voltammograms of tetra *n*-butylammonium bromide and chloride were recorded and clearly showed only two anodic peaks contrasting to the case with iodide where three peaks were observed.

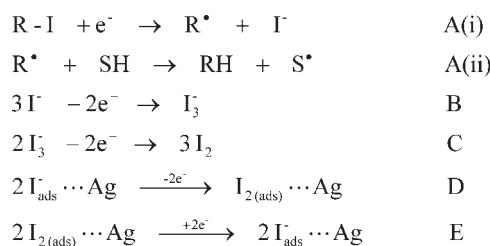
Preparative electrolyses at silver

As the product(s) other than iodide ions are likely to be redox inactive within the potential window we used controlled-potential, bulk electrolyses in order to identify these. In addition, this provided information as to the number of electrons involved in the reductive process. Electrolyses were performed on **I** and **II** at the potentials of -1.7 V and -2.2 V respectively. The results are summarised in Table 2 and experimental details outlined in section 2.3. Using a silver wire, the voltammetric response of the electrolysis reaction was monitored *in situ*. This showed the decreasing response due to the alkyl iodide and an increasing and specific response due to the presence of 'free' iodide ions. By using a chronocoulometric analysis and monitoring, the substrate peak height as a function of Coulombs passed, the number of electrons, n , involved in the reduction process was shown to be 1 in both cases. Electrode filming as reported by some workers²¹ was not observed, although extractions following electrolyses were tailored to incorporate an aqueous saturated sodium thiosulphate wash to remove the significant quantities of iodine by-product. The products were identified by various spectroscopic means; **I** gave percentage yields of adamantane (58%) and the dimer, 1,1'-biadamantane (39%), and **II** yielded a similar mixture of RH (67%) and R-R (25%). No starting material or other significant product(s) were recovered, each starting material showing a full electrochemical

Table 2. Results following preparative bulk electrolysis at controlled-potential

Electrolysis no.	Compound (starting material)	Number of electron(s) (<i>n</i>)	Product(s)	Percentage yield (%)
1	I	1	Adamantane: 1,1'-biadamantane	58 39
2	II	1	RH: R-R	67 25

A silver plate was used ($A = 6.25 \text{ cm}^2$) as the working electrode in a two compartment cell separated by a sintered glass frit in which was housed the counter electrode, a platinum mesh. The reference electrode was a $\text{Fc}/\text{Fc}^+/\text{PF}_6^-$ in THF. THF was the solvent and TBAP (0.1 M) was used as the electrolyte. All reactions were performed at 295 K under constant stirring using a magnetic stirrer bar and their progress monitored at various points after the passage of *X* number of coulombs of charge.

**Scheme 1**

conversion. This contrasts well with the previous attempts at bulk electrolyses using platinum electrodes in THF at 298 K in which a significant fraction of charge passed is consumed by the solvent electroactivity.

CONCLUSIONS

A summary of the electrochemical activity of alkyl iodides is shown in Scheme 1 where SH is either solvent and/or supporting electrolyte in which a hydrogen-abstraction reaction may occur. It has been shown that reduction potentials of alkyl iodides (**I** and **II**) in THF at silver are significantly shifted to more positive values compared with platinum, consistent with the current observation of electrocatalytic activity of silver toward organo-halides. Following a one-electron reduction process, a unique and characteristic pattern of iodide electrochemistry is seen. This corresponds to the oxidation of I^- and I_3^- species in solution, whilst at more positive potentials, a specific oxidation peak is seen corresponding to the oxidation of adsorbed iodide ions, this potential being much more positive than that of iodide ions in solution due to the high affinity of silver towards halide ions. A cathodic peak is seen on potential reversal, which is likely due to the reduction of adsorbed molecular iodine—again the stabilisation inferred by silver responsible for this. Comparisons with TBAI at platinum have shown that such specific effects are indeed, only observed at silver. In addition, other halide ions such as bromide and chloride do not show this specific

response. Finally, preparative electrolyses at controlled-potential have shown that a mixture of reduced monomers and dimers are formed following the passage of charge required for a one-electron reduction.

Acknowledgements

C. A. P and F. L. B wish to thank EPSRC for a joint project studentship (Grant GR/T05011/01).

REFERENCES

- Peters DG, Bard AJ, Stratmann M, Schäfer HJ (eds). *Organic Electrochemistry: Chapter 8 Oxidation and Reduction of Halogen-Containing Compounds*, Vol. 8, 1st ed., Wiley: New York, 2004.
- Peters DG, Lund H, Hammerich O (eds). *Organic Electrochemistry* (4th edn). Marcel Dekker: New York, 2001; Ch 8. pp. 341–377.
- Savéant J-M. *Single Electron Transfer and Nucleophilic Substitutions*, Vol. 26, Academic Press: London, 1990.
- Rondinini S, Mussini PR, Crippa F, Petrone M, Sello G. *Collect. Czechoslovak Chem. Commun.* 2000; **65**: 881.
- Rondinini S, Mussini PR, Crippa F, Sello G. *Electrochem. Commun.* 2000; **2**: 491.
- Isse AA, Ferlin MG, Gennaro A. *J. Electroanal. Chem.* 2005; **581**: 38.
- Isse AA, Gennaro A. *Chem. Commun.* 2002; **23**: 2798.
- Rondinini S, Mussini PR, Cantu G, Sello G. *Phys. Chem. Chem. Phys.* 1999; **1**: 2989.
- Guerrini M, Mussini PR, Rondinini S, Torri G, Vismara E. *Chem. Commun.* 1998; 1575.
- Rondinini S, Vertova A. *Electrochimica. Acta.* 2004; **49**: 4035.
- Rondinini S, Mussini PR, Specchia M, Vertova A. *J. Electrochem. Soc.* 2001; **148**: D102.

12. Delli E, Kouloumtzoglou S, Kyriacou G, Lambrou C. *Chem. Commun.* 1998; **16**: 1693.
13. Andrieux CP, Gallardo I, Savéant J-M. *J Am. Chem. Soc.* 1989; **111**: 1620.
14. Savéant J-M. *J. Am. Chem. Soc.* 1987; **109**: 6788.
15. Andrieux CP, Savéant J-M, Su KB. *J. Phys. Chem.* 1986; **90**: 3815.
16. Isse AA, Falciola L, Mussini PR, Gennaro A. *Chem. Commun.* 2006; **3**: 344.
17. Rondinini S, Mussini PR, Muttini P, Sello G. *Electrochimica. Acta.* 2001; **46**: 3245.
18. Bellomunno C, Falciola BDL, Longhi M, Mussini PR, Doubova LM, Di Silvestro G. *Electrochimica. Acta.* 2005; **50**: 2331.
19. Ardizzone S, Cappelletti G, Doubova LM, Mussini PR, Passeri SM, Rondinini S. *Electrochimica. Acta.* 2003; **48**: 3789.
20. Falciola L, Mussini PR, Trasatti S, Doubova LM. *J. Electroanalyt. Chem.* 2006; **593**: 185.
21. Mussini PR, Ardizzone S, Cappelletti G, Longhi M, Rondinini S, Doubova LM. *J. Electroanalyt. Chem.* 2003; **552**: 213.
22. Ardizzone S, Cappelletti G, Mussini PR, Rondinini S, Doubova LM. *J. Electroanalyt. Chem.* 2002; **532**: 285.
23. Falciola L, Gennaro A, Isse AA, Mussini PR, Rossi M. *J. Electroanalyt. Chem.* 2006; **593**: 47.
24. Foresti ML, Innocenti M, Forni F, Guidelli R. *Langmuir.* 1998; **1**: 7008.
25. Magnussen OM. *Chem. Rev.* 2002; **102**: 679.
26. Datta J, Kundu KK. *Bullet. Electrochem.* 1991; **7**: 4.
27. Kamau GN, Rusling JF. *J. Electroanalyt. Chem.* 1990; **292**: 187.
28. Behl W, Chin DT. *Proc. Electrochem. Soc.* 1987; 441.
29. Macagno VA, Giordano MC. *Electrochimica. Acta.* 1969; **14**: 335.
30. Kolthoff IM, Jordan J. *J. Am. Chem. Soc.* 1953; **75**: 1571.
31. Akkermans RP, Fulian Q, Roberts SL, Suarez MF, Compton RG. *J. Phys. Chem. B.* 1999; **103**: 8319.
32. Breiter MW. *Electrochimica. Acta.* 1963; **8**: 925.
33. Perichon J, Rene B. *Bulletin de la Societe Chimique de France* 1967; **10**: 3707.
34. Pangborn AB, Giardello MA, Grubbs RK, Rosen RK, Timmers RJ. *Organometallics.* 1996; **15**: 1518.
35. Paddon CA, Compton RG. *Electroanalysis.* 2006; **19**: 1919.
36. Fedurco M, Sartoretti CJ, Augustynski J. *Langmuir.* 2001; **17**: 2380.
37. Allen GD, Buzzeo MC, Villagran C, Hardacre C, Compton RG. *J. Electroanalyt. Chem.* 2005; **575**: 311.
38. Allen GD, Buzzeo MC, Davies IG, Villagran C, Hardacre C, Compton RG. *J. Phys. Chem. B.* 2004; **108**: 16322.