Cryoelectrochemical reduction of a phenyl sulfide in tetrahydrofuran: mediated reduction gives different products compared to direct reduction

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ABSTRACT: An electrocatalytic reduction of [(3-{[trans-4-(methoxymethoxy)cyclohexyl]oxy}propyl)thio]benzene (RSPh) in the presence of naphthalene as a mediator is investigated, using steady-state voltammetry at various sized platinum microelectrodes and at low temperature (201 K) in tetrahydrofuran (THF). This mediated process has been found to involve the transfer of one electron, in contrast to the direct electrochemical reduction which involves two electrons. In addition, the mediated reduction proceeds at a potential, some 500 mV less negative than the direct electrochemical reduction. The evidence for the proposed mechanism has been obtained from theoretical simulations, using DIGISIM which shows satisfactory fitting to experimental results and allowed the determination of the rate constant for the homogeneous step. In contrast to direct reduction of RSPh where only one product, *trans*-1-(methoxymethoxy)-4-propoxycyclohexane (RH), has been obtained, the isolation of two products, RH and the dimer, diphenyl disulfide, PhSSPh, following mediated preparative electrolysis of RSPh, in presence of naphthalene shows that this one-electron process may be carried out at the reduction potential of naphthalene at low temperature and has also validated deductions made from voltammetric results. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: phenyl thioether; mediator; cryoelectrochemistry; microelectrode; naphthalene; DIGISIM

INTRODUCTION

Organosulfur compounds are important in many areas of chemistry, including organic electrochemistry. Most of the electrochemical investigations of sulfur compounds were originally conducted in aqueous media,[1,2] with only a few reports of electrochemistry in organic solvents. The reduction of various phenyl sulfides (RSPh) in *N,N*-dimethylformamide, DMF at platinum,[3] mercury, and glassy carbon electrodes[4–6] are notable examples. In general, the reduction of thioethers may be used as a convenient synthetic method for carbon—sulfur bond cleavage and, therefore, there is interest in such processes.

We have recently reported on the cryoelectrochemical reduction in tetrahydrofuran, THF of the thioether, [(3-{[trans-4-(methoxymethoxy)cyclohexyl]oxy}propyl)thio]benzene[7] (Fig. 1). This compound was chosen due to ease of its synthetic functionalization and presence in the

structure alkyl-chain 'tag', which may be successfully used for spectroscopic analyses, following bulk electrolysis. It was shown by microdisk chronoamperometry and bulk electrolysis that only one product, *trans*-1-(methoxymethoxy)-4-propoxycyclohexane (RH), was formed in that process and the number of electrons, *n* involved in the reduction was 2.

Recently, there has been some interest in mediated electrochemistry. This has been most noticeable in the area of biosensor research.[8–12] A few 'aromatic compounds' are known to be good mediators in electrochemical catalytic processes, proceeding according to the so-called EC' mechanism. Numerous electrochemical processes, involving mediation by specific organic and inorganic species have been investigated over the past three decades. For example, naphthalene has been used frequently as a reliable mediator and a review by Simonet[13] has been published. More recently, naphthalene has been used in the dechlorination of various organic compounds such as chlorobenzene,[14] 1-chloronaphthalene,[15] some organic pollutants containing chlorine,[16] and more complicated aromatic compounds.[17]

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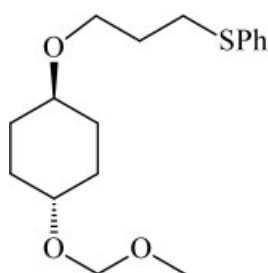E-mail: richard.compton@chem.ox.ac.uk

Figure 1. Phenyl thioether [(3-{[trans-4-(methoxymethoxy)-cyclohexyl]oxy}propyl)thio]benzene, (RSPh)

Herein, we report on the indirect reduction of the phenyl thioether, [(3-{[trans-4-(methoxymethoxy)cyclohexyl]oxy}propyl)thio]benzene (RSPh) (Fig. 1) at low temperature in THF, where naphthalene is used as a mediator. In this case, when the catalytic process is the subject of investigation, low temperature plays an important role, since selectivity over reaction product(s), mechanistic pathways, and kinetics (rate determining steps) may be affected significantly. Specifically, under indirect bulk electrolytic methods, n is shown to be 1, and a different sulfur-containing product, diphenyl disulfide (PhSSPh) is observed, compared to previous work in which $n = 2$. The steady-state waves are shown for additions of RSPh to a solution containing only naphthalene at 196 K in THF and the subsequent catalytic waves fitted using DIGISIM.

EXPERIMENTAL

Reagents

Tetra-n-butylammonium perchlorate, TBAP (Fluka), was used as received, without any further purification. Anhydrous tetrahydrofuran (THF) was purified by filtration through two columns of activated alumina (grade DD-2) as supplied by Alcoa, employing the method of Grubbs et al.[18] Naphthalene (Aldrich) was used as received. The phenyl sulfide, thioether [(3-{[trans-4-(methoxymethoxy)cyclohexyl]oxy}propyl)thio]benzene, was prepared as previously described.[7]

Electrochemical procedures

Cyclic voltammetry (CV). Voltammetric measurements were carried out on a μ-Autolab (Eco-Chemie, Utrecht, Netherlands) PGSTAT 20 potentiostat. A three-electrode arrangement was used in an air-tight, three-necked cryoelectrochemical cell. The cryo-cell with solid electrolyte was dried *in vacuo* overnight, before solvent addition and electrochemical experiments. The working electrodes employed were 1.2, 5.0, and 12.5 μm (radius) platinum electrodes (Cypress Systems, Inc., Kansas, US), with a large area, shiny platinum wire

(Goodfellow Cambridge Ltd., Cambridge, UK) used as the counter electrode. The working electrodes were all carefully polished on a clean polishing pad (Kemet, UK), using 1.0 and 0.3 μm aqueous-alumina slurries (Beuhler, Lake Buff, II., USA), and subsequently rinsed in de-ionized and doubly filtered water of resistivity, no greater than 18 MΩ cm, taken from an Elgastat filter system (Vivendi, Bucks, UK). The electrodes were carefully dried prior to use. Before carrying out electrochemical experiments, the microdisc radius was electrochemically calibrated using a literature methodology.[19] A Fc/Fc$^+$PF$_6^-$ reference electrode was developed for use in THF at low temperature and has been described previously.[20] Tetra-n-butylammonium perchlorate was used as the supporting electrolyte in all electrochemical measurements at a concentration of 0.1 M. The solutions were degassed vigorously for 1 min, using impurity-free argon (BOC gases, Guildford, Surrey, UK) to remove any trace oxygen and an inert argon-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. Low temperature experiments were conducted, using a Julabo FT902 immersion cooler with temperature control for counter-cooling (JULABO UK Ltd.).

Microdisc chronoamperometry. Microdisc chronoamperometry permits the simultaneous determination of the diffusion coefficient, D and the number of electrons, n transferred to an electroactive species of interest, provided no coupled chemistry operates on the timescale of the experiment, and the concentration of the electroactive species is known. The time dependent current response, I, resulting from a diffusion-controlled reductive current after a potential step at a microdisc electrode is given in Eqn (1):

$$I = -4nFDCrf(\tau) \tag{1}$$

where Eqn (2) defines $f(\tau)$:

$$f(\tau) = 0.7854 + 0.8862\tau^{-1/2} + 0.2146e^{-0.7823\tau^{-1/2}} \tag{2}$$

and Eqn (3) defines τ:

$$\tau = \frac{4Dt}{r^2} \tag{3}$$

F is the Faraday constant, r is the radius of the disc electrode, and t the time. The above approximation (Eqns 1–3) were derived by Shoup and Szabo,[21] and describes the current response to within an accuracy of 0.6% over all τ. Experimentally, the chronoamperometric experiment is run over a time scale, incorporating a transition from transient, with a $I \propto D$ dependence, to steady-state with a $I \propto D$ dependent behavior. Accordingly, deconvolution of the parameters D and n is possible from a single scan. Fitting was achieved via ORIGIN 6.0 (Microcal Software, Inc.) where, having input an

accurate value for r and C, the software iterates through values of D and n, until the fit of the experimental data had been optimized.

Preparative electrolysis. Controlled-potential, bulk electrolysis was carried out in a two-compartment cell, the catholyte and anolyte being separated by a sintered glass frit. The cathode was a rectangular platinum plate (area $= 3.25\,cm^2$) (Goodfellow, UK) and the anode, a platinum mesh housed within the separate compartment with 0.1 M TBAP in THF. A $Fc/Fc^+PF_6^-$ reference electrode was used as described above. The electrolysis was vigorously stirred, using a magnetic stirrer bar and the temperature maintained at $195 \pm 1\,K$, using an external system (Julabo FT902, JULABO Labortechnik GmbH, D-77960 Seelbach/Germany). The potential was held constant at the reduction potential of naphthalene (*vs.* $Fc/Fc^+PF_6^-$). Naphthalene was added to the solution at $195 \pm 1\,K$ to minimize any decomposition of the mediator.

Saturated aqueous ammonium chloride (2 mL) followed by water (10 mL) was added to the electrolyzed 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 × 10 mL), saturated sodium bicarbonate (10 mL), and saturated aqueous sodium chloride (10 mL). The organic layer was dried over magnesium sulfate and then evaporated under reduced pressure. Products were initially identified by ^1H NMR (Bruker AV400 (400 MHz) spectrometer) and then separated using TLC/flash chromatography (petrol:diethyl ether elutions). Yields for isolated RH and PhSSPh were 7.1 mg (19%) and 3.5 mg (4%), respectively. Analytical data for these compounds were identical to literature data and are given below.

trans-1-(Methoxymethoxy)-4-propoxycyclohexane (RH)[7]. ^1H NMR (400 MHz, $CDCl_3$): $\delta_H = 4.66$ (2H, s, OCH_2OCH$_3$), 3.43 (1H, m, cyclohexane CH), 3.38 (2H, t, J 6.8, OCH_2), 3.36 (3H, s, OCH$_2$OCH_3), 3.25 (1H, m, cyclohexane CH), 1.99 (4H, m, cyclohexane CH_2), 1.57 (2H, m, OCH$_2$CH_2), 1.33 (4H, m, cyclohexane CH_2), 0.90 (3H, t, J 7.4, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_C = 94.7, 76.5, 74.6, 70.1, 55.2, 30.0, 29.5, 23.3, 10.6$; MS (*CI+*): *m/z* 220 (40%, $[M + NH_4]^+$), 203 (15%, $[M + H]^+$); HRMS $C_{11}H_{23}O_3$ (MH) requires 203.1647, MH^+ found 203.1656 (+4.5 ppm); IR (film) per cm^{-1}: $\nu_{max} = 2937$, 1455, 1377, 1106, 1045.

Diphenyl disulfide (PhSSPh)[22]. ^1H NMR (200 MHz, $CDCl_3$): $\delta_H = 7.19$–7.36 (m, 6H), 7.48–7.53 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_C = 127.1, 127.5, 129.0,$ 137.0, MS (%B): *m/z* 218 ($M^{\bullet+}$, 100), 185 (M-SH, 13), 154 ($C_{12}H_{10}^{\bullet+}$, 32+), 109 ($C_6H_5S^+$, 64); IR (KBr): $\nu = 1573, 1473, 1436, 736, 686\,cm^{-1}$.

Analytical techniques. ^1H NMR spectra were recorded using a Bruker AV400 (400 MHz) spectrometer

in $CDCl_3$ and referenced to tetramethylsilane ($SiMe_4$), as an internal standard. Signal positions were recorded in δ (ppm) with the abbreviations s, d, t, q, quint., sept., br, app., and m denoting singlet, doublet, triplet, quartet, quintet, septet, broad, apparent, and multiplet, respectively. All coupling constants, J, are quoted in Hz.

Crude electrolysis mixture was analyzed by thin-layer chromatography (TLC). TLC was performed on Merck Kieselgel 60 F$_{254}$ 0.25 mm pre-coated aluminum backed silica plates. Compounds were visualized with UV light and/or by staining with basic potassium permanganate solution.

Flash chromatography was used to separate the products, following electrolysis and carried out, according to the method described by Still *et al.* [23] using Merck Kieselgel 60 (40–63 μm). Column fractions were monitored by TLC.

RESULTS AND DISCUSSION

Voltammetric studies of starting compounds: naphthalene and RSPh

A 6.5 mM solution of naphthalene in THF was prepared and cooled to $201 \pm 1\,K$. A platinum microelectrode was used to record a voltammetric response, and a reduction wave with a well-defined plateau was observed at $E = -3.11\,V$ *versus* $Fc/Fc^+PF_6^-$ reference electrode, as shown in Fig. 2. The number of electrons transferred in the reduction, n and the diffusion coefficient, D of naphthalene were obtained using microdisk potential step chronoamperometry.[7,24] Figure 3 depicts a typical chronoamperometric curve with the corresponding fitting applied to deduce the required parameters. Experiments were repeated a number of times and the average D and n
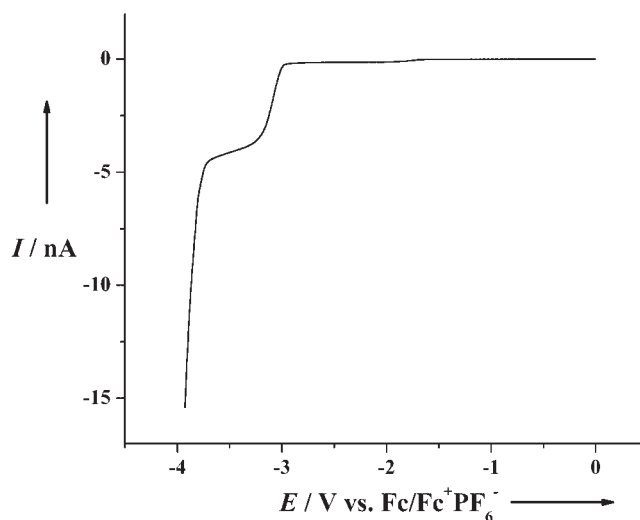

Figure 2. Voltammetric response of naphthalene (6.5 mM) in THF (0.1 M TBAP), using a 5 μm (radius) platinum microelectrode recorded at a scan rate of 10 mV s^{-1}
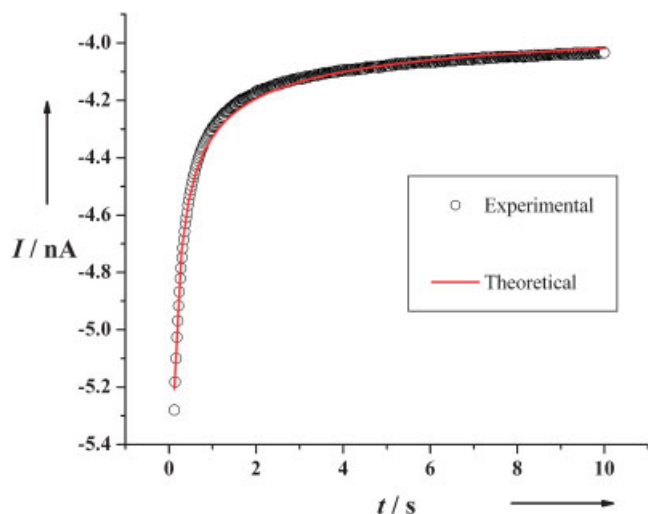
Figure 3. Experimental ((black) circles) and fitted theoretical (solid (red) line) chronoamperometric curve for the one-electron reduction of 6.5 mM naphthalene in THF (0.1 M TBAP), at a 5 μm platinum microelectrode and temperature of 196 ± 1 K. Potential was stepped to −3.50 V *versus* Fc/Fc$^+$PF$_6^-$ in the plateau region of the reductive wave (Figure 2. Fitting by Origin^{TM} software. Diffusion coefficient, $D = 2.4$ (± 0.1) × 10^{-6} cm^2 s^{-1}

corresponding value for naphthalene ($E = -3.11$ V *vs.* Fc/Fc$^+$PF$_6^-$) by some 500 mV. We were interested in whether we could use naphthalene as a catalytic mediator at low temperature to, not only allow reduction at a lower potential, but also to determine whether or not the product(s) following reduction might be altered.

Voltammetric study of catalytic process involving reduction of RSPh via mediation using naphthalene

Figure 5(a) shows the wave for a 1 mM solution of naphthalene in THF at low temperature. Next, three sequential additions of RSPh were made and are shown in Fig. 5. In the Fig. 5, similar increases caused by additions are clearly visible. All the curves are observed at the same potential which is lower than the reduction potential for RSPh itself and almost the same as for naphthalene. This effect may be explained by a mediation-type process involving naphthalene – a type of EC' mechanism as shown by Scheme 1.

The first step of the process involves the one-electron reduction of naphthalene forming the anion radical. The mediator then transfers the electron to a molecule of RSPh, under slow scan rates with the formation of corresponding anion radical and regeneration of naphthalene (hence catalysis). Under such slow timescales, any naphthalene regenerated is immediately re-reduced and, thus, the wave height for naphthalene is increased. The resulting catalytic waves were then simulated and in addition, with no clear way of determining n transferred to RSPh (e.g., RSPh may react with two radical anions), bulk electrolysis was performed.

used. The diffusion coefficient was found to be 2.5 (± 0.1) × 10^{-6} cm^2 s^{-1} and the number of electrons transferred was found to correspond to 1.0 (± 0.1).

Previously[7] under the conditions described above, the steady-state voltammetric wave for a 3 mM solution of RSPh was recorded and is shown again in Fig. 4. Comparing both curves for naphthalene and RSPh, it is easily noticed that the reduction potential of RSPh ($E = -3.58$ V *vs.* Fc/Fc$^+$PF$_6^-$) is more negative than the
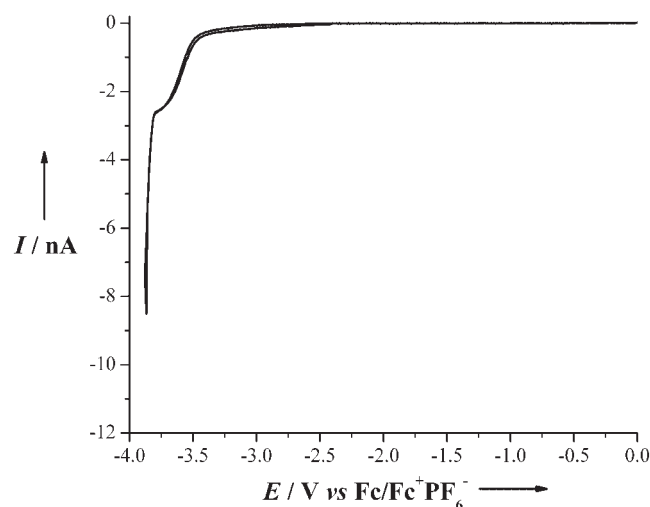

Figure 4. Voltammetric response of [(3-{[trans-4-(methoxymethoxy)cyclohexyl]oxy}propyl)thio]benzene, (RSPh) (3 mM) in THF (0.1 M TBAP), using a 5 μm (radius) platinum microelectrode recorded at a scan rate of 10 mV s^{-1} at 196 ± 1 K
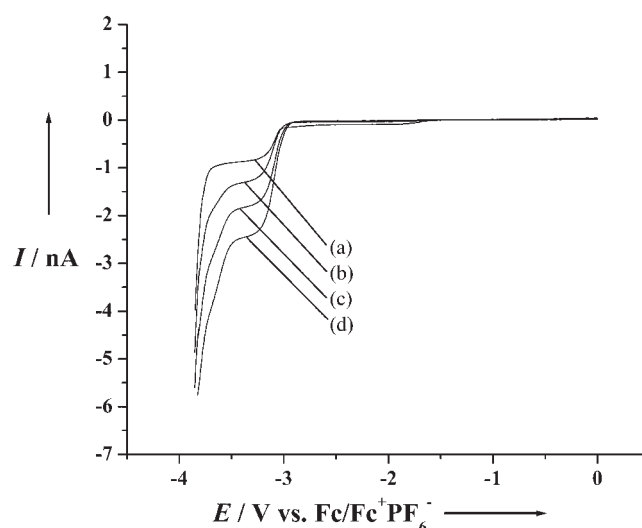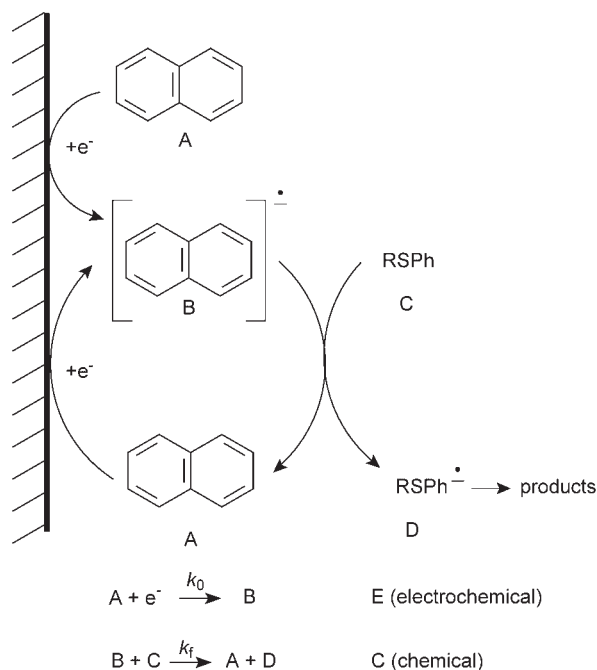

Figure 5. Voltammetric response of (a) naphthalene (1.0 mM) in THF (0.1 M TBAP), using a 5 μm (radius) platinum microelectrode recorded at a scan rate of 10 mV s^{-1} and with RSPh (**2**) (b) 1.8 mM, (c) 3.5 mM, and (d) 5.1 mM

Scheme 1. Mechanism of the process includes initial one-electron reduction of naphthalene, followed by catalytic cycle with formation of RSPh anion radical and regeneration of naphthalene

$$A + e^- \xrightarrow{k_0} B \qquad E \text{ (electrochemical)}$$

$$B + C \xrightarrow{k_f} A + D \qquad C \text{ (chemical)}$$

Figure 6. Overlay of (a) the theoretical simulation result (dotted line) with (b) the RSPh response (1.77 mM, scan rate 10 mV s^{-1}, 5.0 μm (radius)). Parameters used for the simulations were as follows: $T = 201$ K, $\alpha = 0.5$, $D = 2.5 \times 10^{-6}$ cm^2 s^{-1}, $k_s = 1$ cm s^{-1}, $k_f = 5 \times 10^5$ L mol^{-1} s^{-1}

Simulations of voltammograms for RSPh reduction mediated by naphthalene

If the proposed mechanism follows a well-known electrochemical EC' mechanism, it may be successfully simulated using DIGISIM software.[25] In subsequent simulations, the standard EC' mechanism and hemispherical diffusion were assumed as conditions. Diffusion of all species was assumed to be the same as for naphthalene. Therefore, the diffusion coefficient determined from chronoamperometric data for naphthalene (Section 'Voltammetric studies of starting compounds: naphthalene and RSPh') were used. Having constant values such as diffusion coefficient (2.5×10^{-6} cm^2 s^{-1}), radius of electrode (5 μm), initial concentrations of species (1 mM for naphthalene, 1.77 mM for RSPh, and zero for others), temperature (201 K), and scan rate (10 mV s^{-1}), other parameters of simulation E, k_0, and k_f (half wave potential, heterogeneous, and homogeneous rate constants, respectively) were systematically varied, until the best fit of the experimental curve was obtained as shown by Fig. 6. It is clearly visible from the figure that assigning k_0 and k_f values of *ca.* 1 cm s^{-1} and 5×10^5 L mol^{-1} s^{-1}, respectively, and using the measured E of naphthalene, gives satisfactory fitting with deviation of the theoretical limiting current from experimental result, not exceeding 0.1 nA. In order to ensure that the parameters obtained from simulations and the proposed mechanism are correct, the voltammetric curves for two
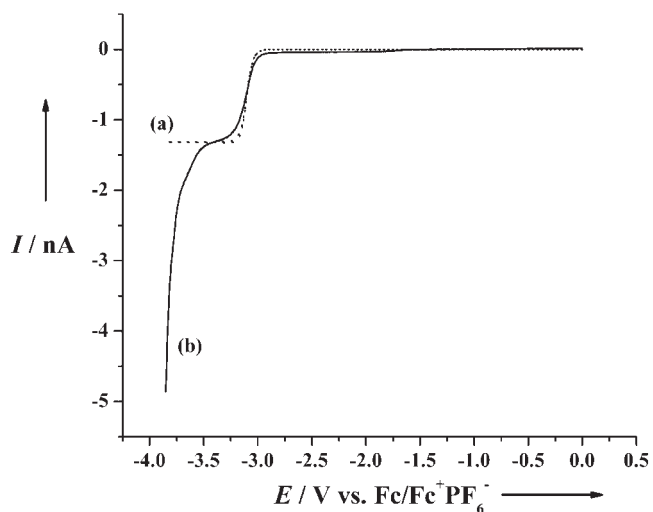
additional electrode sizes were simulated. Keeping all the parameters unchanged except electrode radius, good fittings for 1.2 and 12.5 μm electrodes were achieved as shown in Figs. 7 and 8, respectively. Table 1 contains the observed limiting currents for sets of various electrode sizes and concentrations for both experimental curves and theoretical results. It is obvious from the table that values are consistent.
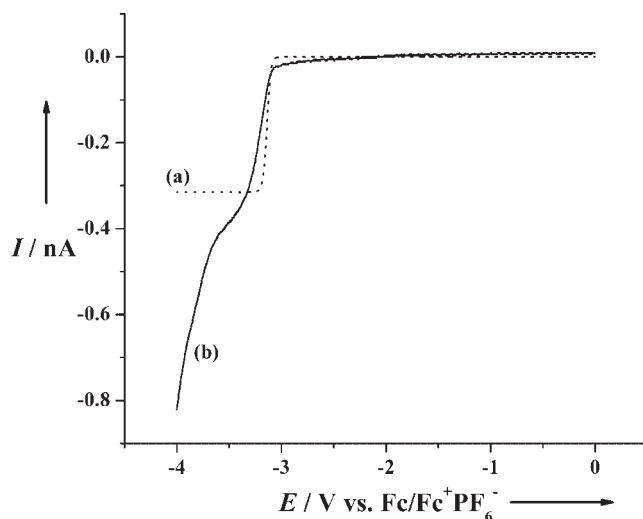

Figure 7. Overlay of (a) the theoretical simulation result (dotted line) with (b) the RSPh response (5.0 mM, scan rate 10 mV s^{-1}, 12.5 μm (radius)). Parameters used for the simulations were as follows: $T = 201$ K, $\alpha = 0.5$, $D = 2.5 \times 10^{-6}$ cm^2 s^{-1}, $k_s = 1$ cm s^{-1}, $k_f = 5 \times 10^5$ L mol^{-1} s^{-1}
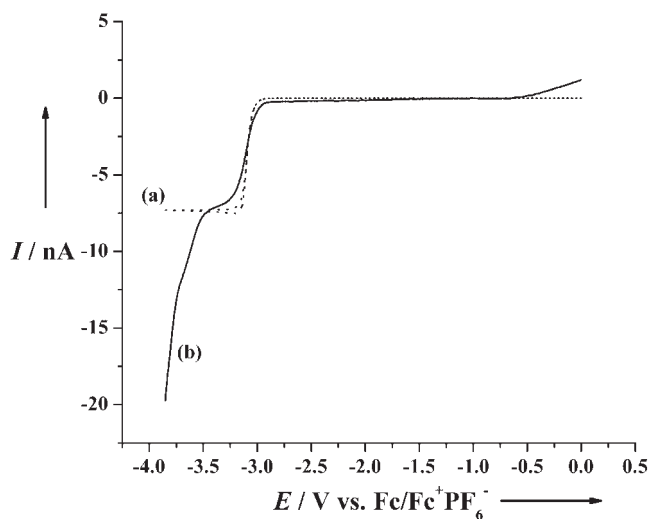
Figure 8. Overlay of (a) the theoretical simulation result (dotted line) with (b) the RSPh response (1.77 mM, scan rate $10\,\text{mV}\,\text{s}^{-1}$, $1.2\,\mu\text{m}$ (radius)). Parameters used for the simulations were as follows: $T = 201\,\text{K}$, $\alpha = 0.5$, $D = 2.5 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$, $k_s = 1\,\text{cm}\,\text{s}^{-1}$, $k_f = 5 \times 10^5\,\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}$

Preparative reduction of RSPh in presence of naphthalene as mediator

The electrolysis was carried out at the potential of naphthalene reduction (-3.1 V *vs.* $Fc/Fc^+PF_6^-$) in THF at low temperature (196 ± 1 K), until a total of $10\,°\text{C}$ was passed. Addition of naphthalene was performed at low temperature, due to the slow decomposition of naphthalene at room temperature in solution. As a result, two products were isolated although in low yield (Table 2). The low yield was a result of both the long timescales required for charge passage through solution at such low temperatures and also lengthy work-up procedures

Table 1. Comparison of limiting currents, observed at various electrodes and concentrations for RSPh with simulated currents

Radius per μm	RSPh per mM	I_{lim}(experimental) per nA	I_{lim}(simulated) per nA
5.0	1.8	1.3	1.3
	3.5	1.8	2.0
	5.1	2.5	2.6
	6.6	2.6	3.1
1.2	0.9	0.266	0.196
	1.3	0.280	0.221
	1.8	0.296	0.242
	4.2	0.375	0.335
	5.8	0.485	0.382
12.5	3.4	6.1	5.4
	5.0	7.1	7.3
	6.6	9.7	9.0
	8.0	10.7	10.7
	9.4	12.4	12.2

required to remove TBAP. Specifically, we isolated the dimer, diphenyl disulfide (PhSSPh) which suggests that RSPh is accepting a single electron homogeneously via a mediated electron transfer and the resulting radical anion cleaves to give carbon anion and the aromatic sulfur radical. In this case, no addition of the produced radical on the aromatic catalyst was observed. In addition, these results show that reduction of RSPh may be conducted indirectly at a much lower potentials than that under direct methods.[7] The following mechanism of decomposition of RSPh anion radical formed in EC'-process (Scheme 1) may be proposed (Scheme 2):

In contrast to direct two-electron reduction, where anion radical of RSPh or its decomposition products underwent further reduction at the same potential with formation of dianion, the first step of this mechanism is decomposition of RSPh, with formation of corresponding anion and radical. The anion may remove a proton from any acidic species, within the electrolytic medium or from the aqueous acid work up, following bulk electrolysis to yield RH. The phenyl sulfide radical thus formed, can dimerise forming diphenyl disulfide. In general, the overall process consumes only one electron per molecule of RSPh and this is in accordance with mechanism proposed from voltammetric data.

CONCLUSIONS

It has been shown that the mediated reduction of the phenyl sulfide at low temperature proceeds via a single electron mechanism (Scheme 1). The mediator used is naphthalene whose potential is *ca.* 500 mV less negative than that of phenyl sulfide *versus* $Fc/Fc^+PF_6^-$. Previous studies into the reduction of thioether have shown that the direct reduction involves two electrons and occurs at much more negative potentials. Mediated electron transfer, therefore, provides a useful electrosynthetic method of reducing functional groups, without the need for extreme potentials and/or electrolyzing at the solvent breakdown limit. Electrocatalytic experiments have been performed in which phenyl sulfide, in the presence of small concentrations of naphthalene, leads to an increase in the wave height, with subsequent additions of the sulfide. Various electrode sizes have been used to gain kinetic information by simulations using DIGISIM. In addition, preparative electrolysis at low temperature has allowed the isolation of the dimer, diphenyl disulfide, although only in low yield. This suggests the transfer of a single electron from the mediator to the phenyl sulfide (Scheme 1). Finally, mediated experiments were only possible at low temperature, due to the decomposition of the mediator at room temperature and the solvent breakdown window *versus* $Fc/Fc^+PF_6^-$. Overall, at low temperature, not only does voltammetric resolution of waves become possible, but a 'clean' mediated electron

Table 2. Summary of preparative electrolysis experiment in which the potential was held constant at 3.1 V *versus* Fc/Fc$^+$PF$_6^-$, until a total of 10 $^\circ$C was passed

Starting material	Mediator	Number of electron(s), n	Product(s) isolated	Yield of product(s) isolated/recovered
I	Naphthalene	1	RH	7.1 mg (19%)
			Diphenyl disulfide[a]	3.5 mg (4%)

[a] Thiophenol was not observed in the products and to ensure that this was not aerial oxidized to diphenyl disulfide, a sample of thiophenol was left overnight in solution, under normal air conditions. ^{1}H NMR revealed the thiol to be stable under these conditions.

$$[RSPh]^{\cdot -} \longrightarrow R^- + PhS^\bullet$$

$$R^- \xrightarrow{H^+} RH$$

$$PhS^\bullet + PhS^\bullet \longrightarrow PhS\!-\!SPh$$
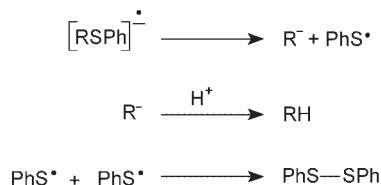
Scheme 2. Mechanism of decomposition of RSPh anion radical, with eventual formation of RH and phenyl disulfide

transfer step allows such electrosynthetic processes to occur.

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