Electrochemical Reduction of Aromatic Dithio and Thiol Esters

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Electrochemical reduction of benzenecarbodithioic esters (*1a–e*) and carbothioic *S*-esters (*2a–e*) in aprotic medium yields diphenylacetylene; in the presence of an alkylating agent *1* forms a dithioacetal. Cyclic voltammetry shows that the heterogeneous electron transfer is quasireversible; it is followed by a relatively slow dimerization of the anion radicals. In the steps following the dimerization dithiobenzil is formed and *1* acts as a thioacylating agent. *2* behaves analogously to *1*, but the follow-up reaction is faster.

Relatively few investigations[1–5] have been published on the electrochemical behaviour of aromatic carbodithioic esters (*1*) and carbothioic *S*-esters (*2*). The half-wave potentials of a number of such compounds[1–5] and EPR spectra[1,2] of some anion radicals of both types have been reported.

Below is reported the electrochemical reduction of *1a–e* and *2a–e*.

$$C_6H_5CSSR \qquad\qquad C_6H_5COSR$$
$$1 \qquad\qquad\qquad\qquad 2$$
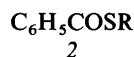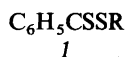
a, R = C_6H_5; *b*, R = 4–ClC_6H_4; *c*, R = $C_6H_5CH_2$; *d*, R = $(CH_3)_3C$; *e*, R = CH_3.

RESULTS AND DISCUSSION

Dithio esters. Cyclic voltammetry of the carbodithioic esters *1a–e* shows a number of peaks (Fig. 1). The first peak, A, caused by the formation of the anion radical *1*$^{.-}$, is irreversible at low sweep rates (^{c}) due to the follow-up reaction, dimerization of *1*$^{.-}$; at higher *v* the reoxidation of *1*$^{.-}$ on the reverse sweep gradually becomes well developed.
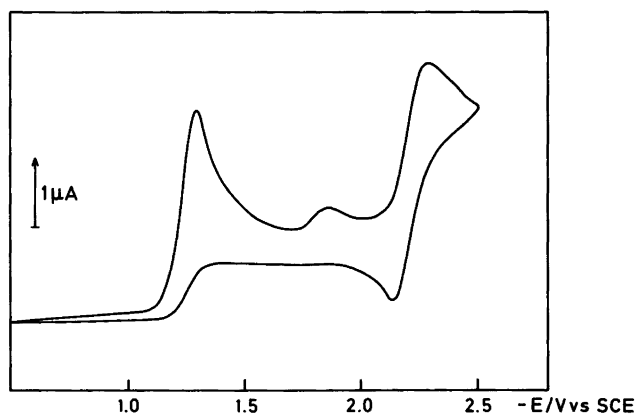

Fig. 1. Cyclic voltammogram of 1.83 mM benzyl benzenecarbodithioate (*1c*) in DMF/0.1 M TBAI at a Pt-electrode. Scan rate: 0.8 V s^{-1}.
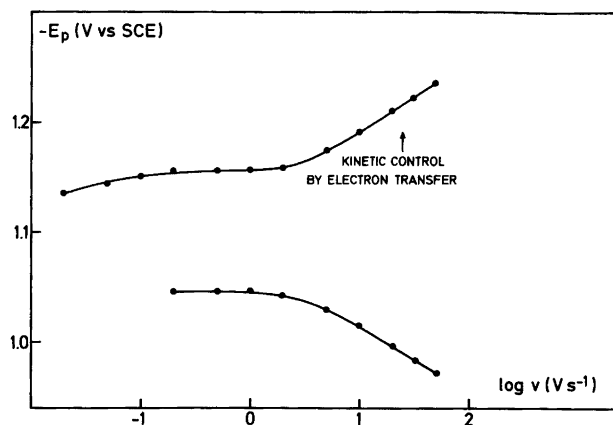
Fig. 2. Variation of the peak potential E_p with the scan rate v for 1.85 mM phenyl benzenecarbodithioate (*1a*) in DMF/0.1 M TBAI at a Pt-electrode.

At high sweep rates ($v \gtrsim 200$ V s^{-1}) the separation between the cathodic and anodic peak of A increases (Fig. 2), which indicates a relatively slow heterogeneous charge transfer.

The second peak, B, caused by the further reduction of $1^{\cdot-}$ to 1^{2-}, is irreversible at all v; at low v its height is small, but grows to the height of a one-electron peak at high sweep rates.

The third peak, C, is reversible and is found at the same potential as that of diphenylacetylene (*3*); the fourth peak, D, is caused by the further reduction of $3^{\cdot-}$. D is not shown in Fig. 1. The relative current function $i_p v^{\frac{1}{2}}$ of peak A varies from 1.0 at high v to about 1.5 at low v.

The peak potential of peak A shifts to more positive potentials with increasing concentration $(dE_p(d \log C)^{-1} \sim 19$ mV), which is consistent with the follow-up reaction after the charge transfer being a second-order reaction (Table 1);[6] the follow-up reaction may thus be a dimerization.

In the presence of an alkylating agent, such as methyl iodide, or a proton donor, *e.g.* phenol, peak A is shifted toward positive potentials and the height grows to that of a two-electron reaction. The reaction of $1^{\cdot-}$ with methyl iodide is too fast for determination of the rate constant from cyclic voltammetric data.

On multicycle cyclic voltammetry at a suitable scan rate a new reversible system grows up at -1.40 V (SCE), which is the same from all the carbodithioates *1a–e*; the wave is presumably due to the reduction of the intermediate 1,2-diphenyl-1,2-di(thiobenzoylmercapto)ethylene, *10*. A peak corresponding to dithiobenzil has not been observed.
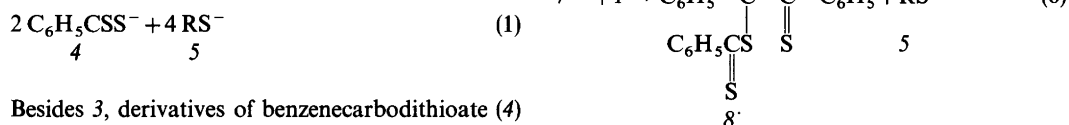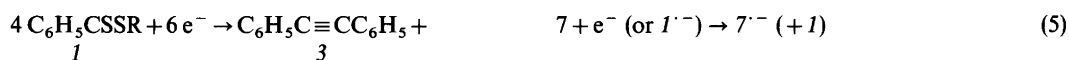
Constant potential electrolysis of *1* in aprotic medium leads to diphenylacetylene (*3*), n being about 1.5 F mol^{-1}.

Table 1. Electrochemical data from cyclic voltammetric analysis of a series of benzenecarbodithioic esters (PhCSSR); the measurements were made in DMF/0.1 M TBAI at a platinum cathode. E° is measured at a v where chemical reversibility was observed (above 1 V s^{-1}).

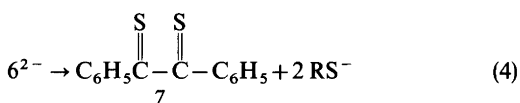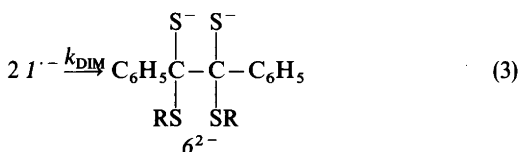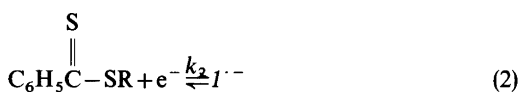| Compound	R	$E^\circ/$ V *vs.* SCE	Conc./ mM	$dE_p (d\log C)^{-1}/$ mV
1a	Ph	-1.10	1.85	-20
1b	4 ClC_6H_4	-1.06	1.92	-18
1c	$PhCH_2$	-1.22	1.57	-21
1d	$(CH_3)_3C$	-1.18	2.11	-19
1e	CH_3	-1.23	1.08	-18

Table 2. Yields (%) from the electrochemical reductions, followed by methylation, of benzenecarbodithioic esters C_6H_5CSSR (*1*).

	$R = C_6H_5$	$4\text{-}ClC_6H_4$	$C_6H_5CH_2$	$(CH_3)_3C$	CH_3
$C_6H_5C \equiv CC_6H_5$	73	80	73	76	76
$C_6H_5CSSCH_3$	92	91	90	89	93
$RSCH_3$	95	96	93	91	—

$$4\,C_6H_5CSSR + 6\,e^- \rightarrow \underset{3}{C_6H_5C \equiv CC_6H_5} +$$
$$\underset{1}{}$$

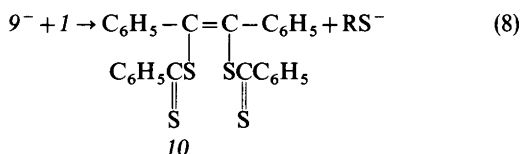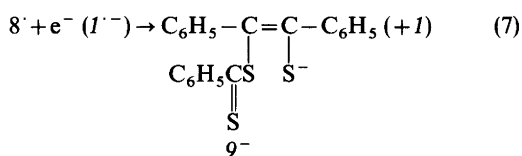$$\underset{4}{2\,C_6H_5CSS^-} + \underset{5}{4\,RS^-} \tag{1}$$

Besides *3*, derivatives of benzenecarbodithioate (*4*) and of a mercaptan (*5*) were isolated after alkylation (Table 2).

The formation of *3* indicates that a dimerization at the central carbon atom takes place somewhere on the reaction path. On the basis of the cyclic voltammetric data and the preparative results the reaction scheme (eqns. 2−4) is proposed.
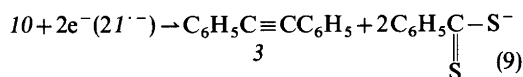
$$C_6H_5\overset{\overset{S}{\|}}{C}-SR + e^- \underset{}{\overset{k_2}{\rightleftharpoons}} 1^{\cdot -} \tag{2}$$

$$2\,1^{\cdot -} \overset{k_{DIM}}{\rightarrow} \underset{\underset{6^{2-}}{RS \quad SR}}{C_6H_5\overset{\overset{S^-}{|}}{C}-\overset{\overset{S^-}{|}}{C}-C_6H_5} \tag{3}$$

$$6^{2-} \rightarrow \underset{7}{C_6H_5\overset{\overset{S}{\|}}{C}-\overset{\overset{S}{\|}}{C}-C_6H_5} + 2\,RS^- \tag{4}$$

After the dimerization the dianion 6^{2-} loses RS^- to give *7*; this elimination does not influence the observed kinetics. It is, however, indicated in the growth of the relative current function on lowering the sweep rate.
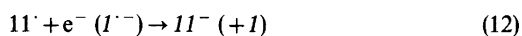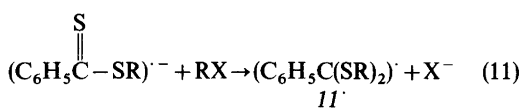
The dithiobenzil (*7*) is more easily reduced than *1*, and it reacts in a process (eqns. 5−8), where the electron transfer steps (eqns. 5 and 7) most probably are homogeneous electron transfer reactions, and the chemical steps (eqns. 6 and 8) are thioacylation of the radical anion (7$^{\cdot -}$) and the anion (9$^-$) by *1*.

$$7 + e^- \text{ (or } 1^{\cdot -}) \rightarrow 7^{\cdot -} \text{ (}+1\text{)} \tag{5}$$

$$7^{\cdot -} + 1 \rightarrow \underset{\underset{\underset{8^{\cdot}}{S}}{C_6H_5CS \quad S}}{C_6H_5-\overset{\overset{\cdot}{}}{C}-\overset{\overset{\|}{}}{C}-C_6H_5} + RS^- \tag{6}$$

$$8^{\cdot} + e^- \text{ (}1^{\cdot -}\text{)} \rightarrow \underset{\underset{9^-}{C_6H_5CS \quad S^-}}{C_6H_5-C=C-C_6H_5} \text{ (}+1\text{)} \tag{7}$$

$$9^- + 1 \rightarrow \underset{\underset{10}{C_6H_5CS \quad SCC_6H_5}}{C_6H_5-C=C-C_6H_5} + RS^- \tag{8}$$

The 1,2-diphenyl-1,2-di(thiobenzoylthio)ethylene (*10*) (*Z* and/or *E*) undergoes then a reductive elimination (eqn. 9) with the loss of two benzenedithioate ions to give diphenylacetylene.

$$10 + 2\,e^- \text{ (}21^{\cdot -}\text{)} \rightarrow \underset{3}{C_6H_5C \equiv CC_6H_5} + 2\,C_6H_5\overset{\overset{}{}}{\underset{\underset{S}{\|}}{C}}-S^- \tag{9}$$

In the presence of an effective alkylating agent the kinetics and the product distribution are changed; *1* forms on reduction in the presence of methyl iodide a dithioacetal of acetophenone in almost quantitative yield. The reaction path changes after eqn. 2 in the way given in eqns. 11−13.
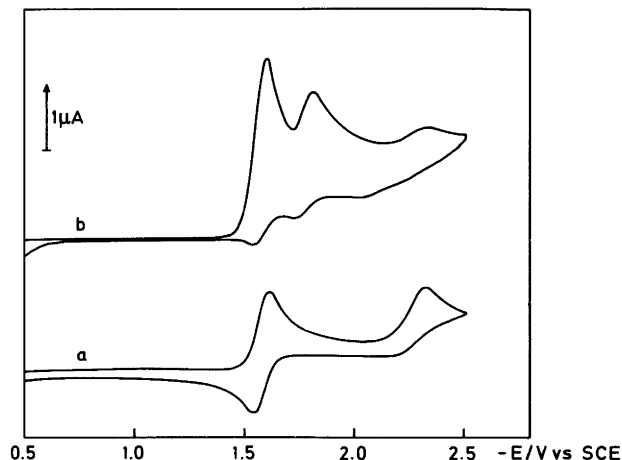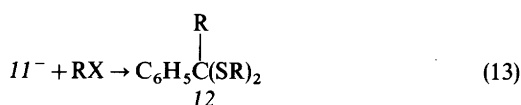
$$(C_6H_5\overset{\overset{S}{\|}}{C}-SR)^{\cdot -} + RX \rightarrow \underset{11^{\cdot}}{(C_6H_5C(SR)_2)^{\cdot}} + X^- \tag{11}$$

$$11^{\cdot} + e^- \text{ (}1^{\cdot -}\text{)} \rightarrow 11^- \text{ (}+1\text{)} \tag{12}$$

Fig. 3. (a) Cyclic voltammogram of 1.57 mM thioxanthon in DMF/0.1 M TBAI at an HMD-electrode; scan rate 0.2 Vs^{-1}. (b) Addition of 1.49 mM S-phenyl 2-chlorobenzenecarbothioate to solution (a); 0.2 Vs^{-1}.

$$11^- + RX \rightarrow C_6H_5\overset{\overset{\displaystyle R}{\displaystyle |}}{C}(SR)_2 \qquad (13)$$
$$12$$

Eqn. 11 thus competes successfully with the dimerization reaction (eqn. 3).
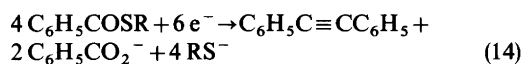
Carbothioic S-esters. CV of the benzenecarbothioic S-esters *2a−e* shows a well-developed peak, which is irreversible at all scan rates (<1000 V s^{-1}), followed by less developed peaks due to products. The interpretation of the cyclic voltammetric data is complicated by the fact that *2* acts as an acylating agent toward some of the intermediates. The current function varies only slightly with *v*, and the addition of an alkylating agent has only a slight effect on the current function and the peak potential.

The follow-up reaction could either be a cleavage (followed by a dimerization) or a dimerization (followed by a cleavage) and the data do not allow a choice between these alternatives.

The follow-up reaction of *2* is fast compared to that of *1*, as no reoxidation wave of *2*$^{-}$ is observed at the sweep rates used.

Indirect reduction of S-phenyl 2-chlorobenzenethioate (*13*) by means of thioxanthone (*14*) anion radical shows a catalytic current in cyclic voltammetry (Fig. 3). As *2a* does not react similarly, it means that the cleavage of the carbon − chlorine bond of *13*$^{-}$ is faster than the follow-up reaction of *2a*. The C − Cl cleavage is not seen as a separate peak on the cyclic voltammetry of *13*.

Constant potential electrolysis of *2a−e* leads to diphenylacetylene in yields comparable to those from *1a−e* (70−90 %) together with benzoate and thiolate (Table 3).

$$4\,C_6H_5COSR + 6\,e^- \rightarrow C_6H_5C \equiv CC_6H_5 + 2\,C_6H_5CO_2^- + 4\,RS^- \qquad (14)$$

A pathway analogous to that of *1*, eqns. 2−9, may be suggested. The scheme requires that the oxygen analogue of *10* is reducible.[8] Cyclic volt-

Table 3. Yields (%) from electrochemical reductions, followed by methylation, of benzenecarbothioic S-esters C_6H_5COSR (*2*).

	R = C_6H_5	4-ClC_6H_5	$C_6H_5CH_2$	$(CH_3)_3C$	CH_3
$C_6H_5C \equiv CC_6H_5$	77	80	87	85	81
$C_6H_5COOCH_3$	96	94	93	95	94
$RSCH_3$	94	93	92	96	−

ammetry of E-1,2-dibenzoyloxy-1,2-diphenylethylene (*14*) shows an irreversible peak followed by the reduction of *3*; the peak potential of *14* is close to that of *2*. Furthermore, the first reversible peak of benzil becomes irreversible on addition of *2* and the height grows to that of a two-electron peak, which is consistent with an acylation of the intermediate enediol by *2*.

EXPERIMENTAL

Materials. The benzenecarbothioic S-esters *2a−e* were prepared according to Reid;[9] *2a−e* were converted to the corresponding benzenedithioic esters *1a−e* using the method of Lawesson *et al.*[10] For preparative purpose *N,N*-dimethylformamide (DMF) was used as received after storage over 4 A molecular sieves; for cyclic voltammetry it was distilled immediately before use. Tetrabutylammonium iodide (TBAI) was used as received.

Apparatus. The electrochemical equipment has been described elsewhere.[11,12] Reference electrode SCE.

General procedure for reductions. The substrate (1 g) was dissolved in dry DMF (150 ml) containing TBAI (7.5 g) and reduced under nitrogen at a mercury pool (area 25 cm^2) or at a Pt-net at the potential of the first peak. After completion of the reduction an excess of methyl iodide was added to the catholyte; after 0.5 h of stirring, the catholyte was diluted with water and the products were extracted with diethyl ether. DMF and basic impurities were removed by washing with dilute acid and water. The organic phase was dried over $MgSO_4$, and after evaporation of the solvent, the crude product was separated by means of column chromatography (silica), gradually changing the eluent from light petroleum (b.p. <50 °C) to diethyl ether.

Reduction of 1a. Pt-electrode; potential −1.25 *vs.* SCE; $n=1.49$ F mol^{-1}. Products: Thioanisole (0.51 g, 95 %), $n_D^{20}=1.5852$, methyl benzenecarbodithioate (0.34 g, 92 %). ^{1}H NMR spectrum (CDCl$_3$); δ 2.75 (3 H, s), 7.1−8.1 (5 H, m), mass spectrum (*m/e*): 168, 153, 121, 78, 76, and diphenylacetylene (0.14 g, 73 %), m.p. 60−61 °C (60−61 °C).[13]

Reduction of 1b. Pt-electrode; potential −1.22 V; $n=1.55$ F mol^{-1}. Products: *p*-Chlorothioanisole (0.575 g, 96 %), methyl benzenecarbodithioate (0.29 g, 91 %), and diphenylacetylene (0.135 g, 80 %).

Reduction of 1c. Pt-electrode; potential −1.49 V; $n=1.6$ F mol^{-1}. Products: Benzyl methyl sulfide (0.525 g, 93 %), $n_D^{20}=1.5620$, methyl benzenecarbodithioate (0.31 g, 90 %), and diphenylacetylene (0.13 g, 73 %).

Reduction of 1d. Pt-electrode; potential −1.37 V;

$n=1.46$ F mol^{-1}. Products: *t*-Butyl methyl sulfide (0.45 g, 91 %), methyl benzenecarbodithioate (0.355 g, 89 %), and diphenylacetylene (0.211 g, 76 %).

Reduction of 1e. Pt-electrode; potential: −1.40 V; $n=1.53$ F mol^{-1}. Products: Methyl benzenecarbodithioate (0.462 g, 93 %) and diphenylacetylene (0.21 g, 79 %). Dimethyl sulfide was lost during work-up.

Reduction of 1e *in the presence of methyl iodide* Compound *1e* (1 g) was reduced at −1.4 V *vs.* SCE at a platinum electrode in the presence of 2 ml of methyl iodide, $n=2.09$ F mol^{-1}. Isolated was 1,1-di(methylthio)-1-phenylethane (1.13 g, 96 %). ^{1}H NMR spectrum (CDCl$_3$); δ 1.96 (3 H, s), 2.13 (6 H, s), 7.2−7.7 (5 H, m). Mass spectrum (*m/e*): 198, 183, 151, 104, 76.

Reduction of 2a. Hg-electrode: potential −1.90 V; $n=1.49$ F mol^{-1}. Products: Thioanisole (0.545 g, 94 %), methyl benzoate (0.305 g, 96 %), and diphenylacetylene (0.16 g, 96 %).

Reduction of 2b. Hg-electrode; potential −1.90 V; $n=1.53$ F mol^{-1}. Products: 4-Chlorothioanisole (0.593 g, 93 %), methyl benzoate (0.258 g, 94 %), and diphenylacetylene (0.144 g, 80 %).

Reduction of 2c. Hg-electrode; potential −2.03 V; $n=1.52$ F mol^{-1}. Products: Benzyl methyl sulfide (0.557 g, 92 %), methyl benzoate (0.278 g, 93 %), and diphenylacetylene (0.170 g, 87 %).

Reduction of 2d. Hg-electrode; potential −1.95 V; $n=1.51$ F mol^{-1}. Products: *t*-Butyl methyl sulfide (0.515 g, 96 %), methyl benzoate (0.333 g, 95 %), and diphenylacetylene (0.195 g, 85 %).

Reduction of 2e. Hg-electrode; potential −2.06; $n=1.48$ F mol^{-1}. Products: Methyl benzoate (0.420 g, 94 %) and diphenylacetylene (0.237 g, 81 %).

Reduction of benzil in the presence of S-*phenyl benzenecarbothioate,* 2a. Benzil (2 g) was reduced at −1.25 V *vs.* SCE at a mercury pool electrode in the presence of 5 g of *2a*, $n=2.09$ F mol^{-1}. Isolated was *14*,[14] m.p. 189 °C. Mass spectrum (*m/e*): 410, 305, 178, 121, 76.

Reduction of E-*1,2-dibenzoyloxy-1,2-diphenylethylene,* 14. Compound *14* (2 g) was reduced at −2.15 V *vs.* SCE at a mercury pool electrode, $n=f$ F mol^{-1}. Products: Methyl benzoate (0.621 g, 96 %) and diphenylacetylene (0.382 g, 88 %).

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