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Electrochemical Reduction of Alkyl Aryl and Dialkyl Trithiocarbonates

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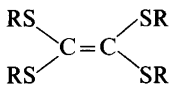
Electrochemical reduction in aprotic medium of alkyl aryl trithiocarbonates (*1a–c*) in the presence of an alkylating agent gives tetraalkyltetrathioethylenes (*2a–c*); under similar conditions dialkyl trithiocarbonates (*3a–c*) also form *2*, but the reaction is complicated by the ability of *3* to act as an alkylating agent. The mechanisms of the reactions are discussed on the basis of the preparative and cyclic voltammetric results.

Diaryl trithiocarbonates (*4*)[1] have been investigated by some electroanalytical techniques and some cyclic trithiocarbonates[2,3] and oxomolybdenum complexes of monoalkyl trithiocarbonates[4] have been studied by cyclic voltammetry (CV) and electrolysis. Alkyl aryl and dialkyl trithiocarbonates have not been investigated electrochemically; below is reported a cyclic voltammetric and electrosynthetic investigation of such compounds.

C_6H_5SCSSR

1a R = CH_3
1b R = C_2H_5
1c R = $(CH_3)_2CH$



2a R = CH_3
2b R = C_2H_5
2c R = $(CH_3)_2CH$

RSCSSR

3a R = CH_3
3b R = C_2H_5
3c R = $(CH_3)_2CH$

ArSCSSAr

4

RESULTS AND DISCUSSION

Aryl alkyl trithiocarbonates. CV of *1a–c* in *N,N*-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium iodide (TBAI) gave at the hanging drop electrode (HMD) a peak which was irreversible at scan rates (v) lower than about 1 V s^{-1}; below that value dE_p (d log v)$^{-1}$ was −30 mV (Fig. 1). In the range 1 V s^{-1} $< v <$ 100 V s^{-1} the cathodic peak potential E_p remains constant and an anodic peak with constant peak potential is observed in this range. At $v >$ 100 V s^{-1} the separation between the cathodic and anodic peaks increases. The relative current function ($i_p v^{-\frac{1}{2}}/i_p^0 v^{-\frac{1}{2}}$, where i_p^0 is the peak height corresponding to a one-electron reduction) increases from 1 to between 1.5 and 2 on decreasing v from ~100 V s^{-1} to 0.04 V s^{-1}.

E_p of *1a–c* is independent of the concentration of the substrate, and addition of an alkylating agent such as methyl iodide has no effect on either the potential or the height of the peak.

The curve E_p *vs.* log v (Fig. *1*) shows three segments; at low v the kinetics of the reaction is determined by the chemical follow-up reactions after the charge transfer step. At medium fast v the follow-up reactions are too slow to seriously influence the kinetics and the rate of the heterogeneous electron transfer is fast compared to v, so the peak behaves reversibly. At high v the charge transfer is no longer fast compared to v and a deviation from the reversible behaviour is observed.

Constant potential electrolysis of *1* yields benzenethiolate and a species, presumably the dianion of dialkyltetrathioethylene (2^{2-}) which after alkylation produces *2*. 2^{2-} is rather unstable, so higher yields of *2* are obtained if the electrolysis is conducted in the presence of an alkylating agent.

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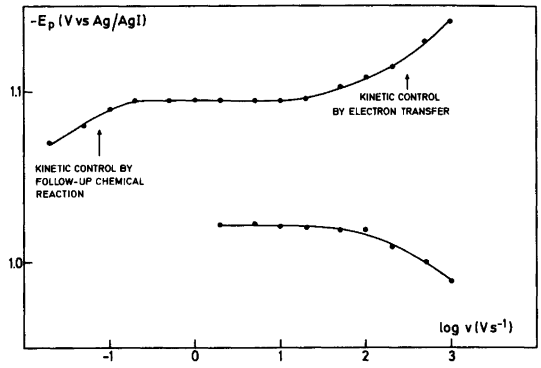

Fig. 1. Variation of the peak potential E_p with the scan rate v for 2.11 mM methyl phenyl trithiocarbonate (*1a*) in DMF/0.1 M TBAI at an HMD-electrode. The upper curve depicts the reduction potentials, the lower curve the reoxidation potentials.

Table 1. Cyclic voltammetric data of a series of phenyl alkyl trithiocarbonates, C_6H_5SCSSR. Medium DMF, reference electrode Ag/AgI, 0.1 M in DMF. The cleavage rate was determined by the intersection method.[5,6]

R	Conc./mM	$E°$/V	$k_{cleavage}/s^{-1}$
1a CH_3	2.11	−1.060	2.8
1b CH_3CH_2	1.67	−1.052	4.3
1c $(CH_3)_2CH$	1.84	−1.040	6.3

The yields are calculated as if the pathway leading to a given product were the only route followed (Table 2).

$$\underset{1}{2C_6H_5SCSSR} \xrightarrow[(2)\,4RX]{(1)\,4e^-} \underset{2}{(RS)_2C{=}C(SR)_2} + \underset{3}{2C_6H_5SR} + 4X^- \quad (1)$$

The yield of *2* is moderate (~40 %), whereas thioanisole (*5*) is isolated in almost quantitative yield.

The cyclic voltammetric behaviour of *1* is similar to that of the diaryl trithiocarbonates (*4*) and the follow-up reaction of $1^{\cdot -}$ being a cleavage reaction is in accordance with $dE_p\,(d\log v)^{-1} = -30$ mV, $dE_p/d\log C = 0$, and the product distribution.

The rate of the follow-up reaction, the cleavage, can be obtained from v at the intersection between the lines $dE_p\,(d\log v)^{-1} = -30$ mV and $dE_p\,(d\log v) = 0$;[5,6] the cleavage rates are listed in Table 1. They increase from *1a* through *1b* to *1c*; an isopropyl group would be expected to stabilize the resulting radical better than a methyl group.

$1^{\cdot -}$ may dissociate in two ways, with either a benzenethiolate (eqn. 2) or an alkanethiolate (eqn. 3) being the leaving group.

$$\underset{1^-}{\left[\begin{array}{l} ArS \\ \quad\diagdown C{=}S \\ RS\diagup \end{array}\right]^{\cdot -}} \rightarrow \underset{7^{\cdot}}{RS\dot{C}{=}S} + ArS^- \xrightarrow{RX} \underset{5}{} \quad (2)$$

$$\underset{7^{\cdot}}{ArS\dot{C}{=}S} + RS^- \xrightarrow{RX} \underset{6}{RSR} \quad (3)$$

In the reduction of *1a* and *1b* the only anion detected is benzenethiolate (8^-); $1c^{\cdot -}$ forms 8^- as the main product, but some 2-propanethiolate is also formed in the primary cleavage reaction, as about one fifth

Table 2. Yields (%) of products from the electrochemical reduction of alkyl aryl trithiocarbonates *1* in DMF/TBAI in the presence of an alkylating agent RX.

C_6H_5SCSSR	$(RS)_2C{=}C(SR)_2$	C_6H_5SR	R_2S	*E*-$RS(C_6H_5S)C{=}C(SC_6H_5)SR$
1a $R{=}CH_3$	47	94	+	–
1b $R{=}C_2H_5$	44	96	49	–
1c $R{=}CH(CH_3)_2$	37	–	81	8

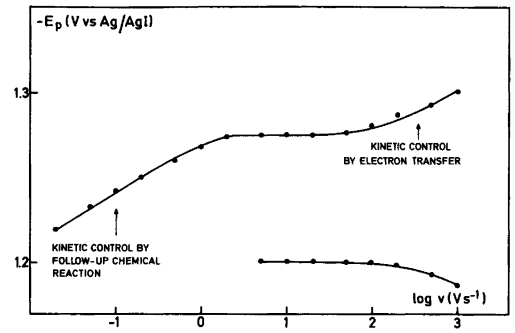

Fig. 2. Variation of the peak potential E_p with the scan rate for 2.59 mM dimethyl trithiocarbonate (*3a*) in DMF/0.1 M TBAI at an HMD-electrode. The upper curve depicts the reduction potentials; the lower one the reoxidation potentials.

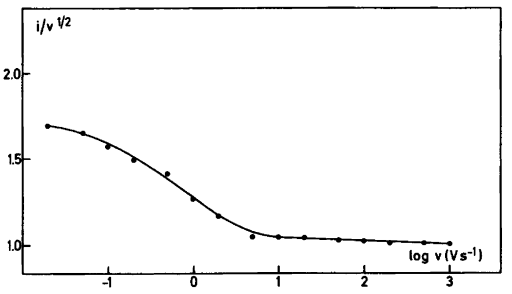

Fig. 3. Variation of the relative current function ($i_p v^{-\frac{1}{2}}$) with scan rate for 2.59 mM dimethyl trithiocarbonate (*3a*) in DMF/0.1 M TBAI at an HMD-electrode.

of the tetrathioethylene obtained is 1,2-bis(isopropylthio)-1,2-bis(phenylthio)ethylene.

The formation of *2* requires a coupling at the central carbon atom; the concentration of *7'* is probably not high enough for a dimerization of *7'* to account for the coupling, as the cleavage rate is so relatively slow that *7'* is formed outside the diffusion layer. A more likely reaction is a coupling of *7'* with *1'⁻* followed by elimination of benzenethiolate, further reduction and alkylation.

Dialkyl trithiocarbonates 3. CV of *3a–c* in DMF–0.1 M TBAI at an HMD-electrode shows one peak, which is irreversible at low scan rates, becoming gradually reversible at higher v. At very high scan rates the peak to peak separation increases, indicating a quasi-reversible heterogeneous charge transfer. The variation of E_p with v for *3b* is shown in Fig. 2. The curve E_p *vs.* log v shows three segments similar to that of *1a* in Fig. 1; the interpretation of the curve is analogous to that given for *1a*. *3a* behaves similarly to *3b*, whereas for *3c* E_p does not become independent of v. This indicates a rather fast chemical reaction after the charge transfer step.

The peak potential shifts to more positive values with increasing concentration of *3*, which is consistent with a second order chemical follow-up reaction. The addition of an alkylating agent also shifts E_p to more posive values; *3* differs in both respects from *1* and *4*. The relative current function of *3a–c* varies with v from 1.0 to between 1.5 and 2 (Fig. 3).

Constant potential electrolysis of *3* gives the following products in the absence of an added alkylating agent RX, $n = 1.0-1.3$ F mol^{-1}:

$$\underset{3}{(RS)_2C{=}S} \xrightarrow{ne^-} \underset{2}{(RS)_2C{=}C(SR)_2} + \underset{10}{HC(SR)_3} + RSCSS^- + RS^- \qquad (4)$$

Besides the products described in eqn. (4) a low yield of hexakis(methylthio)ethane (*11*) was obtained from the reduction of *3a*.

The formation of *2* and *10* without an added alkylating agent RX shows that *3* acts as an alkylating agent, which accounts for the low n-value under these conditions. In the presence of RX n is almost 2 F mol^{-1} (Table 3).

2 is probably formed from *3* in a way similar to that operating in the reduction of *1*. *10* can be

Table 3. Yields (%) of products from the electrochemical reduction of dialkyl trithiocarbonates *3* in DMF/TBAI in the presence of an alkylating agent RX.

$(RS)_2CS$	$(RS)_2C{=}C(SR)_2$	$HC(SR)_3$	$((RS)_3C)_2$	R_2S
3a R = CH_3	38	43	4	+
3b R = C_2H_5	39	47	–	23
3c R = $CH(CH_3)_2$	46	41	–	21

prepared from trialkyltrithiocarbenium fluoroborate (*12*) either on electrochemical reduction[2,7] or by reduction with iodide. A control experiment with *3* showed that the alkylation with an alkyl iodide to *12* was too slow to explain the formation of *10*, and that *3* is not reduced by iodide under the conditions of the electrolysis, so a self-alkylation does not take place. The formation of *10* and *11* can be explained if some of the primarily formed anion radical is alkylated.

The preparative and cyclic voltammetric data indicate thus a mixed follow-up kinetics after the charge transfer step with the relative importance of the available pathways differing somewhat with the alkyl group. From a preparative point of view, factors which could change the relative importance of the reactions leading to *2* and *10* would be of interests. Attempts to find conditions under which the yield of *2* was significantly higher than 50 % have failed.

EXPERIMENTAL

Materials. The trithiocarbonates[8] *1* and *3* and the trimethyltrithiocarbenium tetrafluoroborate (*12*)[9,10] were synthesized according to the references given. Spectroscopic data were in agreement with the literature.[8-10] The purity of the compounds was checked by GLC and HPLC analyses. For preparative purposes *N*,*N*-dimethylformamide (DMF) was used as received, after strorage over 4 A molecular sieves, whereas freshly distilled DMF was used for CV. Tetrabutylammonium iodide (TBAI) was used as received.

Apparatus. The electroanalytical equipment was analogous to that described elsewhere.[11-12] An H-cell[13] was used for preparative reductions. The reference electrode was an Ag/AgI, 0.1 M I^- electrode in DMF.

General procedure for reduction of 1 *and* 3. 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) in the presence of an excess of a suitable alkylating agent. The potential corresponded to the plateau of the first polarographic wave. After completion of the electrolysis the catholyte was diluted with water and the products extracted with diethyl ether, from which 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 on silica, gradually changing the eluent from light petroleum (b.p. < 50 °C) to diethyl ether.

Reduction of 1a. Compound *1a* (1g) was reduced at −1.1 V in the presence of 3 ml of dimethyl sulfate, $n = 1.97$ F mol^{-1}. Isolated were thioanisole (0.583 g, 94 %), $n_D^{20} = 1.5852$ and tetrakis(methylthio)ethylene (0.226 g, 47 %), m.p. 60 °C),[14,15] Dimethyl sulfide was only detected by GLC of the crude product.

Reduction of 1b. Compound *1b* (1g) was reduced at −1.08 V in the presence of 4 ml of ethyl iodide, $n = 2.03$ F mol^{-1}. Isolated were diethyl sulfide (0.174 g, 49 %), $n_D^{20} = 1.4430$,[16] ethyl phenyl sulfide (0.52 g, 96 %), $n_D^{25} = 1.5670$ and tetrakis(ethylthio) ethylene (0.232 g, 44 %), m.p. 52 °C (52.5 − 53 °C).[14,15]

Reduction of 1c. Compound *1c* (1g) was reduced at −1.05 V in the presence of 3 ml of isopropyl iodide, $n = 2.05$ F mol^{-1}. Isolated were diisopropyl sulfide (0.228 g, 44 %), $n_D^{20} = 1.4438$, isopropyl phenyl sulfide (0.540 g, 81 %), tetrakis(isopropylthio)ethylene (0.263 g, 37 %), m.p. 83 °C (82.5 − 84.0 °C)[14,17] and *E*-1,2-bis(isopropylthio)-1,2-bis(phenylthio)ethylene (0.069 g, 8 %), m.p. 121 °C. ^{1}H NMR spectrum ($CDCl_3$): δ 1,17 (6 H, d, *J* 8 Hz), 3.42 (1 H, sept., *J* 8 Hz), 7.23 (5 H, m). Mass spectrum (*m/e*): 392, 349, 317, 283, 109, 77.

Reduction of 3a. Compound *3a* (1 g) was reduced at −1.25 V in the presence of 4 ml of dimethyl sulfate, $n = 1.9$ F mol^{-1}. Isolated were methyl orthothioformate (0.48 g, 43 %, $n_D^{25} = 1.5749$ (1.5713),[18] tetrakis(methylthio)ethylene (0.292 g, 38 %) and hexakis(methylthio)ethane (0.045 g, 4 %), m.p. 56 − 57 °C).[19]

Reduction of 3b. Compound *3b* (1 g) was reduced at −1.25 V in the presence of 4 ml of ethyl iodide, $n = 1.87$ F mol^{-1}. Isolated were diethyl sulfide (0.250 g, 23 %), ethyl orthothioformate (0.555 g, 47 %), $n_D^{25} = 1.5415$ (1.5417)[20] and tetrakis(ethylthio) ethylene (0.315 g, 39 %).

Reduction of 3c. Compound *3c* (1g) was reduced at −1.25 V in the presence of 4 ml of isopropyl iodide, $n = 1.94$ F mol^{-1}. Isolated were diisopropyl sulfide (0.255 g, 21 %) and isopropyl orthothioformate (0.503 g, 41 %), $n_D^{25} = 1.5647$. ^{1}H NMR spectrum (CCl_4): δ 1.28 (18 H, d, *J* 8 Hz), 3.27 (3 H, sept., *J* 8 Hz), 4.93 (1 H, s) and tetrakis(isopropylthio) ethylene (0.384 g, 46 %).

Reduction of 12 *by iodide.* Compound *12* (2g) was poured into a solution of 100 ml DMF containing 5 g of TBAI under nitrogen. The solution turned immediately deep red. After stirring for 0.5 h the solution was worked up as described for the electrochemical reductions. Isolated were hexakis(methylthio)ethane (1.275 g, 45 %), tetrakis(methylthio)ethylene (0.177 g, 20 %) and dimethyl trithiocarbonate (0.138 g, 24 %).

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