The Role of Carbon Monosulfide in the Electrochemical Preparation of 4,5-Bis(methylthio)-1,3-dithiole-2-thione

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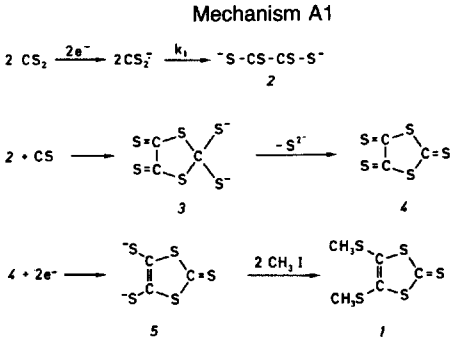
The proposed mechanisms of the electrochemical preparation of 4,5-bis(methylthio)-1,3-dithiole-2-thione (*1*) are reviewed and evidence presented for the uninvolvement of carbon monosulfide in the reaction. Treatment of tetrathiooxalate (*2*) with carbon disulfide, followed by methylation, gave *1* and sulfur. From the methylation of *2* a compound $C_8H_{12}S_6$, previously described as tetrakis(methylthio)-1,4-dithiin, was isolated; however, another structure, 4,5-bis(methylthio)-2-[bis(methylthio)methylene]-1,3-dithiole, is proposed for the compound. The suggested structure was confirmed by X-ray determination.

The major product from the electrochemical reduction of carbon disulfide in dimethylformamide (DMF), followed by methylation, is 4,5-bis(methylthio)-1,3-dithiole-2-thione (*1*);[1] the same compound had previously been obtained by reduction of CS_2 with sodium amalgam, but was assumed to be a tetrathiooxalate.[2] Electrochemical reduction of carbon diselenide gives,[3] after methylation, 4,5-bis(methylseleno-1,3-diselenole)-2-selone. Several papers[1,4–7] have discussed the mechanism of the formation of *1*, but one of the difficulties has been that the reaction components, tetrathiooxalate and carbon monosulfide, CS, have not been available and their properties have been largely unknown. Lately, both tetrathiooxalate salts[8,9] and carbon monosulfide[10–12] have been prepared in synthetically useful quantities which makes it possible to test some of the proposed mechanisms. In the report on the electrochemical synthesis of *1*, mechanism A1 (eqn. (1)–(3)) was proposed.[1] This mechanism was later criticized,[5] partly because coulometric experiments showed the electron consumption $n = 1$ F mol^{-1}, whereas mechanism Al requires $n = 1.33$ F mol^{-1}, and partly because of the evidence for the participation of trithiocarbonate and carbon monosulfide which was presented. An alternative, mechanism B (eqn. (4),(5)), was suggested.[5] Recently Wawzonek[4] altered his proposed mechanism from a dimerization of two anion radicals to *2* (in electrochemical terminology: Dim 1) to a reaction between an anion radical and the substrate (Dim 2), so the following sequence, A2 (eqn. (6)–(10)) was suggested:

Mechanism A1



Mechanism B

$$2\,CS_2 + 2e^- \rightarrow CS_3^{2-} + Cs \quad (4)$$

$$CS_3^{2-} + 2\,CS \rightarrow 5 \quad (5)$$

Mechanism A2

$$CS_2 + e^- \rightleftarrows CS_2^{\bullet-} \quad (6)$$

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$$CS_2^{\cdot-} + CS_2 \xrightarrow{k_7} S{=}\dot{C}\text{-}S\text{-}CS\text{-}S^- \quad (7)$$

$$S{=}\dot{C}\text{-}S\text{-}CS\text{-}S^- + e^- \rightarrow \underset{6}{S{=}\bar{C}\text{-}S\text{-}CS\text{-}S^-} \quad (8)$$

$$\rightleftarrows CS + CS_3^{2-}$$

$$6 + CS_2 \rightarrow \underset{7}{^-S\text{-}CS\text{-}CS\text{-}S\text{-}CS\text{-}S^-} \quad (9)$$

$$2 + CS_2 \rightleftarrows 7 \rightarrow 3 \rightarrow 4 \rightarrow 5. \quad (10)$$

The argument for preferring Dim 2 to Dim 1 was that the first peak of CS_2 in cyclic voltammetry (CV) showed an inflection which was attributed to the two different reductions [eqn. (6) and (8)]. The transformation of *3* to *5* was assumed to proceed as in A1, with the final reduction being either electrochemical or chemical by S^{2-}. Dianion *6* was assumed to be in equilibrium with CS and CS_3^{2-} [eqn. (8)].Besides these mechanisms, a third one (mechanism C) could be suggested in which CS reacted with *2* in a cycloaddition reaction. Carbon monosulfide is analogous to an isonitrile, and cycloadditions of isonitriles to dimethyl tetrathiooxalate are known.[13,14] The reaction would be:

Mechanism C

$$2 + CS \rightarrow 5. \quad (11)$$

Tetrathiooxalate *2* was shown[6] by HPLC to be an intermediate in the electrochemical reduction of CS_2 in DMF. By means of cyclic voltammetry and voltammetry at the rotating ring disc electrode, it was shown[7] that, at concentrations <1 M and current densities above 10 mA cm^{-2}, Dim 1 (eqn. 1) was preferred to Dim 2 (eqn. 6–8) and that the rate constant for the dimerization in DMF was $(6.2\pm2.0)\times10^5$ M^{-1} s^{-1}. The mechanism suggested by Jeroschewski[7,15] was essentially A1 + A2.

Isolation of *2* during the reduction of CS_2 is possible only if *2* can be removed from the solution before it reacts with CS_2. Electrolysis of CS_2 in acetonitrile with tetraethylammonium bromide[8] or potassium iodide[9] permitted the isolation of the salts; X-ray structure determination of the tetraphenylphosphonium salt of *2* identified the compound conclusively.[9] The "dark horse" in selecting a mechanism was carbon monosulfide, since its properties were little known and, until recently, it was not available as a reagent for syntheses. CS can now be generated in the laboratory,[10–12] and, since *2* can also be prepared, it should be possible to gain further information on the reaction mechanism for the formation of *5*. During the reduction of CS_2, a number of compounds have been isolated in various yields after methylation of the reaction mixture. One of the side products, $C_8H_{12}S_6$, which is also obtained from the methylation of *2*, was assumed[19] to be tetrakis(methylthio)-1,4-dithiin. This structure is incompatible with the observed ^{13}C NMR spectrum; hence, another structure is here suggested.

Results and discussion

According to mechanism B, *5* should be formed on reaction between CS and CS_3^{2-} (eqn. 5). To test this, sodium trithiocarbonate was treated with CS in methanol at −78 °C followed by methylation with methyl iodide. Dimethyl trithiocarbonate was isolated in 76 % yield together with minor products, none of which was *1*. Another argument for mechanism B was the isolation of a rhodium complex, $RhCl(PPh_3)_2CS$ (*8*), assumed to be formed from $RhCl(PPh_3)_3$ (*9*) and CS. A stream of nitrogen was bubbled through the catholyte during the reduction of CS_2 and allowed to flow into a benzene solution of *9*. On addition of diethyl ether, *8* precipitated. Previous attempts to prepare *8* from *9* and CS have failed.[11] Treatment of *9* with CS_2 gave $RCl(CS_2)(\pi\text{-}CS_2)(PPh_3)_2$ (*10*), which was identified.[17] Compound *10* could be transformed into *8* in the presence of a catalyst, e.g. methanol.[17] The explanation for the isolation of *8*[5] might possibly be that the nitrogen stream, besides transferring CS_2 also carried a catalyst for the transformation *10* → *8* from the rather complex mixture into the catholyte. It might be mentioned that attempts[15] to detect CS in the way described above[5] or trap it with other reagents[18] have failed. This is not surprising in view of the known reactivity of CS. Some polymerization of CS is unavoidable and no such products have been reported from the reduction of CS_2. Thus, the conclusion from these preparative experiments is that mechanism B is of no importance for the formation of *5*.

Mechanism C requires that CS react fast with *2*. However, attempts to treat CS, with either a

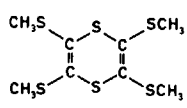
suspension of *2* in DMF at −10 °C or in solution in methanol at −78 °C, lead to no reaction. After treatment of the reaction mixture with methyl iodide, no *1* could be detected. A complex mixture of products was obtained as previously reported for the reaction between *2* and methyl iodide.[19] From this mixture, $C_8H_{12}S_6$ (*11*) was isolated among other products.

Mechanism A1 requires that *2* react with CS_2 to *5*. When a suspension of the tetraethylammonium salt of *2* was treated with an excess of CS_2, the solid dissolved and a dark red solution formed. After methylation with methyl chloride, a high yield of *1* and sulfur was obtained in accordance with previously reported results.[20] The amount of sulfur corresponded to a reduction of *4* to *5* by S^{2-} or CS_3^{2-}. If eqn. (12), shown here,

$$4 + S^{2-}(CS_3^{2-}) \rightarrow 5 + \tfrac{1}{8}S_8 + (CS_2) \qquad (12)$$

is followed by electrochemical reduction of S to S^{2-} and finally formation of CS_3^{2-}, then the electrical consumption in the reduction of CS_2 would be n = 1 F mol^{-1} as found in the coulometric experiment.[5] In eqn. (2), the loss of S^{2-} from *3* to form *4* might be promoted by attack of CS_2 on *3* with simultaneous formation of CS_3^{2-}. The fact that mechanism A1 (with S^{2-} or CS_3^{2-} as reductant in the last step) works does not exclude the possibility of A2. The relative importance of A1 *vs.* A2 is dependent on the ratio k_1 (Dim 1): k_7 (Dim 2). Since k_1 is reported[7] as $(6.2\pm2.0)\times10^5$ M^{-1} s^{-1}, the dimerization takes place in a thin reaction layer close to the electrode. If the potential of the electrode is kept at a value where the diffusion to the electrode is the limiting factor, the concentration of CS_2 in the reaction layer will be small and eqn. (1) favoured. At a potential at the foot of the wave, not all substrate molecules will be reduced and the concentration of CS_2 will be appreciable. This means that, if k_7 is of the same magnitude as k_1, experimental parameters such as electrode potential, cell geometry, stirring rate, and substrate concentration would affect the relative influence of A1 and A2. In the somewhat analogous reduction of CO_2, the Dim 1 rate constant is 10^7 M^{-1} s^{-1}, whereas the Dim 2 rate constant is 3.2×10^3 M^{-1} s^{-1}. Based on electroanalytical results, Jeroschewski and Pragst[7] estimated that, at C_{CS_2} <1 M and current densities <10 mA, eqn. (1) is preferred. This, together with the finding that CS does not play a role in the formation of *5*, makes A1 the most probable reaction path.

From the reaction of *2* with CS followed by methylation $C_8H_{12}S_6$ (*11*) was isolated. The compound $C_8H_{12}S_6$ (*12A*) previously isolated from the reaction mixture after methylation of *2* and thought to be tetrakis(methylthio)-1,4-dithiin



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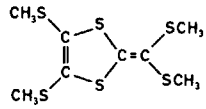

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(*12*)[19] was presumed identical with a side product (*12B*) obtained from the electrochemical reduction of CS_2.[1] The MS of *12A*[19] was identical with that of *11*; the ^1H NMR of *12B*[1] was similar to that of *11*, but contained four methyl signals rather than the two found for *11*. The four signals were explained by restricted rotation of the methylthio groups. From the method of preparation and the MS, it appears that *12A* is identical with *11*; the relationship between *11* and *12B* is less certain. The ^{13}C NMR of *11* has three signals between 100 and 150 ppm, which cannot be explained by *12*. Instead, *11* is proposed to be 4,5-bis(methylthio)-2-[bis(methylthio)methylene]-1,3-dithiole (*13*).

A compound (m.p. 46 °C) with formula *13* was previously obtained from the reaction between dimethyl tetrathiooxalate and triphenylphosphine in dichloromethane.[21] The m.p. and spectral data of *11* are very close to those reported, but to eliminate doubt about the structure of *11*, an X-ray structure determination was made. The crystals of 4,5-bis(methylthio)-2-[bis(methylthio) methylene]-1,3-dithiole, $C_8H_{12}S_6$, (*11*) were monoclinic, $P2_1/n$ (no. 14), with a = 14.612(2) Å, b = 10.320(2) Å, c = 8.984(2) Å, β = 91.333(9)°; Z = 4, V = 1354.3 Å^3, D_x = 1.474 Mg m^{-3}, μMo$K\alpha$ = 0.94 mm^{-1}. The X-ray analysis confirmed that *13* was the correct structure as shown in Fig. 1, which also shows the bond lengths and angles. The molecule contains two nearly localized C-C double bonds. It is flat, (see Table 1), apart from the methyl groups which are arranged three on one side of the plane and one on the other. The shortest unbonded S-CH_3 distance (S(2)−C(6)) is only 3.18 Å, and rotation of the methylthio groups would be possible if the C-S-C angle was widened to about 110°.

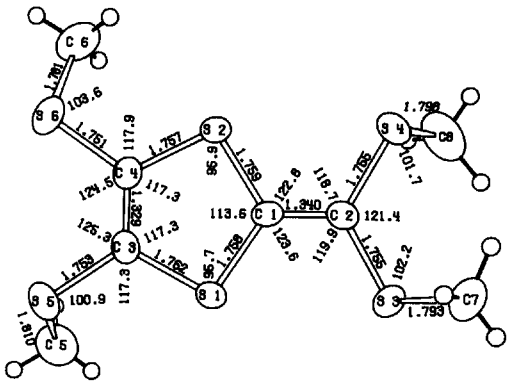

Fig. 1. ORTEP drawing of one molecule of *11* showing the numbering used, and the distances and angles. The standard deviations are: C-S bonds 0.004 Å in the flat part, 0.007 Å to methyl groups; C-C bonds 0.006 Å, C-S-C- angles 0.2–0.3°, S-C-S 0.2° and S-C-C angles 0.3°.

Experimental

^{1}H NMR spectra at 360 MHz on a Varian XL-360 spectrometer. ^{13}C NMR spectra at 25.2 MHz on a Varian XL-100 spectrometer with TMS as internal standard. MS spectra on a Micromass 7070E spectrometer operating at 70 eV using direct inlet. Elemental analyses by Leo Pharmaceutical Products, DK-2750 Ballerup, Denmark.

Carbon monosulfide was generated in a conventional vacuum line by passing CS_2 vapour through a high voltage discharge as previously described.[11,12,27] After leaving the discharge tube, the CS was passed directly into the reaction flask containing a stirred solution or suspension of substrate.

Attempted reaction of $(NaS)_2CS$ with CS. A solution of sodium trithiocarbonate[23] (3.9 g, 25 mmol) in methanol (160 ml) was cooled to −78 °C and treated with CS. Formation of polymeric CS could be observed immediately. After inlet of 25 ml (410 mmol) of CS_2, MeI (14 g, 100 mmol) was added at −78 °C. The reaction mixture was slowly heated to 50 °C under stirring, followed by stirring for 2 h at 50 °C and 16 h at room temperature. Filtration and removal of the solvent *in vacuo*, followed by addition of 150 ml of diethyl ether gave a white precipitate of NaI which was removed by filtration. Removal of the ether *in vacuo* gave a red oil which was separated on a chromatographic column (silica gel, eluent 1:20 mixture of ether/petroleum ether) yielding 2.6 g (76 %) of a yellow oil identified as dimethyl trithiocarbonate[24] together with 4 minor products, none of which was *1* as evidenced by a comparison of the spectral data with the known data of *1*.[25]

Attempted reaction of 2 with CS. Tetraethylammonium tetrathiooxalate[8] (10.3 g) was suspended in DMF (150 ml) and treated at −10 °C with CS. Polymeric CS formed immediately. Addition of 14 g (100 mmol) of MeI to the reaction mixture followed by stirring for 12 h at room temperature and subsequent filtration and removal of the solvent resulted in a complex reaction mixture in which no *1* could be detected neither by comparison on TLC with an authentic sample of *1* nor by comparison of the spectral data of the reaction mixture with the reported data of *1*.[25] Separation by TLC (silica gel, eluent 1:50 mixture of ether/petroleum ether) yielded a small amount of a red oil which could be crystallized from ether/petroleum ether giving yellow crystals (m.p. 51–53 °C) identified as *13*. IR (KBr, cm^{-1}) 1520, 1485, 1420, 1310, 960. MS [IP 70 ef; *m/e* (% rel. int.)]: 300 (98, M), 285 (100, $[M - CH_3]$), 252 (7, $[M - SCH_3]$), 271 (metastb.), 238 (23), 150 (19, $C_4H_6S_3$), 135 (29, $C_3H_3S_3$), 103 (30), 91 (70). ^{1}H NMR ($CDCl_3$):δ 2.296 (6H, s), 2.414 (6H, s). ^{13}C NMR ($CDCl_3$): δ 17.17, 18.74, 108.81, 127.49, 147.44. Anal. $C_8H_{12}S_6$: C,H,S.

Table 1. Final fractional coordinates ×10^4 of the non-hydrogen atoms, and the distances, *d*, in Å from the best plane through all except the methyl groups

	x	*y*	*z*	*d*
S1	9366(1)	1033(1)	1611(1)	0.119(1)
S2	10949(1)	− 356(1)	2919(2)	−0.029(1)
S3	10427(1)	3727(1)	1988(1)	−0.137(1)
S4	12134(1)	2184(1)	2924(2)	0.113(1)
S5	8178(1)	−1339(1)	1486(1)	0.050(1)
S6	9989(1)	−2931(1)	2874(2)	−0.027(2)
C1	10491(3)	1142(4)	2337(5)	0.011(4)
C2	10969(3)	2250(4)	2409(5)	−0.005(4)
C3	9225(3)	− 626(4)	2011(5)	−0.021(4)
C4	9943(3)	−1254(4)	2590(5)	−0.075(4)
C5	7415(4)	− 561(8)	2771(9)	−1.518(7)
C6	10718(5)	−3101(7)	4478(8)	−1.016(8)
C7	11190(4)	4437(6)	682(7)	1.211(6)
C8	12190(6)	3312(8)	4448(8)	−1.331(8)

In a similar way, *2* (10.3 g) in methanol (150 ml) was treated with CS at −78 °C with similar results.

Reaction of 2 *with carbon disulfide.* A suspension of tetraethylammonium tetrathiooxalate (2 g) in dry acetonitrile (25 ml) was stirred under nitrogen with carbon disulfide (2 ml) at ambient temperature until *2* dissolved. After another h, methyl chloride was bubbled through the solution and the system left overnight. The dark red solution turned lighter, a precipitate (100–115 mg) was filtered off and identified as sulfur. The filtrate was analysed by GLC on a glass column (OV-330; 130 °C for 4 min to 240 °C, 8 °C/min): 75–90 % *1* and 25–10 % dimethyl trithiocarbonate.

X-Ray technique. Symmetry and preliminary cell dimensions were obtained from films. A crystal 0.3×0.4×0.4 mm was used for data collection on a Huber 4-circle diffractometer with Mo*K* radiation. The cell dimensions were refined using 36 reflections. Data were collected for *h* positive out to $\theta = 25°$ by the step scan technique, 1 sec/step, 50 steps in ω-2θ scan, scan width 1.0+0.346 tanθ in θ. A total of 5135 reflections were measured, giving 2415 independent and 1610 significant reflections ($I > \sigma I$). Profile analysis was by the Lehmann-Larsen method;[26] Lorentz and polarization but no absorption corrections were applied. The structure was determined by means of the MULTAN programme system,[27] which gave the sulfur atoms, and subsequent Fourier syntheses, and least squares refinement. All hydrogen atoms were clearly visible in a difference map in positions expected for a staggered configuration. Final *R* value =0.041. Coordinates for the non-hydrogen atoms are given in Table 1 together with the distances of these atoms from the best plane through the central part of the molecule. Lists of thermal parameters, hydrogen atoms and observed and calculated structure factors can be obtained from one of the authors (RGH).

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