Formation of Stable Aryldisulphide Ions in Dimethylacetamide from the Reaction of Sulphur with Thiolate Ions

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The conditions for the formation of aryldisulphide ions, RS_2^- during the direct reaction of sulphur with thiolate ions RS^- have been studied by the use of spectroelectrochemistry in dimethylacetamide. The series of derivatives examined was R = *p*-tolyl (**1**), phenyl (**2**), 8-quinolyl (**3**), 2- and 4-pyridyl (**4**), (**5**), *N*-oxido 4-pyridyl (**6**), 2- and 4-nitrophenyl (**7**), (**8**), and 2-(5-nitropyridyl) (**9**). Sulphur reaction leads to RS_2^- ions and precedes the oxidation to diaryldisulphide RS_2R and polysulphide ions S_x^{2-}. With derivatives (**1**)–(**3**), both reactions are successive and practically stoicheiometric, while for derivatives containing electron-withdrawing groups (**6**)–(**9**), the equilibrium constants have been measured. Analysis of the reaction products by methylation of several solutions of thiolate ions [(**2**), (**7**), (**8**)] in the presence of sulphur confirmed the possibility of obtaining aryldisulphide ions stabilized in aprotic dipolar media.

In protic media, alkyl- or aryl-disulphide ions RS_2^- have been proposed as intermediates in the synthesis of trisulphides RS_3R from sulphenylthiocarbonates[1] or *S*-alkylthiosulphate[2] ions, in the course of the desulphurization of trisulphides,[3] and during the neutralisation[4] or attack of hydrodisulphides RS_2H by various nucleophilic reagents.[5] Recently, the structures of several metallic complexes such as Cu(II)[6] and Mo(V)[7], which imply RS_2^- ions as ligands, have been characterised, however we have described in a preliminary communication[8] the formation of stable 2- and 4-nitrophenyldisulphide ions in dimethylacetamide (DMA) by the direct reaction [equation (1)].

$$RS^- + \tfrac{1}{8}S_8 \rightleftharpoons RS_2^- \qquad (1)$$

In reaction (1), the affinity of RS^- ions for sulphur is analogous to that of a number of anions; this was termed 'S-nucleophilicity' or 'thiophilicity' by Kharasch and Parker.[9] Cyanide,[10] sulphite,[11] arsenite,[12] and triarylphosphine ions[13] thus yield thiocyanates, thiosulphates, thioarsenates, and phosphine sulphides, respectively. Nevertheless, the thiophilicity of the anions is often proportional to their reducing nature.[14] Sulphur and RS^- ions belong to the S_8/S_{2x}^{2-}[15] and RS_2R/RS^-[16] redox systems and the oxidation of RS^- ions to RS_2R is generally observed[17] [equation (2)].

$$2\,RS^- + \tfrac{2}{8}xS_8 \longrightarrow RS_2R + S_{2x}^{2-} \qquad (2)$$

Using the example of the CH_3S^- and $C_2H_5S^-$ ions in DMA, we thus verified that solutions of alkylthiolate ions are oxidized according to equation (2); once sulphur is added, the stable radical ion $S_3^{\cdot -}$[15] (in equilibrium with its dimer S_6^{2-}) is immediately detected as explained below (Table 1).

The stabilization of aromatic thiolates bearing an electron-attracting group, NO_2 on the ring previously enabled us to demonstrate the formation of coloured RS_2^- ions[8] without oxidation [equation (2)] being significant. We report here a general pathway to aryldisulphide ions RS_2^- based on the study of reactions between the S_8/S_{2x}^{2-} and RS_2R/RS^- systems for a series of nine aromatic derivatives, R = *p*-tolyl (**1**), phenyl (**2**), 8-quinolyl (**3**), 2-pyridyl (**4**), 4-pyridyl (**5**), *N*-oxido-4-pyridyl (**6**), 2-nitrophenyl (**7**), 4-nitrophenyl (**8**) and 2-(5-nitropyridyl) (**9**). UV or VIS absorption spectrophotometry coupled with classic voltammetry enables these reactions to be followed quantitatively in dilute solutions. DMA was chosen on the basis of prior studies on the sulphur/stable polysulphides system.[15] The analysis of the reaction products by methylation of several solutions of thiolate ions in the presence of sulphur at the preparative scale has confirmed the possibility of obtaining stable aryldisulphide ions in aprotic dipolar media.

Table 1. Spectrophotometric and electrochemical characteristics of S_8, S_8^{2-}, $S_3^{\cdot -}$, and S_6^{2-} in neutral DMA.[15] $E_{\frac{1}{2}}$ at a rotating gold disc electrode *vs.* reference Ag/AgCl, KCl sat. in DMA/Et_4NClO_4 10^{-1} mol dm^{-3}.

Species	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})	Wave ($E_{\frac{1}{2}}$/V)	Reaction[a]
S_8	262 (8 000)	R_1 (−0.34)	$S_8 + 2e^- \longrightarrow S_8^{2-}$
		R_2 (−1.10)	$S_8 + 4e^- \longrightarrow 2\,S_4^{2-}$
S_8^{2-}	515 (4 100)	R_2 (−1.10)	$S_8^{2-} + 2e^- \longrightarrow 2\,S_4^{2-}$
	357 (12 000)	O_1 (−0.20)	$S_8^{2-} - 2e^- \longrightarrow S_8$
$S_3^{\cdot -}$	617 (3 800)	R_2 (−1.10)	$S_3^{\cdot -} + e^- \longrightarrow S_3^{2-}$
		O_1 (−0.20)	$8\,S_3^{\cdot -} - 8e^- \longrightarrow 3\,S_8$
S_6^{2-}	465 (3 100)		
	345 (11 000)		

[a] At the electrode surface.

Results and Discussion

Sulphur/Polysulphide Ions and Diaryldisulphides/Thiolate Ions Characteristics in DMA.—The quantitative study of reactions such as equations (1) and (2) in DMA has been carried out by use of known electrochemical and spectrophotometric characteristics of sulphur and polysulphide ions,[15] the results of which are summarized in Table 1.

Sulphur reduces in two bielectronic steps (waves R_1 and R_2). Controlled-potential electrolysis on the plateau of R_1 shows the disproportionation of the carmine coloured S_8^{2-} ion into sulphur and the intense blue radical anion $S_3^{\cdot -}$[15] [equation (3)].

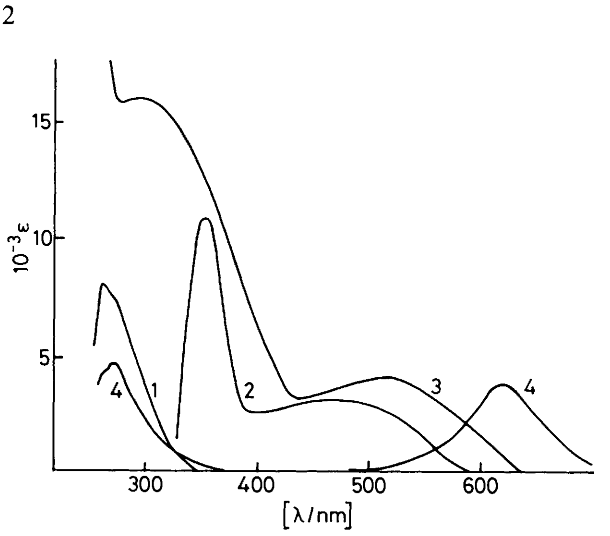

Figure 1. UV–VIS absorption spectra (molar absorption coefficients) of S_8 (1), S_6^{2-} (2), S_8^{2-} (3), and $S_3^{\bullet-}$ (4) in dimethylacetamide.

Table 2. Electrochemical and spectrophotometric characteristics of diaryldisulphides and thiolate ions in dimethylacetamide. Half-wave potentials at a rotating gold electrode *vs.* reference Ag/AgCl, KCl sat. in DMA/Et_4NClO_4 0.1 mol dm^{-3}.

	RS_2R			RS^-		
	$E_{\frac{1}{2}}$ V	$\lambda_{max.}$ nm	ε $dm^3\,mol^{-1}\,cm^{-1}$	$E_{\frac{1}{2}}$ V	$\lambda_{max.}$ nm	ε $dm^3\,mol^{-1}\,cm^{-1}$
(**1**)	−1.25	260	6 500	+0.10	308	21 200
(**2**)	−1.16	260	4 400	+0.16	310	21 800
(**3**)	−1.23	325	11 700	+0.20	282	22 000
					445	5 300
(**4**)	−1.15	282	9 700	+0.38	302	20 000
(**5**)	−0.87	260	7 700	+0.50	320	21 000
(**6**)	−0.90	280	15 100	+0.51	307	15 700
					360	3 000
(**7**)	−0.67	362	7 500	+0.55	300	17 400
					502	2 000
(**8**)	−0.62	322	21 400	+0.67	502	30 000
(**9**)	−0.53	317	21 500	+0.84	475	27 400

$$S_8^{2-} \rightleftharpoons 2\,S_3^{\bullet-} + \tfrac{1}{4}S_8 \qquad (3)$$

$$K_1 = [S_3^{\bullet-}]^2[S_8]^{\frac{1}{4}}[S_8^{2-}] = 5 \times 10^{-5}\ (\text{mol dm}^{-3})^{\frac{5}{4}}$$

The total elimination of sulphur leads to $S_3^{\bullet-}$ in equilibrium with its dimer [equation (4)].

$$S_6^{2-} \rightleftharpoons 2S_3^{\bullet-}$$

$$K_2 = [S_3^{\bullet-}]^2 \cdot [S_6^{2-}]^{-1} = 0.07\ \text{mol dm}^{-3} \qquad (4)$$

The data in Table 1 and the values of K_1 and K_2 can be used to evaluate the concentrations of $S_3^{\bullet-}$, S_6^{2-}, and S_8^{2-} from absorbance A_{617} and A_{515}, as well as that of sulphur by the limiting intensity of R_1 after calibration, or by using A_{262}.

Spectra of the RS_2R species and those arising from it cover in part the sulphur and polysulphide spectra which must be known accurately for data treatment. Thus, we had to determine for this study the spectra represented in Figure 1. For $S_3^{\bullet-}$ and S_6^{2-}, the electrolysis of sulphur for several initial concentrations $[S_8]_0$ at $\frac{8}{3}$ F mol^{-1} leads only to these species and the molar absorption coefficient $\varepsilon(S_3^{\bullet-})$ and $\varepsilon(S_6^{2-})$ then could be deduced at all wavelengths. For S_8^{2-}, spectroscopic modifications during the progressive electrochemical oxidation of $S_3^{\bullet-}/S_6^{2-}$ solutions and constant K_1 enabled $\varepsilon(S_8^{2-}) = f(\lambda)$ to be attained.

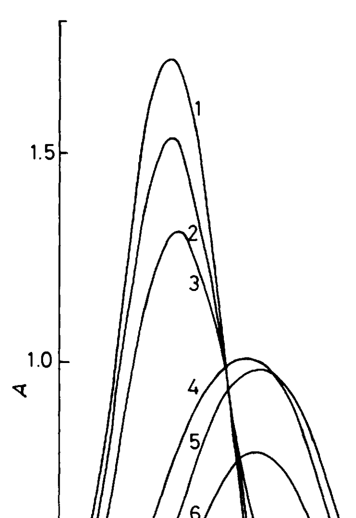

Figure 2. Visible spectroscopic changes during the reaction of sulphur with 8-quinolyl thiolate ions. Thickness of the cell 0.1 cm. $[RS^-]_0$ = 3.28×10^{-3} mol dm^{-3}; $[RS_2R]_0 = 1.12 \times 10^{-4}$ mol dm^{-3}; $y = [S_8]/[RS^-]_0$ = 0 (1); 1/86 (2); 1/26 (3); 1/9.4 (4); 1/7.1 (5); 1/4.8 (6); 1/3.6 (7); 1/2.9 (8); 1/2.0 (9).

In neutral aprotic media, the one-step electrochemical reduction of organic disulphides (**a**) leads to the formation of thiolate ions (**b**)[16] [equation (5)].

$$RS_2R + 2\,e^- \longrightarrow 2\,RS^- \qquad (5)$$

In DMA, RS^- ions were generated at concentrations generally below or equal to 10^{-3} mol dm^{-3} by controlled-potential electrolysis on a gold electrode, of the symmetrical aromatic disulphides RS_2R (**1a**)–(**9a**). The spectrophotometric characteristics of diaryl disulphides and those of the RS^- ions obtained in the course of the electrolysis are summarized in Table 2. In all cases, the redox processes are highly irreversible,[18] as shown by the reduction potential of RS_2R compared with the oxidation potential of RS^- for each example (Table 2). These potentials change in the order predicted by the electronic effects as a function of the nature of R.

Reactivity of Thiolate Ions with Sulphur.—Example of 8-*quinolyl thiolate.* A general presentation of the experimental results can be made with the example of the addition of sulphur to 8-quinolyl thiolate (**3b**) at the initial concentration $[RS^-]_0$. As the ratio $y = [S_8]/[RS^-]_0$ increases, VIS spectroscopic changes are observed (shown in Figure 2) and voltammetric curves (shown in Figure 3). Three domains can be distinguished: (*a*) For the values $y < 0.125$ (Figures 2 and 3, curves 1 to 4 and from the full spectra), it can be observed that the maximal absorbances of RS^- ($\lambda_{max.}$ = 282 and 445 nm) decrease while a new band ($\lambda_{max.}$ = 495 nm) and a shoulder (λ = 325 nm) increase, with the occurrence of three isosbestic points (λ = 295,

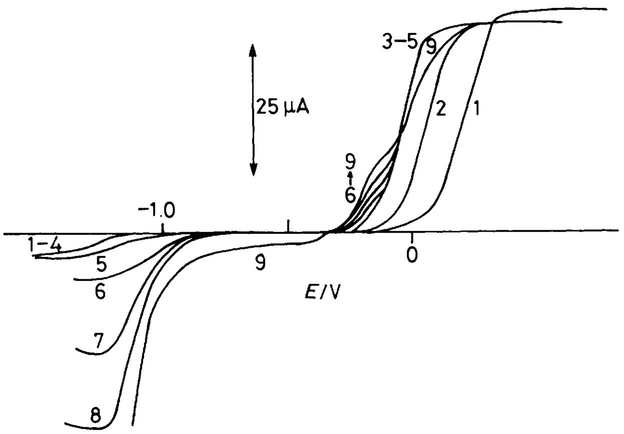

Figure 3. Evolution of voltammograms during the reaction of sulphur with 8-quinolyl thiolate ions. Experimental conditions as in Figure 2. Rotating gold disc electrode $\Omega = 1\,000$ rev min^{-1}, diameter = 2 mm; *E* *vs.* reference Ag/AgCl, KCl sat. in DMA/N(Et)$_4$ ClO$_4$ 0.1 mol dm^{-3}.

Table 3. Electrochemical and spectrophotometric characteristics of aryldisulphide ions RS_2^- and equilibrium constant K_3 (293 K).

	$E_{\frac{1}{2}}$/V	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}	K_3/ (dm^3 mol^{-1})$^{\frac{1}{8}}$
(**1c**)	−0.10	318	7 000	*a*
(**2c**)	−0.08	310	3 200	*a*
(**3c**)	−0.03	495	4 000	*a*
(**4c**)	0.00	360	5 300	*a*
(**5c**)	0.05	385	8 500	*a*
(**6c**)	0.25	280	15 500	0.31
(**7c**)	0.05	362	6 000	14.0
		681	5 000	
(**8c**)	0.27	325	5 500	0.53
		600	11 000	
(**9c**)	0.48	400	21 000	1.2

[a] The reaction (1) is quantitative.

347, and 475 nm). All the sulphur added is consumed (this is assumed because its reduction wave R_1 does not appear). The interpretation of these observations is the same as that for the addition of sulphur to a solution of 2-nitrophenylthiolate,[8] by the formation of RS_2^- ions: the absorbance of the reaction product at the wavelengths where RS_2R and RS^- do not absorb, *i.e.* 520–540 nm becomes maximal for $y = 0.125$. The shoulder at 325 nm is at the same wavelength as the maximum of the band of bis(8-quinolyl) disulphide (**3a**) and may be attributed to the S–S bond found in RS_2^-. Concerning the voltammetry, as soon as traces of sulphur are added to the solution $[RS^-]_0$, the oxidation wave of RS^- ($E_{\frac{1}{2}} = +0.20$ V *vs.* reference) is shifted towards less oxidising potentials, *e.g.* $\Delta E_{\frac{1}{2}} = -150$ mV for $y = 1/86$, while retaining its limiting current unchanged. This phenomenon agrees with the rapid formation of RS_2^- and shows its oxidation to RS_2R which is irreversible to a lesser extent than that of RS^-. The process may be interpreted as being due to the catalytic oxidation of RS^- ions:

$$RS^- + \tfrac{1}{8}S_8 \longrightarrow RS_2^- \qquad (1)$$

$$RS_2^- - e^- \longrightarrow \tfrac{1}{2}RS_2R + \tfrac{1}{8}S_8 \qquad (6)$$

(*b*) For $\frac{1}{8} < y < \frac{3}{8}$ (Figures 2 and 3, curves 5 to 8) sulphur further reacts quantitatively (absence of its reduction wave). The $S_3^{\cdot -}$ ions are detected by their absorbance at 617 nm and by their oxidation wave ($E_{\frac{1}{2}} = -0.20$ V) which increase with *y*. The reduction current increases at the potentials where $S_3^{\cdot -}$ and RS_2R are reducible ($E_{\frac{1}{2}} = -1.10$ V and -1.23 V). Oxidation of RS_2^- reflects the observed stoicheiometry:

$$2\ RS_2^- + \tfrac{1}{2}S_8 \longrightarrow RS_2R + 2\ S_3^{\cdot -} \qquad (7)$$

or calculated from the initial thiolate:

$$RS^- + \tfrac{3}{8}S_8 \longrightarrow \tfrac{1}{2}RS_2R + S_3^{\cdot -} \qquad (8)$$

The 617 nm band remains weak in spite of the high absorption coefficient $\varepsilon(S_3^{\cdot -})$ because a part of the $S_3^{\cdot -}$ ions is in the form of a complex (noted RS_2R, S_6^{2-}) absorbing around 480 nm, as we previously showed[19] and which we will return to below. Its absorbance in this case is masked by that of the RS^- and RS_2^- ions (445 and 495 nm).

(*c*) For $y > \frac{3}{8}$ (for example curve 9), the absorbance of $S_3^{\cdot -}$ ions decreases slightly, while the first reduction wave of sulphur appears ($E_{\frac{1}{2}} = -0.34$ V); when the oxidation of the solution is practically complete, sulphur reacts partially with $S_3^{\cdot -}$ leading to S_8^{2-} ions ($\lambda_{max.} = 515$ nm) according to equilibrium (3).

The following two paragraphs will discuss the oxidation of all the thiolates studied into aryldisulphide ions [equation (1)] and then into RS_2R [equation (7)].

Formation of Aryldisulphide Ions.—Whatever the example (**1**)–(**9**), the reaction $RS^- \longrightarrow RS_2^-$ is shown by an increase of the RS_2^- band(s) at the expense of the RS^- band(s), with one or more isosbestic point and further oxidation of RS_2R remains negligible. The oxidation wave of RS^- is shifted towards more negative potentials once a trace amount of sulphur is added.

(*a*) When the arylthiolates lack an electron-withdrawing group on the aromatic ring (**1b**), (**2b**), (**3b**), reaction (1) is quantitative for $y < \frac{1}{8}$. The same is true for derivatives such as R = 2- or 4-pyridyl (**4b** and **5b**).

(*b*) With thiolate ions stabilized by the high delocalization of the charge, sulphur is detected by voltammetry on its first addition (**6b**), (**8b**), (**9b**) or closer to stoicheiometry (**7b**). This implies that S_8 does not react completely. Reaction (1) now corresponds to an equilibrium, the equilibrium constant of which, K_3 is easily accessible from the RS^- and RS_2^- absorbances and the intensity of the S_8 reduction wave.

$$K_3 = [RS_2^-][RS^-]^{-1}[S_8]^{-\frac{1}{8}}$$

Table 3 lists the electrochemical and spectrophotometric characteristics of the RS_2^- ions (**c**), as well as the available formation constants K_3.

Oxidation of Arylthiolates to Diaryl Disulphides.—(*a*) If the S–S bond of RS_2R disulphides is not weakened by attractive groups (**1**)–(**5**), addition of sulphur to a RS^- solution beyond the ratio 1/8 leads to RS_2R and $S_3^{\cdot -}$ according to the overall reaction (8).

Using a series of RS_xR alkylated derivatives, we previously established[19] that RS_xR and $S_3^{\cdot -}$ ions yield a RS_xR, S_6^{2-} complex (C*) whose structure was not elucidated, by a slow second-order reaction in relation to $S_3^{\cdot -}$ [equation (9)].

$$RS_2R + 2\ S_3^{\cdot -} \rightleftharpoons RS_2R, S_6^{2-} \qquad (9)$$

The same behaviour is observed with diaryl disulphides (**1a**)–(**5a**) and $S_3^{\cdot -}$ ions: the addition of these disulphides to an $S_3^{\cdot -}$ solution decreases the absorption of the radical anion to the benefit of those of its S_6^{2-} complexed form (345 and 470–480 nm). The characteristics of the complex ($\lambda_{max.}$, ε, and $K_4 = [RS_2R][S_3^{\cdot -}]^2[C^*]^{-1}$) can be easily deduced. They are of the same order of magnitude as for (**1a**) and (**2a**) ($\lambda_{max.} = 480$ nm, $\varepsilon = 2\,000$ dm^3 mol^{-1} cm^{-1}, $K_4 = 4.0 \times 10^{-7.8}$ mol^2 dm^{-6}).

Table 4. Equilibrium constants K_5 (293 K) of the reaction of sulphur on aryldisulphide ions in DMA.

R	K_5/mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$
(6)	0.2×10^{-4}
(7)	0.12×10^{-3}
(8)	0.4×10^{-3}
(9)	*a*

[a] No significant oxidation.

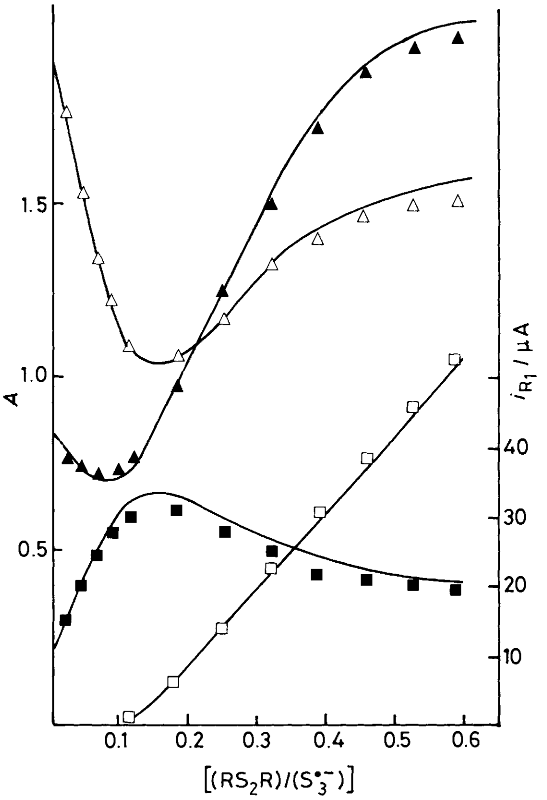

Figure 4. Theoretical variations (——) and experimental values of A_{617} (△), A_{681} (▲), A_{502} (■), and i_{R1} (□) during the reaction of bis(2-nitrophenyl) disulphide with $S_3^{\cdot-}$ ions. $[S_3^{\cdot-}]_0 = 5.80 \times 10^{-3}$ mol dm^{-3}.

Then, the changes in the spectra and voltammograms during the oxidation of aryldisulphide ions (**1c**)–(**5c**) by sulphur occurs according to the following process:

$$2\,RS_2^- + \tfrac{1}{2}S_8 \longrightarrow RS_2R + 2\,S_3^{\cdot-} \qquad (7)$$

$$RS_2R + 2\,S_3^{\cdot-} \rightleftharpoons RS_2R,\,S_6^{2-} \qquad (9)$$

$$2\,S_3^{\cdot-} + \tfrac{1}{4}S_8 \rightleftharpoons S_8^{2-} \qquad (3)$$

Thus, when sulphur is added at $\frac{1}{8} < y < \frac{3}{8}$ to a solution of phenyl or *p*-tolyl disulphide ions (**1c** or **2c**), the absorption bands of $S_3^{\cdot-}$ (617 nm) and of the complex C* (480 nm) increase with *y*. At each addition of S_8, the solution first becomes blue because of the rapid oxidation (7) then slowly turns pale yellow because of the formation of C* (9). Only when *y* becomes higher than 3/8 could sulphur be detected on the voltammetric curves and the absorption maximum at 480 nm shifts towards 500 nm with the partial formation of S_8^{2-} according to (3). Our experimental results are consistent with a near total oxidation of RS_2^- solutions of (**1c**) and (**2c**) and probably (**3c**). At the stoicheiometry $y = \frac{3}{8}$, added sulphur is turned into free and complexed $S_3^{\cdot-}$. In the same conditions, 2- or 4-pyridyl disulphide ions are only partially oxidised, because free sulphur appears just above the ratio 1/8 (**5c**) and 2/8 for (**4c**). Nevertheless, the complexity of the spectra as a result of the simultaneous equilibria (7), (9), and (3) precludes determination of a constant to characterise the level of oxidation (7).

(*b*) The disulphide ions arising from thiolates the structure of which explains the weaker *S*-nucleophilic power (**6b**)–(**9b**), will be slightly (**6c**)–(**8c**) or not at all further oxidised into RS_2R. Both forward and backward shifts of equilibrium (7) have been studied:

$$2\,RS_2^- + \tfrac{1}{2}\,S_8 \underset{b}{\overset{f}{\rightleftharpoons}} RS_2R + 2\,S_3^{\cdot-} \qquad (7)$$

(*i*) addition of sulphur beyond the ratio $y = 1/8$ and determination of the constant $K_5 = [RS_2R][S_3^{\cdot-}]^2[RS_2^-]^{-2}[S_8]^{-\frac{1}{2}}$. In the example of (**7b**), with the addition of S_8, the isosbestic points going with the process $RS^- \longrightarrow RS_2^-$ (407 and 550 nm) are no longer observed beyond $y > 1/7$ and the maximal absorbance of RS_2^- (681 nm) and residual RS^- (502 nm) then decreased slightly. Constant K_5 is calculated from conservation equations (charges, R and S), constants K_1 and K_3, and experimental values of A_{502} and A_{681} expressed by taking into account the absorption of all species (RS^-, RS_2^-, $S_3^{\cdot-}$, S_8^{2-}). Table 4 lists the values of K_5 as a function of the nature of R.

In all cases, oxidation into RS_2R remains low. For example addition of sulphur in the proportion $y = \frac{3}{8}$ to a 4×10^{-3} mol dm^{-3} RS^- solution (**7b**) leads to 2.8×10^{-3} mol dm^{-3} of RS_2^- and only 0.37×10^{-3} mol dm^{-3} of RS_2R.

(*ii*) Reaction of disulphides RS_2R with $S_3^{\cdot-}$ ions in order to observe the shift of reaction (7) in the backward direction. The progressive addition of diaryldisulphides (**6a**)–(**9a**) to a solution of $S_3^{\cdot-}$ entails the substantial reduction of RS_2R:

$$RS_2R + 2\,S_3^{\cdot-} \rightleftharpoons 2\,RS^- + \tfrac{3}{4}S_8 \qquad (8')$$

In the case of (**7a**), Figure 4 shows the experimental changes of absorbance at the wavelengths characteristic of $S_3^{\cdot-}$ (617 nm), RS^- (502 nm), RS_2^- (681 nm) and of the sulphur reduction current. Sulphur does not appear initially, since it is largely consumed in reactions (1) and (3):

$$RS^- + \tfrac{1}{8}S_8 \rightleftharpoons RS_2^- \qquad (1)$$

$$2\,S_3^{\cdot-} + \tfrac{1}{4}S_8 \longrightarrow S_8^{2-} \qquad (3)$$

The oxidation wave of $S_3^{\cdot-}$ or S_8^{2-} ions ($E_{\frac{1}{2}} = -0.20$ V) is progressively compensated by the wave of catalytic oxidation of RS^- ions ($E_{\frac{1}{2}} = +0.05$ V). A_{617} decreases first to the benefit of A_{502} ($RS^- + S_8^{2-}$) then an increase of A_{681} (RS_2^-) and of the R_1 limiting current of S_8 are observed. The satisfactory fit of the parameters A_{617}, A_{502}, A_{681}, and i_{R1} (curves in Figure 4) obtained from the conservation equations and constants K_1, K_3, K_5 confirms the proposed reaction pathway and its characteristics. More generally, when RS_2R and $S_3^{\cdot-}$ are placed together in the ratio 1/2, the spectrum and voltammogram of the equilibrium state are identical with those obtained by mixing RS^- and S_8 in the proportion $y = 3/8$.

Catalytic Electro-oxidation of Thiolate Ions in Presence of Sulphur.—We previously explained the shift of the oxidation wave of RS^- ions in the presence of small amounts of sulphur towards less oxidising potentials by the following scheme:

$$RS^- + \tfrac{1}{8}S_8 \longrightarrow RS_2^- \qquad (1)$$

$$RS_2^- - e^- \longrightarrow \tfrac{1}{2}RS_2R + \tfrac{1}{8}S_8 \qquad (6)$$

This catalytic oxidation process of RS^- ions has been tested on the quantitative electro-oxidation at controlled potential

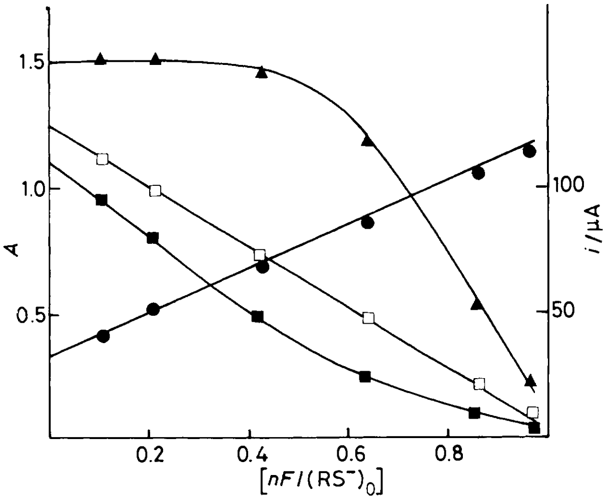

Figure 5. Theoretical variations (——) and experimental values of A_{681} (▲), A_{502} (■), i_0 (□) and i_R (●) during the electro-oxidation at $E = +0.3$ V *vs.* reference of a solution $[RS^-]_0 = 0.77 \times 10^{-2}$ mol dm^{-3}. $[S_8]_0 = 0.40 \times 10^{-3}$ mol dm^{-3}. $[RS_2R]_0 = 0.17 \times 10^{-2}$ mol dm^{-3}.

Table 5. Initial composition (mol%) of RS^-/RS_2^- solutions [(7) and (8)] in comparison with that of their products of reaction with methyl iodide.

R	Ions	(%)	Methyl sulphides	(%)
	RS^-	77	$RSCH_3$	58
4-$NO_2C_6H_4$	RS_2^-	18	RS_2CH_3	34
	Σ y S_x^{y-}	5	Σ $(CH_3)_2$ S_x	8
	RS^-	16	$RSCH_3$	35
2-$NO_2C_6H_4$	RS_2^-	78	RS_2CH_3	57
	Σ y S_x^{y-}	6	$\Sigma(CH_3)_2$ S_x	8

Table 6. Composition (mol%) of the reaction products obtained by the methylation of phenylthiolate solutions in the presence of sulphur in a ratio of $y = [S_8]/[RS^-]_0 = 1/25$; 1/7; 1/4.

Product	$y = 1/25$	$y = 1/7$	$y = 1/4$
RS CH_3	76	12	—
RS_2CH_3	24	65	45
RS_3CH_3	—	10	22
Σ CH_3 S_x CH_3	—	13	33

($E = +0.3$ V *vs.* reference) of a solution of 2-nitrophenylthiolate $[RS^-]_0$ containing sulphur $[S_8]_0$ at the ratio $y = 1/20$. The concentrations of RS^-, RS_2^-, and RS_2R can be determined during the advancement of the electrolysis $nF/[RS^-]_0$ from the initial conditions, the reactions (1), (6), (7) and the constants K_3 and K_5. Figure 5 shows the comparison of the calculated and experimental values of A_{502} (RS^-), A_{681} (RS_2^-), oxidation current ($RS^- + RS_2^-$), reduction current of the regenerated disulphide RS_2R. Their good agreement confirms the validity of the proposed mechanism; as long as the concentration of RS^- ions is higher than 8 $[S_8]_0$, RS_2^- ions remain constant in concentration as a result of the regeneration of sulphur according to (6). It could be noticed that both electro-oxidation of RS_2^- ions or chemical one by sulphur lead to diaryl disulphides.

The spectroelectrochemical study of comparative reactivity of the different thiolate ions towards sulphur leads to the verification that their thiophilicity and reducing power change in the same direction. Sulphur reacts with arylthiolate ions in two distinct steps: the formation of RS_2^- ions precedes their oxidation into RS_2R and the reactions are more quantitative as the groups become as less electron attracting. It was desirable to verify these results at the preparative scale by methylating several solutions of arylthiolate ions containing sulphur.

Synthesis of RS_xCH_3 *Derivatives*.—Syntheses have been performed from 4-nitrophenyl-, 2-nitropheny-, and phenylthiolates (**7b**), (**8b**), and (**2b**) (see Experimental section for preparative electrolysis conditions used to obtain them). Concentrated solutions of RS^- received sulphur in a definite proportion y and were then 'neutralised' with methyl iodide.

(*a*) With (**7b**) and (**8b**), sulphur was added in the ratio $y = 1/7$. The mixtures of products were analysed by proton NMR spectroscopy and GC coupled with mass spectrometry. In each case, the NMR spectra show the presence of six methylated products, of which two aromatic ones (multiplets of ring protons) are predominant. These two major products were identified by mass spectrometry as the expected methyl aryl sulphides: $NO_2C_6H_4SMe^+$ 169 (**8**, 100%; **7**, 33%) and $NO_2C_6H_4S_2Me^+$ 201 [(**8**) 100%; (**7**) 12%] without heavier fragments. The four minor species (less than 8% of the total) are polysulphides $CH_3S_xCH_3$ (x = 3, 4, 6, or 8). We have previously shown[20] that they are the reaction products of methyl iodide with $S_3^{\bullet-}/S_8^{2-}$ solutions because of the equilibria between the radical anions and their dimers, $S_6^{2-}/S_3^{\bullet-}$ and $S_8^{2-}/S_4^{\bullet-}$ all nucleophilic reagents. These ions are present in the reaction medium because of the weak oxidation according to (7).

The addition of known $CH_3S_xCH_3$ mixtures[20] to the synthesis products increases the proportion of secondary species without modifying δ_H or retention times (GC). For nitrophenylmethyl monosulphides then disulphides, the ^1H NMR spectra (90 MHz, CCl_4, standard $SiMe_4$) recorded from the mixtures δ_H (3 H, s, CH_3) at 2.52 (lit.,[21] 2.55) and 2.46 with derivatives (**8**), and at 2.45 (lit.,[21] 2.47) and 2.40 for derivatives (**7**). For $CH_3S_xCH_3$, δ_H increases with the sulphur chain length,[22] but as in the case of 2- or 4-nitrophenyldisulphanes[23] or alkyl nitrophenyl disulphides,[24] δ_H (3 H) of methyl disulphides arising from (**7c**) or (**8c**) are lower than δ_H (3 H) of the corresponding monosulphides. The composition of the mixtures issued from each synthesis was deduced from integration of the NMR or GC peaks. For defined initial concentrations, it can be compared (Table 5) with that of anionic solutions before methylation, estimated with constants K_1, K_2, K_3, and K_5. The differences between the proportions RS^-/RS_2^- and $RSCH_3/RS_2CH_3$ probably correspond to different reactivities of the RS^- and RS_2^- anions: with 4-NO_2 substituents, the nucleophilicity of RS_2^- ions towards iodomethane would be higher than that of RS^-, while the inverse conclusion applies in the case of 2-NO_2 derivatives.

(*b*) With phenylthiolate ions (**2b**), three values of y were chosen (1/25, 1/7, and 1/4) in order to determine better the progress of the formation of RS_2^- ions and then their oxidation. ^1H NMR and GC with detectors in the sulphur mode were used to analyse mixtures of methylated products (results in Table 6). A reference solution composed of commercial thioanisole and of a known mixture[20] of dimethyl polysulphides was used to localise the δ_H (3 H, s, CH_3) values of these species and their retention times.

For $y = 1/25$, only two aromatic products were obtained, in proportion (Table 6) close to that expected if reaction (1) were quantitative thioanisole (δ_H 2.34) and a second less volatile methyl sulphide. With respect to thioanisole the other product is in a ratio close to the RS^-/RS_2^- one for the initial ionic solution. Its proportion changes with y in the same way than RS_2^- and it is thus identified with $C_6H_5S_2CH_3$ (δ_H 2.32). For $y = 1/7$, polysulphides $CH_3S_xCH_3$ (x = 3, 4, 6, or 8) are also detected as expected and their proportion increases for $y = 1/4$ at the expense of RS_2CH_3 (Table 6). A product not detected by GC (δ_H 2.40) is present in the mixtures at $y = 1/7$ and increases relatively at $y = 1/4$. We identify it as methyl phenyl trisulphide. The partial formation of trisulphide ions RS_3^-, from the most *S*-nucleophilic thiolates may be assumed according to equilibrium (10) of the same nature as (1).

$$RS_2^- + \tfrac{1}{8}S_8 \rightleftharpoons RS_3^- \qquad (10)$$

The characteristic absorptions of the RS_2^- and RS_3^- ions are probably similar and so this intermediate reaction cannot be established on the basis of spectroscopic changes in dilute solutions.

Conclusions

In conclusion, the analysis of products obtained in the typical syntheses we have carried out confirms the possibility of obtaining stable aryldisulphide ions in aprotic dipolar medium. With the exception of compounds with highly electron-withdrawing substituents, aryldisulphide ions are the predominant species in solution at the stoicheiometry of their formation from thiolate ions and sulphur. The problem with the synthesis of unsymmetrical disulphides has been extensively studied[25] and the S–S bond has attracted considerable attention because of its biological importance. The present study can be used as the basis for an original method for obtaining the S–S bond from nucleophilic agents RS_2^- and different substrates.

In a similar field, increasing interest is being paid to the synthesis of a number of $[M(SR)_4]^{2-}$ type metallic complexes in aprotic media (DMF, CH_3CN, *etc.*). They are chemical models of enzymes[17] or precursors in the synthesis of heterometallic clusters[26] with M = Fe, Co, Ni, Mn, Zn, *etc.* and very often R = phenyl.

A recent review[7] of dimolybdenum (v) complexes describes the introduction of the RS_2^- ion in SMo_2SSR fragments (R = aryl or alkyl) *via* the classical pathway of access to disulphides, using RSCl derivatives.[7] The formation of some metal–aryldisulphide complexes can be envisaged by directly obtaining RS_2^- ligands by reaction (1).

Experimental

Materials and Equipment.—Sulphur, dimethylacetamide and the diaryl disulphides (**a**) were obtained from Aldrich (**1**), (**2**), (**6**), (**7**), and (**8**) and Serva (**3**), (**4**), (**5**), and (**9**). Sulphur and the nitrophenyldisulphides (**7a**) and (**8a**) were recrystallised in benzene. Solvent purification, equipment used, electrodes and flow-through cell for spectroelectrochemical studies have been described elsewhere.[15]

The mixtures of synthesised product were analysed by gas chromatography (Varian 3300, on-column injection, FID and FPD detectors in the sulphur mode, fused WCOT silica column, length 25 m, 0.5 μm thick film of BP20, equivalent to Carbowax 20 M); ^1H NMR spectroscopy (Varian EM 390, 90 MHz); mass spectrometry (Delsi Ribermag 10 C 10, 70 eV ionization).

Synthesis of RS_xCH_3 *Derivatives.*—(*a*) The solution of arylthiolates (**2b**), (**7b**), or (**8b**) were obtained by the controlled-potential electrolysis of 120 cm^3 of disulphides RS_2R [1.20 g of diphenyl disulphide and 1.50 g of each bis(nitrophenyl) disulphide] on a large gold grid electrode as cathode in a dual compartment preparative cell (platinum foil anode of 20 cm^2 in area). The electrolyte bearing the current was 0.5 mol dm^{-3} tetraethylammonium perchlorate. With (**2a**), electrolysis lasted about 3 h with a 94% yield. With (**7a**) and (**8a**), it could be accelerated and carried to completion by addition of a small quantity of sulphur. In both cases, the over-voltage of sulphur reduction is lower than that for the disulphides, the catalytic reduction[27] of which is observed as summarised below:

$$S_8 + 2\,e^- \longrightarrow S_8^{2-}$$

$$S_8^{2-} + RS_2R \longrightarrow 2\,RS^- + S_8$$

(*b*) The addition of a definite quantity of solid sulphur (w) to the cathode compartment led to the selected ratio $y = [S_8]/[RS^-]_0$: with (**7b**) and (**8b**), $w = 0.34$ g ($y = 1/7$); with (**2b**), $w_1 = 0.103$ g ($y = 1/25$), $w_2 = 0.365$ g ($y = 1/7$), $w_3 = 0.645$ g ($y = 1/4$). After dissolution of S_8, the solutions became coloured as a result of the formation of RS_2^- ions (**7c**) or (**8c**) as well as polysulphide ions S_{2x}^{2-} (**2**).

(*c*) The addition of methyl iodide (dissolved in DMA) bleached the solutions at the expected stoicheiometry was accompanied by the precipitation of tetraethylammonium iodide. After filtration, three volumes of water were added to the reaction medium for the extraction of products with ether, which is partially soluble in DMA. The organic phase was washed with water up to the point of complete elimination of residual DMA verified by GC. After drying (anhydrous Na_2SO_4), ether was removed by evaporation to dryness. The mixtures of products were obtained as oils and analysed without further purification. Methyl nitrophenyl sulphides and disulphides are solid when pure,[28] but are dissolved here in methylpolysulphides $CH_3S_xCH_3$.

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Paper 9/02498K
Received 14*th June* 1989
Accepted 8*th September* 1989