PERKIN 2

Formation and scission of the sulfur–sulfur bond: a new approach to reactions between sulfur/polysulfide ions and thiolate ions/disulfides in *N*,*N*-dimethylacetamide

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The reactivity of sulfur towards a series of thiolate ions RS^- [R = phenyl (1), 4-methylphenyl (2), benzyl (3) ethyl (4), propyl (5), butyl (6), *sec*-butyl (7), *tert*-butyl (8)] has been studied by spectroelectrochemistry in *N*,*N*-dimethylacetamide. Apparently, sulfur reacts in two parallel ways: (*i*) oxidation of RS^- leading to RS_2R and $S_3^{\cdot -}$ ions; (*ii*) preponderant S-nucleophilic process yielding stable RS_x^- ions (x = 2–5). RS_x^- species, whose spectrophotometric characteristics have been determined, are successively obtained in the course of sulfur addition with R = alkyl, whereas equilibria between arylpolysulfide ions were observed. At the junction of these two parallel pathways, the slow key-equilibrium $2RS_4^- \rightleftharpoons RS_2R + 2S_3^{\cdot -}$ has been investigated by addition of RS_2R R = 1–8 to $S_3^{\cdot -}$ solutions. In fact, our study is consistent with at first, a monoelectronic transfer between RS^- (or RS_2^-) ions and the very reactive S_2 molecules in equilibrium with S_8. The fast and competing couplings of the radicals $RS^{\cdot}$ (or $RS_2^{\cdot}$), $S_2^{\cdot -}$ (or $S_3^{\cdot -}$) agree with the simultaneous formation of RS_2R, RS_x^- and polysulfide ions. More generally, the $S_2/S_2^{\cdot -}$ redox system is believed to be involved in thiophilic reactions of a number of anions such as RS^- towards sulfur rather than the initial opening of the cyclic S_8 form.

Alkyl polysulfide† ions RS_x^- ($x \geqslant 2$) are known as transient species in the synthesis of RS_nR' compounds,[1] from inorganic polysulfides S_x^{2-} and alkyl halides, from monoorganic polysulfanes and various electrophilic reagents, from sulfenylthiocarbonates or *S*-alkylthiosulfates (x = 2, n = 3). We recently showed[2] that aryldisulfides ArS_2^- are stabilised in dimethylacetamide (DMA), an aprotic dipolar medium. These ions were obtained from sulfur and a set of aromatic thiolates by reaction (1). Sulfur further oxidizes ArS_2^- ions [reaction (2)]

$$ArS^- + \tfrac{1}{8}S_8 \rightleftharpoons ArS_2^- \qquad (1)$$

$$2ArS_2^- + \tfrac{1}{2}S_8 \rightleftharpoons ArS_2Ar + 2S_3^{\cdot -} \qquad (2)$$

with at first the fast appearance of the characteristic blue anion radical $S_3^{\cdot -}$ which then slowly decreases in concentration. Using a series of di-alkyl and -phenyldisulfides, we previously proposed[3] that RS_2R and $S_3^{\cdot -}$ yield a RS_2R-S_6^{2-} complex whose structure has not been elucidated [reaction (3)].

$$RS_2R + 2S_3^{\cdot -} \overset{k}{\rightleftharpoons} RS_2R\text{-}S_6^{2-} \qquad (3)$$

Reaction (3) appeared to us to be the slow shift of the equilibrium between $S_3^{\cdot -}$ and S_6^{2-} to the benefit of the dimeric form in presence of RS_2R. When the synthesis was carried out[2] by addition of methyl iodide to a solution $[C_6H_5S^-]_o$ and $[S]_{ad}$ ($[S]_{ad} = 8[S_8]$) at $y = [S]_{ad}/[RS^-]_o = 1.1$, the following mixture (mol%) was obtained: $C_6H_5SCH_3$ = 12%; $C_6H_5S_2CH_3$ = 65%; $C_6H_5S_3CH_3$ = 10%; $\Sigma CH_3S_xCH_3$ = 13% and the proportion in $C_6H_5S_3CH_3$ increased by increasing y. With alkyl thiolates CH_3S^- or $C_2H_5S^-$, the oxidation by sulfur seemed to be dominating because $S_3^{\cdot -}$ was immediately detected.[2]

We report here on the general reactivity of sulfur towards the following aryl or alkyl RS^- ions in DMA: R = phenyl (1), 4-methylphenyl (2), benzyl (3), ethyl (4), propyl (5), butyl (6), *sec*-butyl (7), *tert*-butyl (8). To this purpose, the reactions between $S_3^{\cdot -}$ ions and the corresponding disulfides RS_2R R = **1**–**8** will also be examined. The known electrochemical and spectrophotometric characteristics of the sulfur-polysulfide ions system,[2,4] and those that we determined for species **1**–**8** enabled the reactions to be followed by UV–VIS absorption spectrophotometry coupled with classic voltammetry. The concept of 'S-nucleophilicity' or 'thiophilicity'[5] for the cleavage of the S–S bond of sulfur or polysulfide species by a number of anions such as RS^- will be questioned on the basis of our statements.

Results

Sulfur–polysulfide ions and thiolate ions characteristics in DMA

The partial dissociation [reaction (4)] of cyclooctasulfur into S_2

$$S_8 \rightleftharpoons 4S_2 \qquad (4)$$

molecules in DMA was recently proposed by our group from the results of two sets of experiments:[4] (*i*) further studies of the disproportionation of S_8^{2-} ions; (*ii*) kinetics of the reaction between triarylphosphines and sulfur. The S_8 dissociation

$$K_1\,(297\ \text{K}) = [S_2]^4\,[S_8]^{-1} = 10^{-7}\ \text{mol}^3\ \text{dm}^{-9} \qquad (5)$$

would attain 50% at $[S_8]_T{}^{\circ} = 1.5 \times 10^{-3}$ mol dm^{-3}. The reduction of sulfur into polysulfide ions has been extensively studied in aprotic media.[4] As in the same type of solvents (DMF, DMSO, CH_3CN *etc.*) the electroreduction of sulfur in DMA occurs in two bielectronic steps with respect to S_8 molecules[4,6] (waves R_1, $E_{\frac{1}{2}} = -0.40$ V *vs.* ref. and R_2, $E_{\frac{1}{2}} = -1.10$ V, on a rotating gold-disc microelectrode). The disproportionation [reaction (7)] of the carmine-red S_8^{2-} ions

$$S_8 + 2e^- \longrightarrow S_8^{2-} \qquad (6)$$

$$S_8^{2-} \rightleftharpoons S_6^{2-} + S_2 \qquad (7)$$

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† Alkyl polysulfide ion = alkylpolysulfanide.

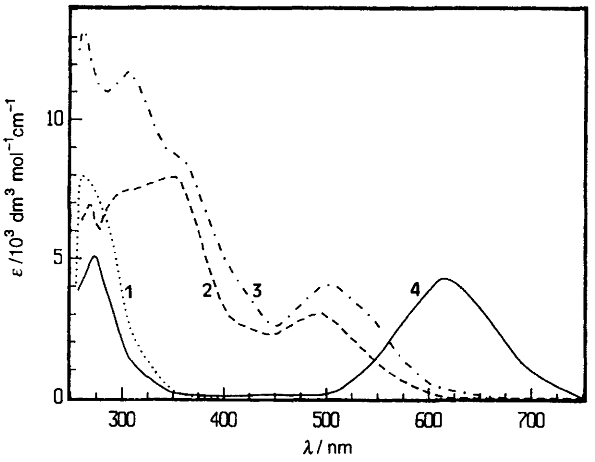

Fig. 1 UV–VIS absorption spectra (ε_i/dm^3 mol^{-1} cm^{-1}) of S_8 (**1**), S_6^{2-} (**2**) S_8^{2-} (**3**) and $S_3^{\cdot -}$ (**4**) in dimethylacetamide[‡]

(λ_{max} = 515 nm, $\varepsilon^8{}_{515}$ = 3800 dm^3 mol^{-1} cm^{-1}) leads to the stable product of the electrolysis of sulfur at controlled-potential on the plateau of R_1, the blue anion radical $S_3^{\cdot -}$ (λ_{max} = 617 nm, $\varepsilon^3{}_{617}$ = 4390 dm^3 mol^{-1} cm^{-1}). $S_3^{\cdot -}$ ions are in equilibrium (9) with their dimer S_6^{2-} (λ_{max} = 465 nm,

$$K_2\,(297\text{ K}) = [S_6^{2-}][S_2][S_8^{2-}]^{-1} = 4.0 \times 10^{-5}\text{ mol dm}^{-3} \quad (8)$$

$$S_6^{2-} \rightleftharpoons 2S_3^{\cdot -} \quad (9)$$

$$K_3\,(297\text{ K}) = [S_3^{\cdot -}]^2\,[S_6^{2-}]^{-1} = 0.043\text{ mol dm}^{-3} \quad (10)$$

$\varepsilon^6{}_{465}$ = 3100 dm^3 mol^{-1} cm^{-1}). S_8^{2-} and $S_3^{\cdot -}$ ions can be oxidized (O_1, $E_{\frac{1}{2}}$ = −0.20 V) and reduced (R_2, $E_{\frac{1}{2}}$ = −1.10 V) at the same potentials. The electrolysis of sulfur (reduction), or $S_3^{\cdot -}$ ($\rightleftharpoons S_6^{2-}$) ions (oxidation) for several initial concentrations enabled spectra of S_8, S_6^{2-}, $S_3^{\cdot -}$, S_8^{2-} to be attained;[2,4] they have been represented in Fig. 1. All these characteristics and the values of K_1, K_2 and K_3 will be used for data treatment.

As was previously performed for the generation of the ArS$^-$ species, thiolate ions were obtained by electrolysis at a controlled potential on a gold electrode of disulfides RS_2R^2 (**1**–**4**) or thiols RSH (**3**, **5**–**8**). RSH reduces according to the totally irreversible reaction (11),[8] whereas reduction of disulfides is

$$RSH + e^- \longrightarrow RS^- + \tfrac{1}{2}H_2 \quad (11)$$

$$RS_2R + 2e \longrightarrow 2RS^- \quad (12)$$

highly irreversible in neutral aprotic media.[7,8] The electrochemical ($E_{\frac{1}{2}}$) and/or spectrophotometric (λ_{max}, ε_{max}) characteristics of RSH, RS_2R and those of RS$^-$ ions are summarized in Table 1.

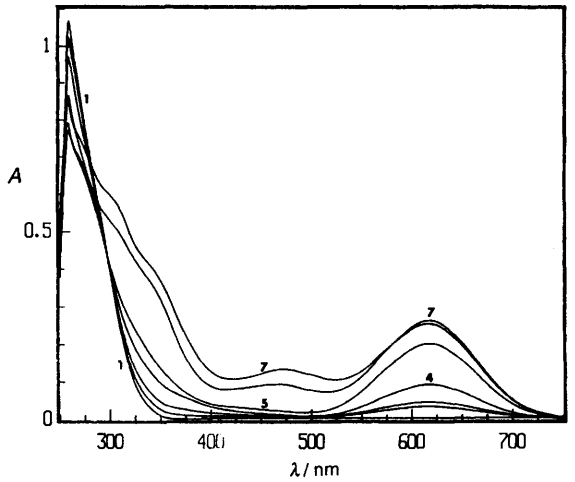

Fig. 2 Evolution of UV–VIS spectra during the addition of sulfur to a solution of propylthiolate ions $[RS^-]_o = 2.0 \times 10^{-3}$ mol dm^{-3}. $y = [S]_{ad}/[RS^-]_o$ = 0 (1); 0.25 (2); 0.50 (3); 1.20 (4); 1.80 (5); 2.80 (6); 3.1 (7). Thickness of the cell, l = 0.1 cm

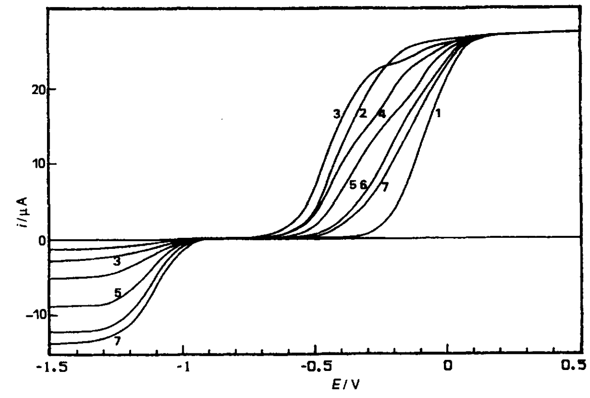

Fig. 3 Evolution of voltammograms during the reaction of sulfur with propylthiolate ions. Same conditions as for Fig. 2. Rotating gold-disc electrode Ω = 1000 rev min^{-1}, diameter = 2 mm; *E vs.* reference Ag/AgCl, KCl sat. in DMA–N(Et)$_4$ ClO$_4$ 0.1 mol dm^{-3}

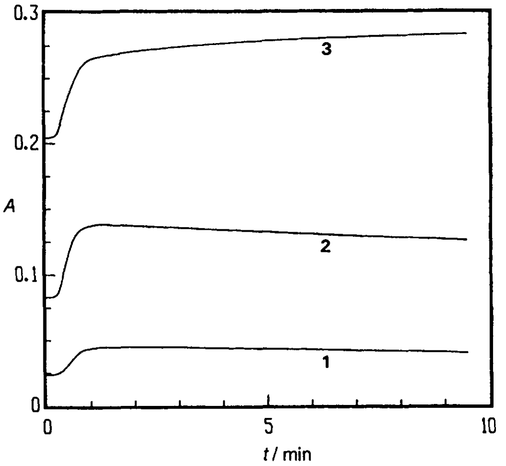

Fig. 4 Variation in A_{617} *vs.* time in the course of sulfur additions to propylthiolate ions $[RS^-]_o = 2.0 \times 10^{-3}$ mol dm^{-3}; y = 0.50 (1); 1.40 (2); 2.8 (3)

Reactivity of thiolate ions with sulfur

As an example (R = propyl), Figs. 2 and 3 show the general evolution of the UV–VIS spectra and voltammograms when a concentrated solution of sulfur was added to a solution of thiolate ions, $[RS^-]_o = 2.0 \times 10^{-3}$ mol dm^{-3}, with ratio $y = 8[S_8]/[RS^-]_o = [S]_{ad}/[RS^-]_o$. As long as y remained less than *ca.* 4.5, the total consumption of sulfur was evidenced by the lack of its reduction wave R_1. The partial oxidation of RS$^-$ ions according to the overall reaction (13) agrees with the

$$2RS^- + 3S_2 \longrightarrow RS_2R + 2S_3^{\cdot -} \quad (13)$$

progressive appearance of $S_3^{\cdot -}$ ions. These species were detected by the simultaneous increase in their absorption at 617 nm and those of their waves of reduction (R_2, $E_{\frac{1}{2}}$ = −1.10 V) and oxidation (O_1, $E_{\frac{1}{2}}$ = −0.20 V). Whatever the y values, sulfur was quantitatively recovered by the exhaustive

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[‡] More accurate spectra of sulfur species than those previously reported[2] (especially for S_8^{2-} ions) have been estimated in the course of recent electro-oxidations of $S^{1/3-}$ solutions.[4]

Table 1 Electrochemical and/or spectrophotometric characteristics of thiols RSH, disulfides RS_2R, RS^- and RS_2^- ions in *N*,*N*-dimethylacetamide–$E_{\frac{1}{2}}$ at a rotating gold disc electrode *vs.* reference Ag/AgCl, KCl sat. in DMA–$N(Et)_4$ ClO_4 0.1 mol dm^{-3}

	RSH	RS_2R			RS^-			RS_2^-
R	$E_{\frac{1}{2}}$(R)/V	λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}	$E_{\frac{1}{2}}$(R)/V	λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}	$E_{\frac{1}{2}}$(O)/V	$E_{\frac{1}{2}}$(O)/V
4-$NO_2C_6H_4$[a]	—	322	21 400	−0.62	507	30 000	+0.67	+0.27
2-$NO_2C_6H_4$[a]	—	362	8 500	−0.67	502	1 860	+0.55	+0.05
C_6H_5(**1**)	—	260	4 100	−1.10	309	18 200	+0.20	−0.03
4-$CH_3C_6H_4$(**2**)	—	260	6 000	−1.17	309	21 200	+0.22	+0.02
$C_6H_5CH_2$(**3**)	−1.63	260	1 850	−1.53	260	5 300	+0.06	−0.40
C_2H_5(**4**)	—	260	350	−1.75	260	5 400	−0.28	−0.45
C_3H_7(**5**)	−1.72	259	400	—	259	5 300	−0.11	−0.43
C_4H_9(**6**)	−1.75	259	400	—	260	5 300	−0.08	−0.42
sec-C_4H_9(**7**)	−1.70	257	320	—	257	5 400	−0.10	−0.35
tert-C_4H_9(**8**)	−1.80	257	250	—	257	5 100	−0.18	−0.35

[a] Values previously determined.[2,12]

electrolysis of the solutions at an anodic potential (E = +0.20 V).

However, with the exception of R = *tert*-C_4H_9, A_{617} changed with time with each addition of sulfur, as reported in Fig. 4 for propylthiolate ions (same experimental conditions as given for Figs. 1 and 2): after a fast increase in concentration, $[S_3^{\bullet -}]$ decreased (curves 1 and 2; $y \lesssim 2$), or increased (curve 3, $y > 2$), more slowly with R = alkyl than with R = aryl. The variations in concentrations during spectra recordings (t = 15 s) were insignificant. The total concentration X_T of sulfur in the oxidation state $S^{\frac{1}{3}-}$ [*i.e.* $S_3^{\bullet -}$ and S_6^{2-} ions in equilibrium (9)] was calculated from A_{617} (or A_{675}) measurements giving $[S_3^{\bullet -}]$, and $[S_6^{2-}]$ by the use eqn. (14) and (10). Comparing $3X_T$ and $[S]_{ad}$, it was possible to show that sulfur ($[S]_R$) was mainly consumed by RS^- to give polysulfide ions RS_x^-, with an average $\bar{x}$ value obtained from reaction (13) and conservation equations [eqns. (15)–(18)].

$$X_T = [S_3^{\bullet -}] + 2[S_6^{2-}] \qquad (14)$$

$$[S]_R = [S]_{ad} - 3X_T \qquad (15)$$

$$X_T = 2[RS_2R] \qquad (16)$$

$$[RS_x^-]_T = [RS^-]_o - X_T \qquad (17)$$

$$\bar{x} - 1 = [S]_R/[RS_x^-]_T \qquad (18)$$

(*a*) With $\bar{x} < 2$, and as soon as traces of sulfur ($y < 1/50$) were added, the oxidation wave of RS^- ions ($E_{\frac{1}{2}} = -0.11$ V) totally shifted over towards more cathodic potentials (curve 2, Fig. 3, $E_{\frac{1}{2}} = -0.43$ V) as observed with aromatic thiolates.[2] RS_2^- ions oxidize into RS_2R faster than RS^- *via* the electrocatalytic process given by reactions (19) and (20). This

$$2RS^- + S_2 \longrightarrow 2RS_2^- \qquad (19)$$

$$2RS_2^- - 2e^- \longrightarrow RS_2R + S_2 \qquad (20)$$

mechanism was previously tested by the electrolysis of a solution of 2-$NO_2C_6H_4S^-$ ions (λ_{max} = 502 nm) in the presence of sulfur at y = 0.41.[2] As long as $[ArS^-]_T = [ArS^-] + [ArS_2^-]$ was greater than $[S]_{ad}$, $[ArS_2^-]$ (λ_{max} = 681 nm) remained constant as a result of the regeneration of sulfur [reaction (20)]. ArS_2^- ions react faster than ArS^- towards alkyl halides in DMA.[9] The S–S bond does not transmit the conjugation,[10] so the anionic charge could be supposed to be more localized on the terminal S in ArS_2^-. The same phenomena [reactions (19) and (20)] with both alkyl and aryl RS^- or RS_2^- species may be rather explained by the 'α-effect'[11] in RSS^-, due to the unshared electron pairs on the sulfur atom adjacent to the nucleophilic centre of RS^-. Half-wave potentials for RS_2^- ions which were measured at $\bar{x}$ = 2 are listed in Table 1. $E_{\frac{1}{2}}$ (R) of disulfides RS_2R and $E_{\frac{1}{2}}$ (O) of RS^- and RS_2^- species evolve with the nature of R in agreement with the electronic effects. Diethyldisulfide probably contains traces of sulfur; this would explain the more cathodic value $E_{\frac{1}{2}}$ (O) for $C_2H_5S^-$. In the course of the successive additions of sulfur, with R = alkyl and $\bar{x} \leqslant 2$ the evaluation of concentrations when A_{617} quickly reached a maximum value showed that $\Delta RS_x^-/\Delta X_T \approx 2$: according to reactions (13) and (19), about $\frac{1}{3}$ of the thiolate ions oxidizes into RS_2R and $\frac{2}{3}$ goes to RS_x^- species ($\bar{x}$ = 2).

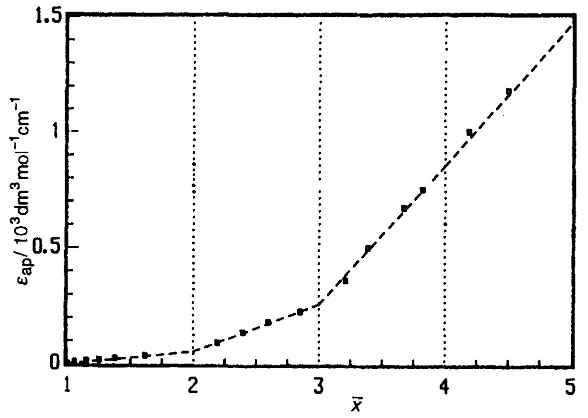

Fig. 5 Variation in $\varepsilon_{ap} = A_{460}/l[RS_x^-]_T$ as a function of $\bar{x}$ during the addition of sulfur to propylthiolate ions

(*b*) With $\bar{x} > 2$, RS_x^- ions are characterised by the growth of a VIS absorption band ($\lambda_{max} \approx$ 460–470 nm, curves 5–7, Fig. 2) and their oxidation wave shifts again, but towards anodic potentials, close to the RS^- one. With R = alkyl (**3**–**8**), the specific absorptions A_λ of RS_x^- species were studied as a function of $\bar{x}$ at 15 wavelengths between 260 and 600 nm. For each of them, the absorptions of RS_2R, $S_3^{\bullet -}$ and S_6^{2-} which were estimated from their concentrations, and spectrophotometric characteristics (Fig. 1) were substracted from the measured A values. The evolution of the molar apparent absorbance, $\varepsilon_{ap} = A_\lambda/l[RS_x^-]_T$ *versus* $\bar{x}$ is represented in Fig. 5 for λ = 460 nm and R = C_3H_7. Whatever λ and R, the variations $\varepsilon_{ap} = f(\bar{x})$ were linear between entire $\bar{x}$ values. This important result implies the quantitative and successive formation of RS_x^- species (x = 2–5) as summarized by reaction (21). The molar absorptions ε_x, which were deduced, satisfy eqn. (22), with x

$$RS_{x-1} + \tfrac{1}{2}S_2 \longrightarrow RS_x^- \qquad (21)$$

$$\varepsilon_{ap} = \bar{x}(\varepsilon_{x+1} - \varepsilon_x) + (x + 1)\varepsilon_x - x\varepsilon_{x+1} \qquad (22)$$

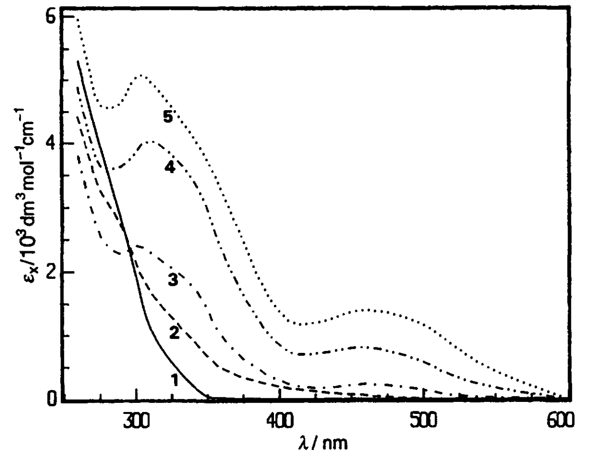

Fig. 6 Calculated UV–VIS spectra (ε_x/dm^3 mol^{-1} cm^{-1}) of propylthiolate (1) and polysulfide ions RS_x^-, $x = 2$ (2); 3 (3); 4 (4); 5 (5)

Table 2 Spectrophotometric characteristics of RS_x^- ions (x = 1–5) at 330 or 360 and 460 nm in dimethylacetamide

		ε_x/dm^3 mol^{-1} cm^{-1}				
R^a	λ/nm	RS^-	RS_2^-	RS_3^-	RS_4^-	RS_5^-
1	360	550	4000	*b*	*b*	—
	460	—	—	400	900	—
2	360	1100	4100	3300	3900	—
	460	—	—	250	800	—
3	360	200	900	1400	2600	2900
	460	—	~40	200	900	1600
4	330	250	1600	2400	3600	*b*
	460	—	100	300	800	*b*
5	330	100	1100	2000	3700	4400
	460	—	~50	250	850	1500
6	330	200	1300	2000	3700	*b*
	460	—	100	350	850	*b*
7	330	100	950	2000	3000	*b*
	460	—	~50	250	1000	*b*
8	330	500	1200	3000	3400	5200
	460	—	100	200	750	1300

[a] $4\text{-}NO_2C_6H_4S_2^-$: λ_{sh} = 600 nm (ε = 11 000 dm^3 mol^{-1} cm^{-1}); $2\text{-}NO_2C_6H_4S_2^-$: λ_{max} = 681 nm (ε = 5200 dm^3 mol^{-1} cm^{-1}), from ref. 2.
[b] ε_x values uncalculated.

(entire) $< \bar{x} < (x + 1)$. The UV–VIS spectra of $C_3H_7S_x^-$ ions (x = 1–5) so obtained have been reported in Fig. 6. The absorption generally increases with x in the spectral regions UV (λ_{max} 320–360 nm) and VIS (λ_{max} 450–470 nm). The analogous results concerning the alkylpolysulfide ions are summarized for two wavelengths (λ = 330 and 460 nm) in Table 2.

(*c*) With $\bar{x} > 5$ (the experiments were only performed with R = benzyl, propyl and *tert*-butyl), the maximal VIS absorptions shift towards *ca.* 500 nm, $i(R_1)$ appears on voltammograms ($E_{\frac{1}{2}} = -0.40$ V) and A_{617} slightly decreases; sulfur now reacts with $S_3^{\bullet -}$ leading to S_8^{2-} ions (λ_{max} = 515 nm) according to equilibrium (23) [=(7) + (9)]. The partial formation of RS_6^- could not be revealed.

$$2S_3^{\bullet -} + S_2 \rightleftharpoons S_8^{2-} \qquad (23)$$

With aromatic groups **1** and **2** (R = C_6H_5 and $4\text{-}CH_3C_6H_4$) the oxidation reaction (13) of RS^- was weaker than that with R = alkyl. When adding sulfur ($y > 2$), the solutions first became blue (λ_{max} = 617 nm, $S_3^{\bullet -}$ formation) then turned pale yellow (λ_{max} = 470 nm) in a few minutes. However the slope $\varepsilon_{ap} = f(\bar{x})$ smoothly varied at all the selected wavelengths (5 values for **1**, 10 values for **2**, between 300–600 nm), without the presence of sulfur ($\bar{x} < 4.5$) in solution [lack of $i(R_1)$]. This general evolution agrees with equilibriums (24), (25), (27) and (28) between the different species RS_x^- (x = 1–4). At fixed λ, approximate values of $\varepsilon_2(RS_2^-)$, $\varepsilon_3(RS_3^-)$ and $\varepsilon_4(RS_4^-)$ could be attained with eqn. (30) derived from eqn. (22).

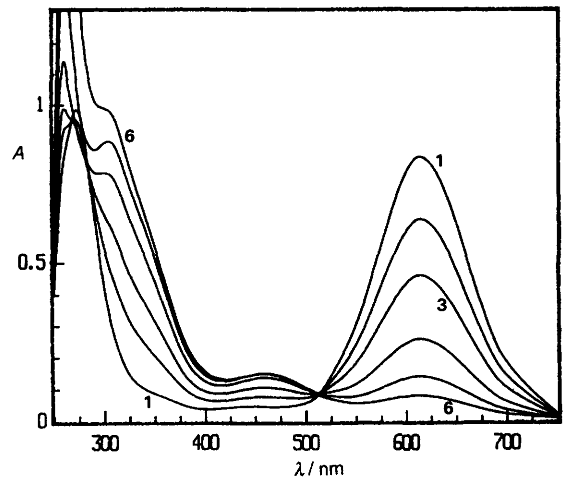

Fig. 7 Variation in spectra during the addition of dibenzyldisulfide to $S^{\frac{1}{3}-}$ ions at $X_T{}^{\circ} = 2.12 \times 10^{-3}$ mol dm^{-3}. $[RS_2R]_{ad}/X_T{}^{\circ}$ = 0 (1); 0.125 (2); 0.25 (3); 0.56 (4); 1.42 (5); 4.30 (6)

$$RS^- + S_2 \rightleftharpoons RS_3^- \qquad (24)$$

$$RS_3^- + RS^- \rightleftharpoons 2RS_2^- \qquad (25)$$

$$K_4 = [RS_3^-][RS^-][RS_2^-]^{-2} \qquad (26)$$

$$RS_2^- + S_2 \rightleftharpoons RS_4^- \qquad (27)$$

$$RS_4^- + RS_2^- \rightleftharpoons 2RS_3^- \qquad (28)$$

$$K_5 = [RS_4^-][RS_2^-][RS_3^-]^{-2} \qquad (29)$$

$$\lim_{\bar{x}\rightarrow 1\text{–}3} \frac{d\varepsilon_{ap}}{dx} = \varepsilon_{x+1} - \varepsilon_x \qquad (30)$$

For $1 < \bar{x} < 2$, the supposed major species in solution were ArS^-, ArS_2^- and ArS_3^-. Their concentrations were estimated at first from corrected A_λ values, ε_x and conservation equations related to $[RS_x^-]_T$ and $[S]_R$. Better values of ε_x (see Table 2), and then of concentrations $[ArS_x^-]$ were deduced from iterative calculations at several other λ′ wavelengths until linear plots of eqn. (31) could be produced. The following

$$(A_\lambda'/l - \varepsilon'_1[ArS^-])/[ArS_2^-] = \varepsilon'_2 + \varepsilon'_3\,[ArS_3^-]/[ArS_2^-] \qquad (31)$$

disproportionation constants K_4 (298 K) of aromatic RS_2^- ions have been determined (±10%): K_4 (**1**) = 0.06; K_4 (**2**) = 0.35. K_4 (**2**) is close to the value which was previously obtained[12] when sulfur was added to a mixture of coloured $2\text{-}NO_2C_6H_4S^-$ (λ_{max} = 502 nm) and $4\text{-}CH_3C_6H_4S^-$ ions, *i.e.* K_4 (**2**) = 0.43. 33% (**1**) and 55% (**2**) of ArS_2^- species dissociate into ArS^- and ArS_3^- when $\bar{x} = 2$.

The same method was applied to $2 < \bar{x} < 3$ and afforded more accurate coefficients ε_4 (Table 2) and approximate values (±20%) of the disproportionation constants K_5 (298 K) of RS_3^- ions: K_5 (**1**) = 0.07; K_5 (**2**) = 0.05.

The slow evolution of $S_3^{\bullet -}$ (Fig. 4) resulting from the partial oxidation of RS^- [reaction (13)] led us to reinvestigate the reactivity of $S^{\frac{1}{3}-}$ ions towards disulfides RS_2R, taking into account the possible formation of RS_x^- species.

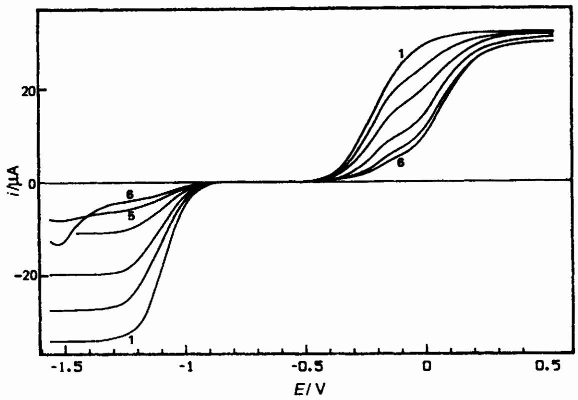

Fig. 8 Evolution of voltammograms during the reaction of dibenzyldisulfide with $S^{\frac{1}{3}-}$ ions. Same conditions as for Fig. 7

Table 3 'Dissociation' constants K_6 (298 K) of RS_4^- ions. Ionic strength = 0.1 mol dm^{-3}

R	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
$K_6/10^4$ mol dm^{-3}	2.0	4.2	1.2	0.13	0.50	0.30	0.10	*a*

[a] No reaction.

Table 4 Successive formation constants [(mol dm^{-3})$^{-\frac{1}{2}}$] at 298 K of aromatic RS_x^- ions. Ionic strength = 0.1 mol dm^{-3}

R	$K(RS_2^-)$	$K(RS_3^-)$	$K(RS_4^-)$
$4\text{-}NO_2C_6H_4$	4.0	—	—
$2\text{-}NO_2C_6H_4$	1.05×10^2	—	—
C_6H_5	5.8×10^4	3.5×10^3	2.4×10^2
$4\text{-}CH_3C_6H_4$	5.5×10^4	1.9×10^4	9.5×10^2

Reactivity of disulfides RS_2R with $S^{\frac{1}{3}-}$ ions

Whatever the nature of R (**1–7**), when RS_2R and $S_3^{\bullet-}$ were brought together in the ratio $\frac{1}{2}$, spectra and voltammograms recorded at equilibrium were the same as those obtained by mixing sulfur and thiolate ions in the proportion $y = [S]_{ad}/[RS^-]_o = 3$. Except for $(tert\text{-}C_4H_9)_2S_2$ (R = **8**), which was practically unreactive at room temperature, with R = alkyl (**3–7**), the experimental results can be generally described as the reaction between dibenzyldisulfide and $S_3^{\bullet-}$ ions at $X_T^o = 2.12 \times 10^{-3}$ mol dm^{-3} (spectra and voltammograms in Figs. 7 and 8). At this level of concentration the solutions reached a stable composition in less than 20 min, according to equilibrium (32). With the addition of RS_2R, A_{617} ($S_3^{\bullet-}$) decreases to the

$$RS_2R + 2S_3^{\bullet-} \rightleftharpoons 2RS_4^- \qquad (32)$$

$$K_6 = [RS_2R]\,[S_3^{\bullet-}]^2\,[RS_4^-]^{-2} \qquad (33)$$

benefit of a new VIS band (λ_{max} = 460 nm), with the occurrence of an isosbestic point at 512 nm. The absorption also increases in the spectral UV region 320–360 nm. The ratio $\Delta X_T/[RS_2R]_{ad}$ has initial values equal to 2 : 1 and then progressively drops down. At the same time, the reduction current R_2 ($E_{\frac{1}{2}} = -1.10$ V) of $S_3^{\bullet-}$ ions decreases in parallel with A_{617} while their O_1 wave ($E_{\frac{1}{2}} = -0.20$ V) diminishes to the benefit of the oxidation current of RS_x^- ions ($E_{\frac{1}{2}} \approx +0.04$ V). K_6 values (see Table 3) were easily deduced from A_{617} measurements and conservation equations in sulfur and RS_2R. The molar absorbances obtained for RS_4^- ions at 460 nm (Table 2) were in very good agreement with those obtained by the addition of sulfur to RS^- solutions.

With aromatic disulfides (R = **1**,**2**), the solutions reached equilibrium in under 2 min. The ratio $\Delta X_T/[RS_2R]_{ad}$ was at first restricted to between 3 and 4. In both cases, $S_3^{\bullet-}$ ions were able to displace partially sulfur from ArS_4^- ions which were stabilised to a lesser degree than RS_4^-. Simultaneous reactions (32) and (34) have to be considered. The formation of S_8^{2-}

$$2RS_4^- + 2S_3^{\bullet-} \rightleftharpoons 2RS_3^- + S_8^{2-} \qquad (34)$$

$$K_7 = [RS_3^-]^2\,[S_8^{2-}]\,[RS_4^-]^{-2}\,[S_3^{\bullet-}]^{-2} \qquad (35)$$

explained the shift of λ_{max} from 460 nm (RS_4^-, R = alkyl) to *ca.* 480 nm ($RS_x^- + S_8^{2-}$). All the concentrations were calculated with eqns. (36)–(38) and by analysis of the spectra.

$$2[RS_2R]_{ad} = 2[RS_2R] + [RS_3^-] + [RS_4^-] \qquad (36)$$

$$X_T^o = X_T + [RS_3^-] + [RS_4^-] + 2[S_8^{2-}] \qquad (37)$$

$$3X_T^o = 3X_T + 2[RS_3^-] + 3[RS_4^-] + 8[S_8^{2-}] \qquad (38)$$

X_T was again evaluated from A_{617} (or A_{675}), and A_{480} was expressed by eqn. (39) after substraction of $S_3^{\bullet-}$ (ε = 90 dm^3

$$A_{480}/l = \varepsilon_3\,[RS_3^-] + \varepsilon_4\,[RS_4^-] + 3500\,[S_8^{2-}] \qquad (39)$$

mol^{-1} cm^{-1}) and S_6^{2-} (ε = 2900 dm^3 mol^{-1} cm^{-1}) absorbances. Constants K_6 have been reported in Table 3, and K_7 (298 K) have the following values (±20%): K_7 (**1**) = 10 dm^3 mol^{-1}; K_7 (**2**) = 0.64 dm^3 mol^{-1}. With the values of K_1, K_2 and K_3 for the equilibria between S_8 and S_2; S_8^{2-} and S_6^{2-}; S_6^{2-} and $S_3^{\bullet-}$, of K_7, K_5 and K_4, the successive constants of formation of RS_2^-, RS_3^-, RS_4^-] (R = **1**, **2**) were deduced and are listed in Table 4: $K(RS_2^-) = [RS_2^-]\ [RS^-]^{-1}[S_2]^{-\frac{1}{2}}$, $K(RS_3^-) = [RS_3^-]\,[RS_2^-]^{-1}[S_2]^{-\frac{1}{2}}$ and $K(RS_4^-) = [RS_4^-]\,[RS_3^-]^{-1}[S_2]^{-\frac{1}{2}}$.

Discussion

The rates of reactions leading to equilibrium (32) were not

$$RS_2R + 2S_3^{\bullet-} \underset{b}{\overset{f}{\rightleftharpoons}} 2RS_4^- \qquad (32)$$

quantitatively examined in the present study. The electrochemical reduction of disulfides RS_2R is usually described in protic or aprotic media[13] according to the mechanism (40)–(42). The

$$RS_2R + e^- \longrightarrow RS_2R^{\bullet-} \qquad (40)$$

$$RS_2R^{\bullet-} \longrightarrow RS^- + RS^{\bullet} \qquad (41)$$

$$2RS^{\bullet} \longrightarrow RS_2R \qquad (42)$$

intermediate anion radical $RS_2R^{\bullet-}$, whose EPR detection has been reported in organic solvents,[14] rapidly cleaves to give RS^- and the thiyl radical $RS^{\bullet}$; $RS^{\bullet}$ undergoes dimerization at a rate which was roughly estimated at 10^9–10^{10} dm^3 mol^{-1} s^{-1} in aqueous solutions.[15] The indirect electrochemical reduction of RS_2R by homogeneous redox catalysis (SET) has been carried out in DMF, by the use of activated olefins[16] or aromatic compounds [reaction (43)].[7a,16] With $S_3^{\bullet-}$ ions, the monoelectronic transfer [reaction (44)] can be suggested as the rate-determining step of reaction (32, f), favoured by the fast chemical follow-up reactions (41), (42) and (45). However

$$RS_2R + A^{\bullet-} \xrightarrow{k} RS_2R^{\bullet-} + A \qquad (43)$$

$$RS_2R + S_3^{\bullet-} \xrightarrow{k(f)} RS_2R^{\bullet-} + 3/2\,S_2 \qquad (44)$$

$$RS_2R^{\bullet-} \longrightarrow RS^- + RS^{\bullet} \qquad (41)$$

$$2RS^{\bullet} \longrightarrow RS_2R \qquad (42)$$

$$RS^- + \tfrac{3}{2}\,S_2 \longrightarrow RS_4^- \qquad (45)$$

dimeric S_6^{2-} ions in low concentrations are perhaps the $S_3^{\cdot-}$ effective reagents rather than $S_3^{\cdot-}$, as was established for the substitution of nitroaromatic halides[17] or dehalogenation of *vic*-dibromides.[18] The slow dissociation of RS_4^- affording the stable $S_3^{\cdot-}$ ion and the very reactive thiyl radical could be the initial step of reaction (32,b).

Reaction (44) appears to be similar to those involving the superoxide radical ion $O_2^{\cdot-}$ and disulfides RS_2R.[19] The latter is faster in more polar solvents (pyridine, acetonitrile) than in less polar media (chloroforme, benzene).[19c] Sterically hindered disulfides such as $(t\text{-}C_4H_9)_2S_2$ react at very low rates with both $S_3^{\cdot-}$ and $O_2^{\cdot-}$ ions (more than 30 h at room temperature[19] with superoxide). After an initial nucleophilic attack of $O_2^{\cdot-}$ on their S–S bond, aryl and alkyl disulfides yield both sulfinate and sulfonate ions. Furthermore the reactions between electrogenerated thiolates and dioxygen in DMF afforded mixtures of disulfides RS_2R and sulfinates at a preparative scale in accordance with the following scheme.[20]

$$RS^- + O_2 \longrightarrow RS^{\cdot} + O_2^{\cdot-} \qquad (46)$$

$$2RS^{\cdot} \longrightarrow RS_2R \qquad (42)$$

$$RS^{\cdot} + O_2^{\cdot-} \longrightarrow RSO_2^- \qquad (47)$$

The thiyl radicals produced in reaction (46) dimerize [reaction (42)] or react with $O_2^{\cdot-}$ [reaction (47)] to form the intermediate peroxylsulfenate $RSOO^-$ before its rearrangement into sulfinate RSO_2^-. The formation of transient peroxysulfur species such as $RSOO^-$ was proposed during the alkaline autooxidation of thiols in *tert*-butyl alcohols[21] and confirmed by Oae *et al.*[19b] by the use of trapping agents added to the reactions of organic sulfur compounds with $O_2^{\cdot-}$ ions: 'when thiol is oxidized, much of the reaction goes through direct oxidation to the peroxysulfenate and only a fraction *via* thiyl radical formation of disulfide'.[22] It can be conceived that sulfur reacts with thiolate ions in a similar process.

$$S_8 \rightleftharpoons 4S_2 \qquad (4)$$

$$RS^- + S_2 \longrightarrow RS^{\cdot} + S_2^{\cdot-} \qquad (48)$$

$$2RS^{\cdot} \longrightarrow RS_2R \qquad (42)$$

$$RS^{\cdot} + S_2^{\cdot-} \longrightarrow RS_3^- \qquad (49)$$

$$2S_2^{\cdot-} \longrightarrow S_4^{2-} \qquad (50)$$

$$S_4^{2-} + S_2 \longrightarrow S_6^{2-} \qquad (51)$$

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

The monoelectronic transfer [reaction (48)] implicates the S_2 molecule as the reactive form of sulfur rather than the cyclic S_8 one. The fast competing reactions (42), (49) and (50) entail the formation of disulfides RS_2R, RS_x^- and polysulfide ions. Unlike $O_2^{\cdot-}$, $S_2^{\cdot-}$ dimerizes into S_4^{2-} ions [reaction (50)] whose quantitative reaction (51) with sulfur was reported in many instances.[23] As shown at the beginning of our study, the oxidation remains weaker with R = aryl (and negligible with R = 2- or 4-$NO_2C_6H_4$) than with R = alkyl; the better stabilisation of the aromatic intermediate $ArS^{\cdot}$ radicals probably lower the rate of dimerization [reaction (42)]. $S_3^{\cdot-}$ ions stemming from reaction (51) slowly reduce RS_2R produced in reaction (42) into RS_4^- [reaction (32)]. For $y = [S]_{ad}/[RS^-]_o \lesssim 2$ (curves 1, 2 of Fig. 4), RS^- (or RS_2^-) ions can themselves react with RS_4^-, with the successive formation of RS_x^- (R = alkyl, $x = 2,3$), the only thermodynamically stable species [reactions (28) and (25)]. For y values greater than 2–

$$RS_4^- + RS_2^- \longrightarrow 2RS_3^- \qquad (28)$$

$$RS_3^- + RS^- \longrightarrow 2RS_2^- \qquad (25)$$

2.5, the 'instantaneous' formation of RS_4^- in excess of the concentrations at equilibrium (32) entails its slow dissociation into RS_2R and $S_3^{\cdot-}$ (growth of A_{617}, curve 3, Fig. 4).

Reactions (24) [=(48) + (49)] and (25) are analogous to those which were proposed in the course of thiol oxidation by the $O_2/O_2^{\cdot-}$ system.[21] The addition of sulfur to ArS^- ions of

$$RS^- + O_2 \longrightarrow RSOO^- \qquad (52)$$

$$RSOO^- + RS^- \longrightarrow 2RSO^- \qquad (53)$$

weaker reducing power yields species in equilibrium. (*i*) ArS^-, ArS_2^-, ArS_3^- [reactions (24) and (25) for $1 < y < 2$]; ArS_2^-, ArS_3^- ArS_4^- [reactions (27) and (28) for $2 < y < 3$] with R = **1**, **2**; (*ii*) ArS^-/ArS_2^- only with R = 2- or 4-$NO_2C_6H_4{}^2$, the thiolates being even more stabilized.

More generally, the affinity of RS^- ions for sulfur is analogous to that of many other 'S-nucleophiles'. The thiophilicity[5] of various Y^- anions in protic media or triarylphosphines in non-polar solvents was found to be in the reactivity order:[5,24] $C_2H_5S^- > C_6H_5S^- > Ar_3P > CN^- > SO_3^{2-} > N_3^-$, from their reactions on unsymmetrical RSSR′ disulfides, the more stable $R'S^-$ thiolate being displaced [reaction (54)]. A close correlation was established for some

$$RSSR' + Y^- \rightleftharpoons RSY + R'S^- \qquad (54)$$

Y^- ions between their ease of oxidation to Y–Y and their thiophilicity.[25] With elemental sulfur, the same species (*e.g.* CN^- and SO_3^{2-}) give the corresponding thioanions according to the mechanism proposed by Foss[25] and Bartlett and co-workers[26] [reactions (55) and (56)]. The nucleophilic attack

$$S_8 + Y^- \xrightarrow{k} Y\text{–}S_7\text{–}S^- \qquad (55)$$

$$Y\text{–}S_7\text{–}S^- + 7Y^- \longrightarrow 8YS^- \qquad (56)$$

[reaction (55)] of Y^- on cyclic S_8 with ionic scission of the S–S bond is assumed to be the rate-determining step. The highly reactive intermediate would then be rapidly and successively degradated by additional Y^- ions.

With the same stoichiometry, we recently established[4] that reactions between triarylphosphines and sulfur in DMA were first-order in each reactant Ar_3P and S_2, and we proposed a very different pathway [reactions (4), (57) and (58)]. The

$$S_8 \rightleftharpoons 4S_2 \qquad (4)$$

$$Ar_3P + S_2 \xrightarrow{k} Ar_3P^+SS^- \qquad (57)$$

$$Ar_3P^+\,SS^- + Ar_3P \longrightarrow 2Ar_3PS \qquad (58)$$

reactions which were performed in the present work involve the initial monoelectronic transfer [reaction (48)]. We think that the reactions of the different 'S-nucleophiles' towards the S–S bond of sulfur and disulfides RS_2R' could also be thought to occur *via* similar redox reactions [reactions (59)–(61) and (62)–

$$Y^- + S_2 \longrightarrow Y^{\cdot} + S_2^{\cdot-} \qquad (59)$$

$$Y^{\cdot} + S_2^{\cdot-} \longrightarrow YS_2^- \qquad (60)$$

$$YS_2^- + Y^- \rightleftharpoons 2YS^- \qquad (61)$$

$$Y^- + RS_2R' \longrightarrow Y^{\cdot} + RS_2R'^{\cdot-} \qquad (62)$$

$$RS_2R'^{\bullet -} \longrightarrow RS^{\bullet} + R'S^{-} \qquad (63)$$

$$RS^{\bullet} + Y^{\bullet} \longrightarrow RSY \qquad (64)$$

(64)]. The key redox system $S_2/S_2^{\bullet -}$ (analogous to the $O_2/O_2^{\bullet -}$ one) in reaction (59) is implied rather than the 'S_N2' opening of cyclic S_8. We believed that the same species were involved in the first step of the electrochemical reduction of sulfur in aprotic

$$S_2 + e^{-} \longrightarrow S_2^{\bullet -} \qquad (65)$$

media.[4] $S_2^{\bullet -}$ ions were characterized in HMPA,[27] with a thorough comparison of the force constants, harmonic frequencies and anharmonicity constants for diatomic sulfur and oxygen species X_2 and $X_2^{\bullet -}$. Reaction (51) of the dimeric form S_4^{2-} with sulfur can be regarded as another example of reactions (59) and (60). Other reactions between the Y^- species

$$S_4^{2-} + S_2 \longrightarrow S_4^{\bullet -} + S_2^{\bullet -} \qquad (66)$$

$$S_4^{\bullet -} + S_2^{\bullet -} \longrightarrow S_6^{2-} \qquad (67)$$

and sulfur, with concurrent couplings of intermediates such as $RS^{\bullet}$ and $S_2^{\bullet -}$ are at present carried out in our group.

Experimental

Materials and equipment

Disulfides RS_2R (R = **1**–**4**) and thiols (R = **3**, **5**–**8**) were obtained from Aldrich and used as received (purity > 98%). The purification of *N*,*N*-dimethylacetamide (Aldrich) and its storage after addition of tetraethylammonium perchlorate (Fluka, 0.1 mol dm^{-3}) as supporting electrolyte has been reported elsewhere.[6] Electrochemical and spectrophotometric equipment, as well as the thermostatted (25 ± 0.5 °C) flow-through cell, were the same as previously described.[4] A rotating gold disc (diameter = 2 mm; 1000 rev min^{-1}) was used as working electrode. The counter electrode was a gold wire in a separated compartment. The potentials were expressed in comparison to the reference electrode Ag/AgCl, KCl saturated in DMA–$N(Et)_4ClO_4$ 0.1 mol dm^{-3}. All experiments were performed under a dry nitrogen atmosphere.

Generation of RS^- ions and $S^{\frac{1}{3}-}$ species

Solutions of RS^- ions (V = 40 cm^3) were generated at concentrations near 2 × 10^{-3} mol dm^{-3} by reduction at a controlled potential on a large gold grid electrode of disulfides or thiols [eqns. (11) and (12)]. The molar absorbances of the RS^- species (Table 1) were determined in the course of their quantitative electrolysis at fixed E values on their well defined anodic wave. Definite volumes (V_{max} = 5 cm^3) of a 'concentrated' sulfur solution at 9.0 × 10^{-3} mol dm^{-3} (close to saturation in DMA at 25 °C) were progressively added to the thiolate solutions.

$S^{\frac{1}{3}-}$ solutions were prepared before addition of RS_2R by electroreduction of sulfur on the plateau of its second reduction wave R_2. When the absorbance reached a maximum at 617 nm, $S^{\frac{1}{3}-}$ ions ($S_3^{\bullet -} \rightleftharpoons S_6^{2-}$) were the only species in solution, according to the overall stoichiometry of reaction (68). All

$$S_8 + 8/3\,e^{-} \longrightarrow 8/3\,S_3^{\bullet -} \qquad (68)$$

initial concentrations $X_T{}^{\circ} = [S_3^{\bullet -}] + 2[S_6^{2-}]$ were included between (2–3) × 10^{-3} mol dm^{-3}. $X_T{}^{\circ}$ values were obtained from A_{675} measurements. At this wavelength $S_3^{\bullet -}$ ions are the only absorbing species[4] ($\varepsilon^3{}_{675}$ = 1825 dm^3 mol^{-1} cm^{-1}).

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