Preparation of S_4^{2-} polysulfide from a sacrificial sulfur cathode and its use as a nucleophile in an electrochemically induced $S_{RN}1$ substitution reaction

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Polarization in deaerated acetonitrile of a sacrificial sulfur cathode constituted of a 2 : 1 mixture of S_8 and graphite powder contained in a graphite envelope, at a potential corresponding to the first reduction step of S_8, led to the $S_3^{\cdot -}$ ($\rightleftharpoons S_6^{2-}$) polysulfide. After reduction of the total amount of S_8, the further reduction of $S_3^{\cdot -}$ at a potential corresponding to the second reduction step of S_8, and using the graphite envelope as a cathode, gave exclusively S_4^{2-}. Addition of one equivalent of 3-bromoquinoline (BrQ) followed by its mediated reduction by redox catalysis led to a mixture of QS_3Q, QS_2Q and QSQ in similar yields (22 ± 4%), resulting from $S_{RN}1$ substitution reactions involving the S_4^{2-}, QSS^- and QS^- nucleophiles, respectively.

Préparation de polysulfures S_4^{2-} à partir d'une cathode consommable de soufre, et leur utilisation dans une réaction de substitution nucléophile $S_{NR}1$ induite électrochimiquement. Une électrode consommable de soufre, constituée d'un mélange de soufre S_8 et de poudre de graphite (2 : 1) contenu dans une enveloppe de graphite, et polarisée dans de l'acétonitrile à un potentiel correspondant au premier stade de réduction de S_8 conduit à l'anion polysulfure $S_3^{\cdot -}$ ($\rightleftharpoons S_6^{2-}$). Après réduction totale de S_8, la réduction de $S_3^{\cdot -}$ au potentiel correspondant à la seconde vague de réduction de S_8 et en utilisant l'enveloppe de graphite comme cathode, conduit exclusivement à S_4^{2-}. L'addition d'un équivalent de 3-bromoquinoléine (BrQ) suivie de sa réduction par l'intermédiaire d'un médiateur redox conduit à un mélange de QS_3Q, QS_2Q et QSQ avec des rendements voisins (22 ± 4%), ces produits résultant de réactions de substitution de type $S_{NR}1$ mettant respectivement en jeu les nucléophiles S_4^{2-}, QSS^- et QS^-.

A sacrificial mixed sulfur/graphite cathode (S–C electrode) has been proposed as a source of polysulfide ions reactive towards aliphatic or activated aromatic molecules.[1–8] For instance, polarization of a sacrificial sulfur cathode in the presence of halogenonitrobenzene[5,6] or 4-bromobenzophenone[5] leads mainly to an aryl disulfide by nucleophilic substitution. The use of this electrode was developed by Le Guillanton's group,[4] following the pioneering work by Berge *et al.*[1,2]

In continuation of the electrochemical synthesis of aromatic chalcogeno derivatives by $S_{RN}1$ substitutions reaction in acetonitrile, using a sacrificial cathode (Se or Te) and an unactivated aryl halide,[9–12] the present work describes the use of an S–C electrode in combination with 3-bromoquinoline (BrQ). Experimental conditions were defined that allowed the exclusive preparation of S_4^{2-} polysulfide and its use as a nucleophile in the $S_{RN}1$ substitution reaction with BrQ.

Experimental

Reagents and equipment

Analytical grade acetonitrile (Janssen Chimica) was dried on neutral alumina. Bu_4NPF_6 (electrochemical grade, Fluka), $Et_4NF \cdot 2H_2O$ (99%, Janssen Chimica), BrQ (98%, Aldrich), $K_3Fe(CN)_6$ (99+%, Aldrich), and CH_3I (99%, Prolabo) were used as received. Sulfur (Prolabo) was recrystallised from toluene. To prepare a saturated solution in dry acetonitrile, sulfur was stirred mechanically for 24 h at room temperature and then filtered. Complete evaporation of the solvent under vacuum allowed the amount of dissolved sulfur to be evaluated, *i.e.* 0.10 g l^{-1} (*ca.* 4×10^{-4} M S_8). Graphite powder of average diameter 100 μm was supplied by Johnson Matthey and graphite cloth was obtained from Carbone Lorraine.

Voltammograms at a glassy carbon rotating (650 rpm) or stationary disc electrode (V25 Carbone Lorraine; 3 mm diameter) or Pt disc electrode (Tacussel EM-EDI-CVJ; 2 mm diameter) were recorded by using a Tacussel PRT 20-2X potentiostat connected to a Tacussel ADTP differential amplificator and a Sefram T6M 101 X-Y recorder. An Amel 552 potentiostat and an Amel 731 integrator were used in preparative electrolysis under controlled potential and in coulometry. All potentials are referred to the aqueous saturated calomel electrode (SCE).

High performance liquid chromatography (HPLC) was carried out on a Gilson apparatus equipped with a UV117 detector (210 nm) and a Phase Sep reverse phase column (S5ODS2).

Large-scale electrolysis

The electrolyses were carried out in an H-type cell filled with acetonitrile containing 0.1 M Bu_4NPF_6 as supporting electrolyte. The three compartments were separated by ion-exchange membranes [Ionax MA 3475 (anodic side) and MC 3470 (cathodic side)]. The cathodic solution (100 ml) was stirred mechanically and deaerated with argon prior to and during electrolysis. The sacrificial sulfur cathode was a mixture of S_8 (200 or 400 mg) and graphite powder (2 : 1 ratio) contained in a graphite envelope (tea-bag type electrode[10]) and it was prepared by a method similar to that used by Le Guillanton's group.[13]

The tea-bag type electrode was introduced in a glass tube, which was smoothly heated in an oil bath. As soon as the sulfur melted, the glass tube was removed from the oil bath, so

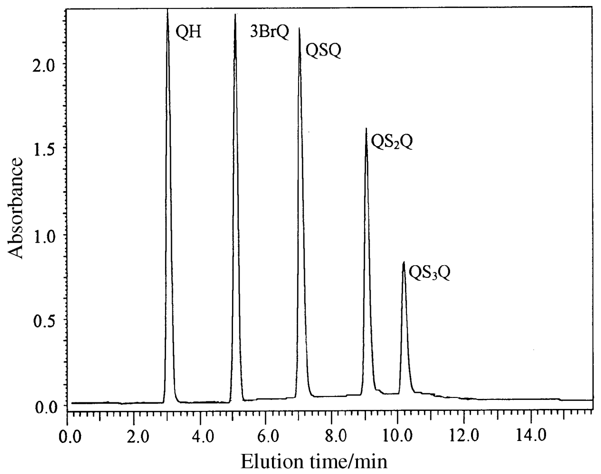


Fig. 1 HPLC of a mixture containing QH, BrQ, QSQ, QS_2Q, and QS_3Q

that the electrode was easily taken out of the glass tube at room temperature. The counter electrode was a Pt grid, but a magnesium rod (Aldrich) was used preferentially for the electrochemical generation of $S_3^{\cdot -}$ (-0.8 to -1.0 V) from an S–C electrode containing 400 mg S_8. The rod was placed in the cathodic compartment, thus constituting a one-compartment electrolysis cell. The degradation of the ion-exchange membranes, which normally occurs under electrolysis conditions,[10] was thus avoided. Moreover, 0.06 M $Et_4NF \cdot 2H_2O$ was present in the cathodic compartment because the formation of MgF_2 predominated at the expense of a MgS_x salt.[10] The further reduction of $S_3^{\cdot -}$ to S_4^{2-} (-1.4 to -1.9 V) proceeded in the three-compartment cell, after removing the Mg rod, and no longer in an undivided cell, because the anodic oxidation of S_4^{2-} occurred more readily than the Mg rod oxidation. After total cathodic reduction of $S_3^{\cdot -}$ to S_4^{2-}, BrQ was added and reduced, either without redox mediator (-1.55 to -1.65 V) or with phthalonitrile as redox mediator (-1.40 to -1.60 V). The electrolysis was followed-up by HPLC and it was stopped after almost complete consumption of BrQ (less than 2% was left). The electrolysis solution was diluted with 400 ml water containing 10 mmol $K_3Fe(CN)_6$, and the products were extracted with methylene chloride (100 ml) and diethyl ether (2 × 100 ml). In two experiments methyl iodide (1.5 or 2 ml) was added immediately after electrolysis and the electrolysis products were extracted as above, after dilution by water (400 ml). The products were purified by preparative HPLC using a gradient of 50–95% acetonitrile in water as eluent, and they were eluted in the order: quinoline (QH), 3-bromoquinoline (BrQ), 3,3′-diquinolyl sulfide (QSQ) mp 124–125 °C (lit.[14] mp 123–124 °C), 3,3-diquinolyl disulfide (QSSQ) mp 149–151 °C (lit.[15] mp 150–151 °C) and 3,3′-diquinolyl trisulfide (QSSSQ). A typical HPLC recording in the case of a standard mixture is shown in Fig. 1. The trisulfide derivative was identified by MS: *m/z* (relative intensity) 352 (M, 36); 320 (M − S, 100); 160 (QS, 93). An attempt to recrystallize it failed and led to a mixture of QSSSQ and QSSQ. In the two experiments with MeI, 3-methylthioquinoline (QSMe)[16] was eluted prior to QSQ in preparative HPLC.

Results and Discussion

Voltammetric behavior of elemental sulfur in acetonitrile

The solubility of elemental sulfur is poor in the usual organic solvents; a saturated acetonitrile solution was evaluated to contain *ca.* 4×10^{-4} mol l^{-1} of S_8 at room temperature. Tebbe *et al.*[17] have shown that S_8 is the only species initially present, whereas small amounts of S_6 (0.30 ± 0.05%) and S_7 (0.8 ± 0.1%) are formed later, one or two days being necessary to reach the equilibrium.

The voltammetric behavior of S_8 in deaerated acetonitrile was previously examined at a Pt rotating disc electrode (RDE) by Fujinaga *et al.*[18] Two waves of similar amplitudes (limiting currents i_I and i_{II}) were recorded, which were attributed so the reduction steps (1) and (2) of Scheme 1.

1st wave $\quad S_8 + 2e \rightarrow S_8^{2-} \quad (1)$

2nd wave $\quad S_8^{2-} + 2e \rightarrow 2S_4^{2-} \quad (2)$

Scheme 1

UV-visible spectrophotometric studies allowed the equilibrium constants K and K_d corresponding to reactions (3) and (4), respectively, to be determined ($K = 1.6 \times 10^{-2}$ mol$^{\frac{1}{4}}$ l$^{-\frac{1}{4}}$; $K_d = 1.2 \times 10^{-3}$ mol l^{-1}).[18]

$$S_8^{2-} \rightleftharpoons S_6^{2-} + \tfrac{1}{4}S_8 \qquad (3)$$

$$S_6^{2-} \rightleftharpoons S_3^{\cdot -} \qquad (4)$$

A voltammetric study carried out at a glassy carbon RDE indicated a third reduction wave visible beyond −2 V (Fig. 2), which was masked at the Pt RDE, owing to the discharge of the supporting electrolyte (see Fig. 1 of ref. 18). The limiting current i_{III} of the third wave increased at the expense of i_{II} as the electrode rotation speed ω was increased, whereas the sum $i_{II} + i_{III}$ remained close to i_I. A similar effect was observed when the temperature was decreased and the third wave was no longer visible at 55 °C. Moreover, the ratio i_{II}/i_I was the same at a Pt and a glassy carbon RDE for a given temperature. These data and the voltammetric curve shown in Fig. 2 can be interpreted according to Scheme 2.

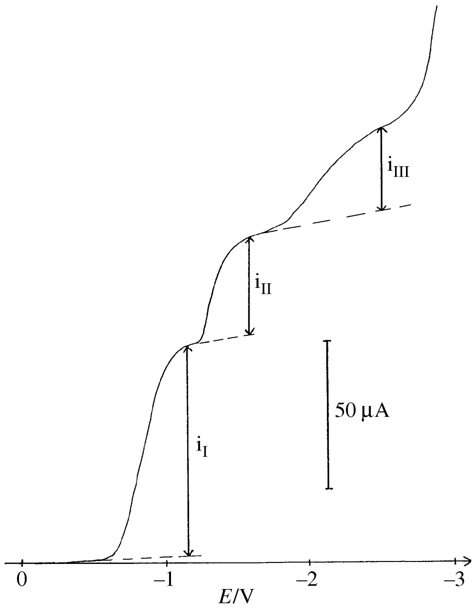


Fig. 2 Voltammetric curve on a glassy carbon rotating electrode of S_8 (0.4 mmol l^{-1}). Scan rate is 50 mV s^{-1}

1st wave ($E_{\frac{1}{2}} = -0.8$ V) $$S_8 + 2e \rightarrow S_8{}^{2-} \quad (1)$$

$$S_8{}^{2-} \rightleftharpoons S_6{}^{2-} + \tfrac{1}{4}S_8 \quad (3)$$

$$S_6{}^{2-} \rightleftharpoons 2S_3{}^{\bullet -} \quad (4)$$

2nd wave ($E_{\frac{1}{2}} = -1.25$ V) $$S_3{}^{\bullet -} + e \rightleftharpoons S_3{}^{2-} \quad (5)$$

3rd wave ($E_{\frac{1}{2}} = -2.0$ V) $$S_8{}^{2-} + 2e \rightarrow 2S_4{}^{2-} \quad (6)$$

Scheme 2

In the first reduction step, the two-electron generation of $S_8{}^{2-}$ is followed by its disproportionation [reaction (3)], as previously claimed by Fujinaga *et al.*[18] At high rotation speeds ω and/or low temperature, this reaction takes place far from the electrode in the bulk solution and so the further cathodic reduction of the regenerated sulfur does not occur. Consequently, two electrons are involved in the first reduction step on the voltammetric scale and the third wave, well-developed under these conditions at a glassy carbon RDE, corresponds to the further reduction of $S_8{}^{2-}$ to $S_4{}^{2-}$ [reaction (6)]. On the other hand, $S_6{}^{2-}$ and S_8 are generated close to the electrode according to reaction (3) when ω is decreased and/or the temperature is increased, and so S_8 is reduced immediately. Consequently, $S_3{}^{\bullet -}$ and $S_6{}^{2-}$ are formed according to the global reaction (7) during the first step, which involves 2.7 electrons, and the well-developed second wave under these conditions corresponds most probably to the further reduction of $S_3{}^{\bullet -}$ to $S_3{}^{2-}$ [eqn. (5) of Scheme 2].

$$S_8 + \tfrac{8}{3}e \rightarrow \tfrac{8}{3}S_3{}^{\bullet -}(\rightleftharpoons \tfrac{4}{3}S_6{}^{2-}) \quad (7)$$

This interpretation is consistent with recent results in liquid ammonia by Levillain *et al.*[19] who have shown that $S_3{}^{\bullet -}$ is more easily reduced than $S_6{}^{2-}$. Moreover, the reduction of $S_6{}^{2-}$ is expected to take place at potentials similar or more negative than those for $S_8{}^{2-}$, *i.e.*, beyond −2 V. The voltammogram recorded at a stationary glassy carbon electrode (curve B of Fig. 3) shows the presence of a redox peak system for the second reduction step at a stationary electrode, indicating that the electron exchange [reaction (5)] is fast. Moreover, no peak is associated with the third reduction step at the stationary electrode, since the disproportionation reaction (3) takes place close to the electrode surface in the absence of convection.

Table 1 summarizes the anionic species electrogenerated at each reduction step and the corresponding number of electrons involved on the voltammetric scale. It is assumed that the transformation of $S_6{}^{2-}$ to $S_3{}^{\bullet -}$ [reaction (4)] is very rapid and therefore quantitative during the kinetic process preceding the second reduction step (5). The data given in Table 1 show that the total number of electrons involved in step I is the same as in steps II + III [$(i_{\mathrm{II}} + i_{\mathrm{III}})/i_{\mathrm{I}} \cong 1$], which is consistent with the experimental results. In the extreme case where $x = 0$ in Table 1 (stationary electrode, high temperature) the first and second steps take place exclusively and $\frac{8}{3}$ electrons are consumed in each step, whereas in the opposite limiting case where $x = 1$ (very high rotation speeds, low temperatures) only waves I and III are expected to be observed at a glassy carbon electrode.

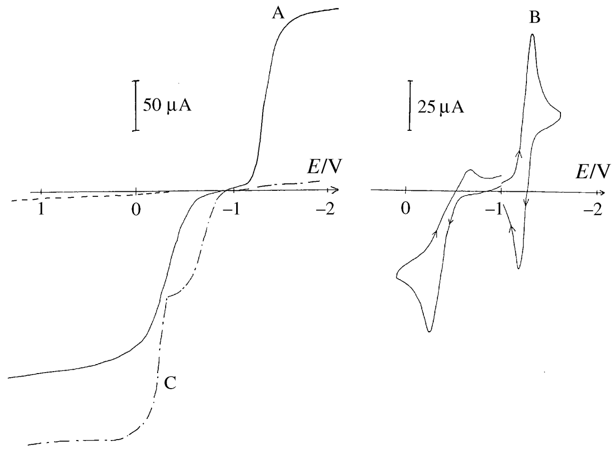


Fig. 3 Voltammetric curves on a glassy carbon rotating (A, C) or stationary (B) electrode recorded after electrolysis of S_8 (1.56 mmol) and consumption of 4.2 mF (A, B) and 6.7 mF (C). Scan rate is 50 (A, C) or (B) 100 mV s^{-1}

Clearly, the voltammetric study of S_8 carried out in deaerated acetonitrile at a glassy carbon electrode leads to the conclusion that the second reduction wave does not correspond to the two-electron reduction of $S_8{}^{2-}$ to $S_4{}^{2-}$, as suggested by Fujinaga *et al.* [eqn. (2) of Scheme 1][18] but to the reversible one-electron reduction of $S_3{}^{\bullet -}$ to $S_3{}^{2-}$ [eqn. (5) of Scheme 2]. A similar conclusion was drawn by Delamar's group in *N*,*N*-dimethylsulfoxide and *N*,*N*-dimethylformamide (DMF).[20,21]

Large-scale electrochemical preparation of polysulfide anions

To overcome the poor solubility of S_8 in acetonitrile, sulfide anions were generated at a sacrificial sulfur cathode immersed in deaerated acetonitrile (100 ml) and polarized at controlled potential. The electrode was usually composed of a mixture of sulfur (400 mg, *i.e.*, 1.56 mmol S_8) and graphite powder (200 mg) contained in a bag of graphite tissue (tea-bag type electrode[10]).

When the sacrificial cathode was polarized at a potential corresponding to the *first reduction step* of S_8 (−0.8 V to −1.0 V) the solution turned blue and the reduction of the total amount of S_8 contained in the graphite bag consumed 4.2 mF ($n = 2.7$ electrons per S_8 unit), confirming the reduction of S_8 to $S_3{}^{\bullet -}$ and $S_6{}^{2-}$ according to the global reaction (7). A voltammogram was recorded at a glassy carbon RDE after electrolysis and dilution (1 : 10) and it showed a cathodic and an anodic wave (curve A of Fig. 3). The reversible peak system recorded at a stationary electrode (curve B of Fig. 3) and corresponding to the reduction wave is consistent with reaction (5) of Scheme 2. In Fig. 3A, the limiting currents of the cathodic ($E_{\frac{1}{2}} = -1.25$ V) and anodic ($E_{\frac{1}{2}} = -0.3$ V) waves does not differ significantly, suggesting that S_8 is anodically regenerated according to reaction (8), in

Table 1 Electrochemically generated species and number of electrons involved in each step of the voltammetric reduction of S_8 at a glassy carbon RDE

	Electrochemical species	Fraction	Number of electrons
First wave	$S_8{}^{2-}$	x	$2x$
	$S_6{}^{2-} + S_3{}^{\bullet -}$	$1 - x$	$\frac{8}{3}(1 - x)$
Second wave	$S_3{}^{2-}$	$(1 - x)$	$\frac{8}{3}(1 - x)$
Third wave	$S_4{}^{2-}$	x	$2x$

agreement with previous results obtained in *N*,*N*-dimethylacetamide (DMA).[19]

$$2S_3^{\bullet -}\ (\text{or } S_6^{2-}) - 2e \rightarrow \tfrac{3}{4}S_8 \qquad (8)$$

The large-scale electrolysis was prolonged by shifting the applied potential to more negative values corresponding to the *second reduction step* of S_8 (−1.3 V to −1.8 V). The cathode was thus constituted by the graphite envelope. The solution turned orange and the electrolysis was stopped when the current became negligible, after consumption of 2.5 mF, *i.e.*, 1.6 electrons per S_8 unit in the second electrolysis step. The total amount of electricity consumed in the two-step electrolysis (6.7 mF, *i.e.*, 4.3 electrons per S_8 unit) is consistent with the formation of S_4^{2-} (*ca* 3.1 mmol) according to the global reaction (9).

$$S_8 + 4e \rightarrow 2S_4^{2-} \qquad (9)$$

The S_3^{2-} anions generated during the second step of electrolysis (5) reacted slowly with $S_3^{\bullet -}$ to give S_4^{2-} [reaction (10)] as previously observed in aprotic solvents (ref 22 and references therein). On the voltammetric time scale this reaction is negligible, since the $S_3^{\bullet -}/S_3^{2-}$ peak system is reversible (curve B of Fig. 3). In other words, the reduction of S_8 to S_4^{2-} proceeds at the potential of the third wave on the voltammetric time scale, but occurs already at the potential of the second wave on the electrolysis time scale.

$$S_3^{2-} + S_3^{\bullet -} \rightarrow \tfrac{3}{2}S_4^{2-} \qquad (10)$$

The voltammogram recorded at a glassy carbon RDE after electrolysis and dilution (1 : 10) showed two anodic waves with $E_{\frac{1}{2}} = -0.75$ V and −0.25 V and with limiting currents in a ratio of *ca.* 2 (curve C of Fig. 3). These data suggest that the anodic oxidation of S_4^{2-} proceeds according to Scheme 3.

The anodic waves of S_4^{2-} and $S_3^{\bullet -}$ were observed previously, with $E_{\frac{1}{2}}$ values of −0.32 and −0.05 V, respectively, in DMA using a Ag–AgCl salt reference electrode.[22] Anodic oxidation of S_4^{2-} to the S_6^{2-} and $S_3^{\bullet -}$ polysulfides was shown recently by Levillain *et al.* in liquid ammonia.[23] It was verified by cyclic voltammetry that the S_4^{2-} anions were stable in deaerated acetonitrile for 24 h.

The above results show that two stable sulfide anions, *i.e.*, $S_3^{\bullet -}$ (in equilibrium with S_6^{2-}) and S_4^{2-} are available from a sacrificial sulfur electrode polarized in acetonitrile. The $S_3^{\bullet -}$ species is exclusively generated by exhaustive electrolysis of S_8 at the potentials of its first reduction step. The further exhaustive reduction of $S_3^{\bullet -}$ at potentials more negative than −1.2 V and using the graphite envelope as cathode leads exclusively to S_4^{2-}. Clearly, this latter polysulfide is the only nucleophile (Nu^-) usable for electrochemically induced $S_{RN}1$ substitution reactions,[24,25] owing to its cathodic inactivity. It allows the cathodic reduction [reaction (12)] of a large variety of aryl halides ArX to take place, with formation of an aryl radical $Ar^{\bullet}$ [reaction (13)] and its subsequent reaction with S_4^{2-} [reaction (14)].

$$ArX + e \rightarrow [ArX]^{\bullet -} \qquad (12)$$

$$[ArX]^{\bullet -} \rightarrow X^- + Ar^{\bullet} \qquad (13)$$

$$Ar^{\bullet} + S_4^{2-} \rightarrow [ArS_4^{-}]^{\bullet -} \qquad (14)$$

Large-scale electrolysis of 3-bromoquinoline in the presence of S_4^{2-} anions

The cathodic reduction of 3-bromoquinoline to quinoline occurs with $E_{\frac{1}{2}} = -1.78$ V. No spontaneous reaction took place when BrQ (3 mmol) was added to a solution of S_4^{2-} (3.12 mmol) electrogenerated as described above from a sacrificial sulfur cathode containing 1.56 mmol S_8, in a two-step electrolysis. The cathodic reduction of BrQ proceeded when a potential of −1.6 ± 0.1 V was applied at the graphite envelope, and its disappearance was followed by HPLC until *ca.* 2% of BrQ was left. Chemical oxidation by $K_3Fe(CN)_6$, followed by treatment of the electrolysis solution led to a mixture of quinoline and mono-, di-, and trisulfide derivatives (QSQ, QS_2Q and QS_3Q, respectively) (entry 1 of Table 2). HPLC follow-up indicated that the formation of QH and QSQ took place during electrolysis, whereas QS_2Q and QS_3Q resulted from the chemical oxidation step after electrolysis. These two latter derivatives were not isolated when the chemical oxidation step was replaced by the addition of methyl iodide in excess, and so the main thio derivative was QSMe (entry 2 of Table 2). The yield of quinoline dropped to a negligible value (⩽2%) when electrolyses were carried out in the presence of phthalonitrile (standard redox potential $E^0 = -1.7$ V) as the redox mediator (entries 3–6). The yields of QSQ, QS_2Q and QS_3Q were similar when one equivalent of S_4^{2-} was present initially (entries 3 and 4), whereas the yield of QSQ decreased when S_4^{2-} was in excess (entry 5). The trisulfide QS_3Q derivative was rather unstable, since any attempt to purify it failed and led to a mixture of QS_3Q and QS_2Q, and so the yields of QS_3Q indicated in Table 2 are probably underestimated. Diorganyl trisulfides of moderate stability have also been prepared from a sacrificial sulfur anode (generation of S^{2+}) and thiolates.[6]

These above results indicate that the synthesis of the isolated thio derivatives involved an electrochemically induced

1st wave ($E_{\frac{1}{2}} = -0.75$ V) $\qquad S_4^{2-} - \tfrac{2}{3}e \rightarrow \tfrac{4}{3}S_3^{\bullet -}\ (\text{or } \tfrac{2}{3}S_6^{2-})$ $\qquad$ (11)

2nd wave ($E_{\frac{1}{2}} = -0.25$ V) $\qquad \tfrac{4}{3}S_3^{\bullet -}\ (\text{or } \tfrac{2}{3}S_6^{2-}) - \tfrac{4}{3}e \rightarrow \tfrac{1}{2}S_8$ $\qquad$ (8′)

Scheme 3

Table 2 Yields of the products isolated after reductions of BrQ in the presence of electrogenerated S_4^{2-} anions and final addition of an aqueous solution of $K_3Fe(CN)_6$

				Yields[a] of electrolysis products/%				
Entry	BrQ/ mmol	S_4^{2-}/ equiv	med[b]/ equiv	QH	QSQ	QS_2Q	QS_3Q	$QSCH_3$
1	3	1	0	30	18.4	23.7	14.5	
2	3	1.1	0	21	16.7	—	—	48[c]
3	3	1	1 : 3	2.1	25.8	20.9	17.9	
4	1.5	1	1 : 2	2.0	23.4	21.5	20.3	
5	0.5[d]	3	1 : 2	0	10.6	24.7	24.9	
6	1.5	1	1 : 3	1.8	19.8	2.0	0.8	65.8[c]

[a] HPLC determination. [b] Phthalonitrile. [c] Addition of CH_3I in excess after electrolysis. [d] 14.5% BrQ was left.

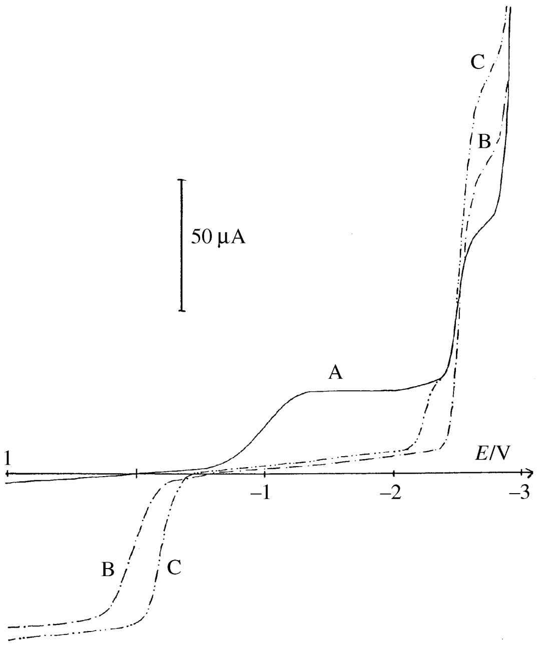


Fig. 4 Voltammetric curves on a glassy carbon rotating electrode recorded before (A) and after (B) electrolysis of QSSQ (3 mmol l^{-1}), and further addition of S_8 (0.4 mmol l^{-1}) (C). Scan rate is 50 mV s^{-1}. Dilution factor of 5

$S_{RN}1$ substitution reaction.[24,25] The cathodic cleavage of BrQ [reaction (12′)] with formation of a $Q^{\bullet}$ radical [reaction (13′)] was followed by the key step [reaction (14′)], which competed eventually with two side reactions, *i.e.*, the further cathodic reduction of $Q^{\bullet}$ [reaction (15)] with formation of quinoline [reaction (16)], and H-atom transfer [reaction (17)], since acetonitrile is an H-atom donor.[26–28]

In the presence of a redox mediator (med), the $Q^{\bullet}$ radicals were generated in the bulk solution[29–31] according to reactions (18), (19) and (13′), avoiding the cathodic side reaction (15) with formation of quinoline [reaction (16)]. The very low yields of QH under these conditions (entries 3–6 of Table 2) indicate that the second side reaction, *i.e.*, the radical hydrogenation by the solvent [reaction (17)] was negligible.

$$\mathrm{BrQ} + e \rightarrow [\mathrm{BrQ}]^{\bullet -} \qquad (12')$$

$$[\mathrm{BrQ}]^{\bullet -} \rightarrow \mathrm{Br}^{-} + \mathrm{Q}^{\bullet} \qquad (13')$$

$$\mathrm{Q}^{\bullet} + \mathrm{S_4}^{2-} \rightarrow [\mathrm{QS_4}^{-}]^{\bullet -} \qquad (14')$$

$$\mathrm{Q}^{\bullet} + e \rightarrow \mathrm{Q}^{-} \qquad (15)$$

$$\mathrm{Q}^{-} + \mathrm{CH_3CN} \rightarrow \mathrm{QH} + {}^{-}\mathrm{CH_2CN} \qquad (16)$$

$$\mathrm{Q}^{\bullet} + \mathrm{CH_3CN} \rightarrow \mathrm{QH} + {}^{\bullet}\mathrm{CH_2CN} \qquad (17)$$

$$\mathrm{med} + e \rightarrow \mathrm{med}^{\bullet -} \qquad (18)$$

$$\mathrm{med}^{\bullet -} + \mathrm{BrQ} \rightarrow \mathrm{med} + [\mathrm{BrQ}]^{\bullet -} \qquad (19)$$

The key step [reaction (14′)] was followed by a reductive cleavage, most probably with formation of a new nucleophile QS_2^{-} [reaction (20)], which could compete with S_4^{2-} and lead to QS^{-} [reactions (21)–(23)]. A partial and competing dissociation of QS_2^{-} to QS^{-} can be also envisaged.[32] Finally, the thiolate anion QS^{-} thus generated could be involved in an $S_{RN}1$ process [reactions (24) and (25)].

$$[\mathrm{QS_4}^{-}]^{\bullet -} \rightarrow \mathrm{QS_2}^{-} + \tfrac{1}{2}\mathrm{S_4}^{2-} \qquad (20)$$

$$\mathrm{Q}^{\bullet} + \mathrm{QS_2}^{-} \rightarrow [\mathrm{QSSQ}]^{\bullet -} \qquad (21)$$

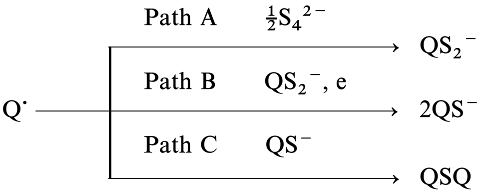
$$[\mathrm{QSSQ}]^{\bullet -} \rightarrow \mathrm{Q}^{\bullet}\ (\text{or } \tfrac{1}{2}\mathrm{QSSQ}) + \mathrm{QS}^{-} \qquad (22)$$

$$\mathrm{Q}^{\bullet}\ (\text{or } \tfrac{1}{2}\mathrm{QSSQ}) + e \rightarrow \mathrm{QS}^{-} \qquad (23)$$

$$\mathrm{Q}^{\bullet} + \mathrm{QS}^{-} \rightarrow [\mathrm{QSQ}]^{\bullet -} \qquad (24)$$

$$[\mathrm{QSQ}]^{\bullet -} + \mathrm{BrQ} \rightarrow \mathrm{QSQ} + [\mathrm{BrQ}]^{\bullet -} \qquad (25)$$

Scheme 4 summarizes the three suggested competing reactions. The chemical oxidation of QS_2^{-} by $K_3Fe(CN)_6$ would lead to QSSSQ [reaction (26)].



Scheme 4

$$2\mathrm{QS_2}^{-} \xrightarrow{\text{oxidation}} \mathrm{QSSSQ} + \tfrac{1}{8}\mathrm{S_8} \qquad (26)$$

The formation of organyl disulfide anions RSS^{-} was claimed previously when polysulfide anions S_x^{2-} were generated from a sacrificial sulfur cathode in the presence of 2-chloronitrobenzene[5] or a vinylic derivative bearing a leaving group.[6] The addition of methyl iodide in excess after electrolysis led to RSSMe. Aryl sulfide anions $ArSS^{-}$ were also formed during the direct reaction of sulfur with thiolate anions ArS^{-} in DMA, as shown by Paris and his group.[32–34] It was accompanied by a positive shift of the oxidation wave of ArS^{-} in voltammetry at a gold RDE, while its limiting current was unchanged. This phenomenon was interpreted as being due to the catalytic oxidation of ArS^{-} [reactions (27) and (28)]. Moreover, the addition of MeI led to ArSSMe [reaction (29)].

$$\mathrm{ArS}^{-} + \tfrac{1}{8}\mathrm{S_8} \rightarrow \mathrm{ArS_2}^{-} \qquad (27)$$

$$\mathrm{ArS_2}^{-} - e \rightarrow \tfrac{1}{2}\mathrm{ArS_2Ar} + \tfrac{1}{8}\mathrm{S_8} \qquad (28)$$

$$\mathrm{ArS_2}^{-} + \mathrm{MeI} \rightarrow \mathrm{ArSSMe} + \mathrm{I}^{-} \qquad (29)$$

Surprisingly, entries 2 and 6 in Table 2 indicate the formation of monosulfide QSMe, but not of disulfide QSSMe as expected from path A in Scheme 4, after addition of MeI in the electrolysis solution. It suggests that the formation of QSSMe occurred but that the compound was too unstable to be isolated. Its decomposition led to QSMe, which could be proved with the help of the following experiments. Thiolate anions QS^{-} (*ca.* 6 mmol l^{-1}) were generated by cathodic reduction of QSSQ, which proceeds in two steps with $E_{\frac{1}{2}} = -1.0$ and -2.5 V, and it was followed by addition of S_8 (*ca.* 0.4 mmol l^{-1}). These experiments were accompanied by a voltammetric study at a glassy carbon RDE (Fig. 4). Curves A and B were recorded before and immediately after electrolysis of QSSQ, and curve C after addition of S_8 (dilution factor 5 in each case). The cathodic waves of curve A with $E_{\frac{1}{2}} = -1$ and -2.5 V are associated with the successive reduction of QSSQ and QS^{-}. The more negative wave was still visible after electrolysis (curve B), whereas the anodic wave with $E_{\frac{1}{2}} = 0.05$ V corresponds to the oxidation of QS^{-} to QSSQ. The anodic wave shifted negatively ($E_{\frac{1}{2}} = -0.17$ V) after addition of S_8 (curve C) and a supplementary cathodic wave with $E_{\frac{1}{2}} = -2.25$ V was observed. These results are consistent with the observations of the Paris group,[32–34] *i.e.*, the formation of aryl disulfide upon addition of S_8 to arylthiolate [reaction (27)]. The oxidation and reduction of QS_2^{-} proceeded with $E_{\frac{1}{2}} = -0.17$ and -2.25 V, respectively. In the next step, methyl iodide was added to a part of the electrolysis solution (60%), while the other part was oxidised chemically. An HPLC study of the latter solution indicated the presence of QS_2Q as the major compound, QS_3Q, which is consistent with reaction (26), and a minor unidentified product, possibly a more sulfur-loaded diaryl. HPLC analysis of the former solution revealed the formation of $QSCH_3$ as the major compound and of a minor unstable compound that might be $QSSCH_3$.

Conclusion

Electrolysis conditions were found that allowed the exclusive formation of S_4^{2-} in acetonitrile. This nucleophile reacted by an electroinduced $S_{RN}1$ substitution reaction with an unactivated aryl halide, *i.e.*, 3-bromoquinoline, to give a disulfide anion QS_2^- and the corresponding moderately stable trisulfide QSSSQ by chemical oxidation. Several sulfur-containing nucleophiles were generated as the electrolysis proceeded, and they interfered with S_4^{2-}.

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