

Short Communication

## Preparation of a Stable Diaryl Trisulfide from a Sacrificial Sulfur Cathode and 2-Chloropyrimidine

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**Dedicated to Professor Henning Lund on the occasion of his 70th birthday.**

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Polarization of a sacrificial mixed sulfur/graphite cathode (S–C cathode) generates polysulfide ions  $S_x^{\cdot-}$  and  $S_x^{2-}$  with nucleophilic properties.<sup>1–10</sup> These ions react with activated aromatic molecules<sup>1,5–7</sup> such as 2-halogenonitrobenzene or 4-bromobenzophenone (ArX), giving the intermediate  $ArS_2^-$  anions<sup>5,6</sup> and  $ArSSAr$  after oxidation. Similar results were obtained in the case of polysulfide ions  $S_3^{\cdot-}$  and  $S_8^{2-}$  electrogenerated from dissolved sulfur in *N,N*-dimethylacetamide.<sup>11–13</sup> The ions readily reacted with aromatic halides activated by nitro substituents with formation of  $ArS_2^-$  ions, anodically oxidized to  $ArSSAr$ . Conversely our group has recently shown that 3-quinolyl disulfide anions ( $QS_2^-$ ) are chemically oxidized to the moderately stable diaryl trisulfide  $QSSSQ$ . These anions were prepared by electrochemically induced  $S_{RN}1$  substitution reaction, from 3-bromoquinoline and  $S_4^{2-}$  polysulfide anions generated in acetonitrile from a S–C cathode. On the other hand, diaryl trisulfides have also been prepared from a sacrificial sulfur anode (generation of  $S^{2+}$ ) and thiolates.<sup>7</sup>

The present work describes the electrochemical synthesis of a stable aromatic trisulfide isolated as the major compound after addition of 2-chloropyrimidine (ClPyr) to a solution of  $S_4^{2-}$  anion in acetonitrile, and then anodic oxidation of the intermediate thiolate anion. Thus the oxidation of  $ArS_2^-$  ions to  $ArSSSQ$  can be achieved both chemically and electrochemically.

### Results and discussion

The voltammetric behaviour of elemental sulfur  $S_8$  in deaerated acetonitrile has previously been examined at a

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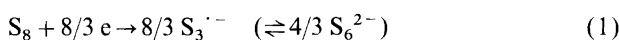
Table 1. Voltammetry results of  $S_8$  at a glassy carbon RDE.<sup>a</sup>

Reduction wave	$E_{1/2}/V$ vs. SCE	Generated species
First wave	–0.8	$S_8^{2-}$ , $S_3^{\cdot-}$ + $S_6^{2-}$
Second wave	–1.25	$S_3^{2-}$
Third wave	–2.0	$S_4^{2-}$

<sup>a</sup>0.4 mM substrate in acetonitrile–0.1 M  $Bu_4NPF_6$ . Rotation speed: 650 rpm.

Pt<sup>14</sup> or a glassy carbon<sup>15</sup> rotating disc electrode (RDE). Three reduction waves were observed at a glassy carbon RDE, whereas the third reduction wave was not visible at the Pt RDE, owing to cathodic discharge. Table 1 indicates for each wave recorded at a glassy carbon RDE, its half-wave potential ( $E_{1/2}$ ) and the polysulfide ions generated on the voltammetric timescale.<sup>15</sup>

The two-step electrochemical synthesis of  $S_4^{2-}$  was carried out as previously described<sup>15</sup> in a three-compartment cell and with an S–C cathode to overcome the poor solubility of  $S_8$  in acetonitrile (ca.  $4 \times 10^{-4}$  M at room temperature). The electrode was composed of a mixture (2:1) of  $S_8$  (218 mg; 0.85 mmol) and graphite powder contained in a bag of graphite tissue, and it was immersed in deaerated acetonitrile (100 ml) and polarized at a controlled potential corresponding to the first reduction step of  $S_8$ . The solution turned blue, indicating the reduction of  $S_8$  to the blue  $S_3^{\cdot-}$  anion according to the global reaction (1).

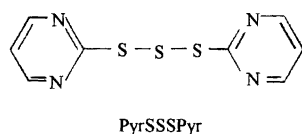


After reduction of the total amount of  $S_8$  contained in the graphite bag (2.3 mmol  $S_3^{\cdot-}$  was thus generated) the applied potential was shifted to more negative values

corresponding to the second reduction step of  $S_8$ , the cathode being the graphite envelope. The solution turned orange and the electrolysis was stopped when the current became negligible. As previously shown,<sup>15</sup>  $S_3^{2-}$  anions were reversibly generated ( $S_3^{2-} + e \rightleftharpoons S_3^{3-}$ ) which reacted slowly with  $S_3^{3-}$  to give the orange  $S_4^{2-}$  anion ( $S_3^{2-} + S_3^{3-} \rightarrow 3/2 S_4^{2-}$ ). The total amount of electricity consumed in the two-step electrolysis (consumption of 3.65 mF;  $n=4.3$  electrons per  $S_8$  unit) was consistent with the formation of  $S_4^{2-}$  (1.7 mmol) according to the global reaction (2).

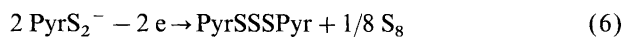
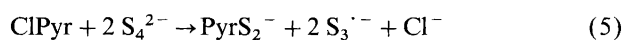
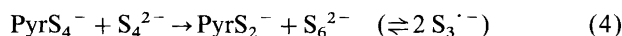
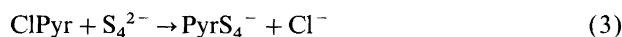


After addition of ClPyr (1.2 mmol; 0.7 equivalent), the electrolysis solution turned blue within a few minutes, indicating the consumption of  $S_4^{2-}$  and the reappearance of  $S_3^{3-}$ . As shown in Ref. 15 (Fig. 3), the anodic oxidation of  $S_4^{2-}$  proceeds in two steps with  $E_{1/2} = -0.75$  V and  $-0.25$  V, and the anodic oxidation and cathodic reduction of  $S_3^{3-}$  are observed with  $E_{1/2} = -0.25$  V and  $-1.25$  V, respectively. Consequently, it was possible to follow by voltammetry the fate of the known electroactive species, i.e., total disappearance of  $S_4^{2-}$ , regeneration of  $S_3^{3-}$  in an amount similar to the consumed  $S_4^{2-}$  anions (1.7 mmol), non-generation of elemental sulfur  $S_8$ , and consumption of ClPyr (this compound is reduced in two steps with  $E_{1/2} = -2.05$  V and  $-2.5$  V). A potential of 0 V was finally applied to oxidize the remaining polysulfide ions and the generated thiolate anions, and so the stable compounds PyrSSSPyr and PyrSSPy were successively isolated in 40% and 25% yields, respectively, after the usual work-up and chromatographic purification. The voltammograms of the isolated compounds were recorded in acetonitrile at a glassy carbon RDE. The cathodic reduction of PyrSSSPyr and PyrSSPy proceeded in two steps ( $E_{1/2} = -0.95$  V and  $-1.7$  V) and one step ( $E_{1/2} = -1.8$  V), respectively.



The two isolated compounds were generated during the final anodic oxidation step, since the voltammogram recorded prior to this step did not reveal their presence. These results suggest that the initial substitution reaction (3) was followed by the formation of  $PyrS_2^-$  (4) resulting for example from a substitution reaction, or a bulk reductive cleavage. Consequently, the generation of  $PyrS_2^-$  would proceed according to the global reaction (5) involving equivalent amounts of  $S_4^{2-}$  and  $S_3^{3-}$ . The anodic oxidation of  $PyrS_2^-$  at 0 V would lead to a trisulfide derivative (6), as previously observed with

$QS_2^-$  anions.<sup>15</sup>



The formation of the minor disulfide generated during the final oxidation could not result from a substitution reaction involving the  $PyrS_2^-$  nucleophile. Nor could it involve the  $S_3^{3-}$  nucleophile, because no spontaneous reaction took place when ClPyr was added to a solution of  $S_3^{3-}$ . Partial oxidation of  $PyrS_2^-$  to PyrSSPy and/or its partial dissociation to  $PyrS^-$  might occur, as previously observed with aromatic halides activated by nitro and/or keto substituents.<sup>5,6,11-13</sup>

## Experimental

Analytical grade acetonitrile (Janssen Chimica) was dried on neutral alumina.  $Bu_4NPF_6$  (electrochemical grade, Fluka), and 2-chloropyrimidine (95%, Aldrich) were used as received. Sulfur (Prolabo) was recrystallised from toluene. Graphite powder (average diameter 100  $\mu$ m) was supplied from Johnson Mathey and graphite cloth by Carbone Lorraine. The synthesis of 2,2'-dipyrimidyl disulfide was carried out as previously described.<sup>16</sup> The electrochemical equipment has been previously described.<sup>15</sup> Voltammograms were recorded at a rotating (650 rpm) or stationary glassy carbon electrode (V25, Carbone Lorraine; 3 mm diameter). All potentials were referenced to an aqueous saturated calomel electrode (SCE).

*Electrogeneration of  $S_4^{2-}$  and reaction with ClPyr.* The electrochemical generation of  $S_4^{2-}$  was carried out in an H-type cell equipped with ion-exchange membranes [Ionax MA 3475 (anodic side) and MC 3470 (cathodic side)] and filled with MeCN-0.1 M  $Bu_4NPF_6$ . The cathodic solution (100 ml) was stirred mechanically and deaerated with argon prior to and during electrolysis. The S-C cathode was prepared as described in Ref. 15 by a method similar to that used by Le Guillanton's group.<sup>17</sup> The counter electrode was a Pt grid. The electrochemical generation of  $S_4^{2-}$  proceeded in two steps, i.e. blue  $S_3^{3-}$  anions were first generated by polarizing the S-C electrode at a potential of  $-0.8$  V to  $-1.0$  V. The potential was then shifted negatively ( $-1.3$  V to  $-1.8$  V) and the reduction of the blue  $S_3^{3-}$  anions to the orange  $S_4^{2-}$  anions took place at the graphite envelope constituting the cathode. After addition of ClPyr, which is very volatile, the cathodic solution turned blue within a few minutes. A potential of 0 V was then applied and the electrolysis was stopped when the anodic current became negligible. Addition of water (400 ml) was followed by extraction by methylene chloride (100 ml  $\times$  3). The electrolysis products were extracted with a Soxhlet from the crude product obtained after

evaporation of the solvent. They were purified by column chromatography (Kieselgel; diethyl ether as the eluent), and the stable and original trisulfide PyrSSSPyr (61 mg, 0.24 mmol) and the disulfide PyrSSPyr (33 mg, 0.15 mmol; identified by comparison with an authentic sample<sup>16</sup>) were successively isolated in 40% and 25% yields, respectively.

*2,2'-dipyrimidyl trisulfide*. White solid, m.p. 145–147 °C (diethyl ether) Anal. Found: C 37.44; H 2.38; N 21.53; S 38.50. Calc for: C<sub>8</sub>H<sub>6</sub>N<sub>4</sub>S<sub>3</sub>: C 37.78; H 2.38; N 22.03; S 37.78. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.15 (2 H, d, *J* = 4.83 Hz), 8.68 (4 H, d, *J* = 4.83 Hz).

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