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Anodic Oxidation of Disulfides: Detection and Reactions of Disulfide Radical Cations

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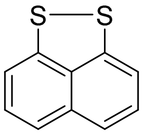
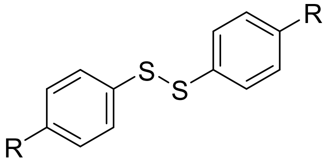
Abstract

The anodic oxidation of five diaryldisulfides have been studied in a dichloromethane/$[NBu_4][B(C_6F_5)_4]$ electrolyte. Cyclic voltammetry (CV) scans of $(p\text{-}RC_6H_4)_2S_2$ (R = Me, **1a**; R = F, **1b**; R = OMe, **1c**) show modest chemical reversibility for the $\mathbf{1}^{0/+}$ couple ($E_{1/2}$ values *vs* ferrocene: 1.04 V for **1a**, 1.21 V for **1b**, 0.92 V for **1c**), providing the first voltammetric evidence for the radical cation $[Ar_2S_2]^+$. A dimer dication, $[Ar_4S_4]^{2+}$, is proposed as an intermediate in the formation of the electrolysis product, the trisulfide $[Ar_3S_3]^+$. The chemical reversibility of the one-electron oxidations of Ar_2S_2 vanishes in $[PF_6]^-$ - containing electrolytes. The radical cations of the more sterically constrained *ortho*-substituted analogues dimesityldisulfide (**2a**, $E_{1/2}$ = 1.01 V) and bis(2,4,6-triisopropylphenyl)disulfide (**2b**, $E_{1/2}$ = 0.98 V) show less tendency to dimerize. In all cases except **2b**, the bulk electrolysis product is $[R_3S_3]^+$, consistent with earlier literature reports. A mechanism is proposed in which the trisulfide is formed by reaction of the dimer dication $[Ar_4S_4]^{2+}$ with neutral Ar_2S_2 to afford the trisulfide in a net 2/3 e^- process. Oxidation of Ar_2S_2, either anodically or by a strong one-electron oxidant, in the presence of cyclohexene gives an efficient synthetic route to 1,2-substituted cyclohexyldisulfides.

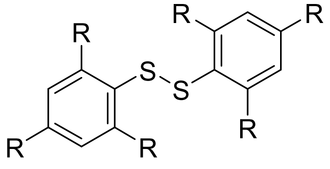
Introduction

Owing in part to the importance of organic disulfides in structural biology,[1] the electrochemical oxidation of this class of compounds continues to draw study, adding to an already extensive body of papers.[2] For simple RSSR disulfides, the anodic electrolysis products and the (1 e^- *vs* 2 e^-) electron-transfer stoichiometry depend principally on the nature of R and the temperature and chemical makeup of the solvent/supporting electrolyte system. An important general finding is that the radical cations of this series, $[RSSR]^+$, have low kinetic stability. A few radical cations of cyclic disulfides (such as dithionaphthalene shown below) have been confirmed by optical or ESR spectroscopy.[3,4] However, to the best of our knowledge, radical cations of the linear disulfides $[RSSR]^+$, R = alkyl or aryl, although frequently invoked as intermediates, have not been confirmed even as a transient species by spectroscopy or cyclic voltammetry (CV). Rather, $[RSSR]^+$ has been reported to be kinetically unstable with respect to sulfur-sulfur cleavage,[5-8] thereby initiating routes to formation of more stable *in situ* products such as the sulfenium ion $[RS]^+$ [5-13] or the trisulfide $[R_3S_3]^+$.[5,10,11,14] With the goals of finding direct electrochemical evidence for $[RSSR]^+$ and adding to mechanistic understanding of the oxidatively-induced conversion of disulfides to their cationic products, we have investigated the anodic oxidation of several diaryl disulfides and dimethyldisulfide in dichloromethane using the weakly coordinating anion (WCA) $[B(C_6F_5)_4]^-$ as the supporting electrolyte anion. Although the low nucleophilicity of this anion[15] has been extremely valuable in promoting the stability of highly electrophilic organometallic systems,[16,17] it has seen relatively few applications to organic redox chemistry.[14,18] The present paper reports our findings on five diaryldisulfides (**1a**-**1c**, **2a** and **2b**) and dimethyldisulfide. With the exception of the sterically hindered compound **2b**, the





1a, R = Me
1b, R = F
1c, R = OMe



2a, R = Me
2b, R = iPr

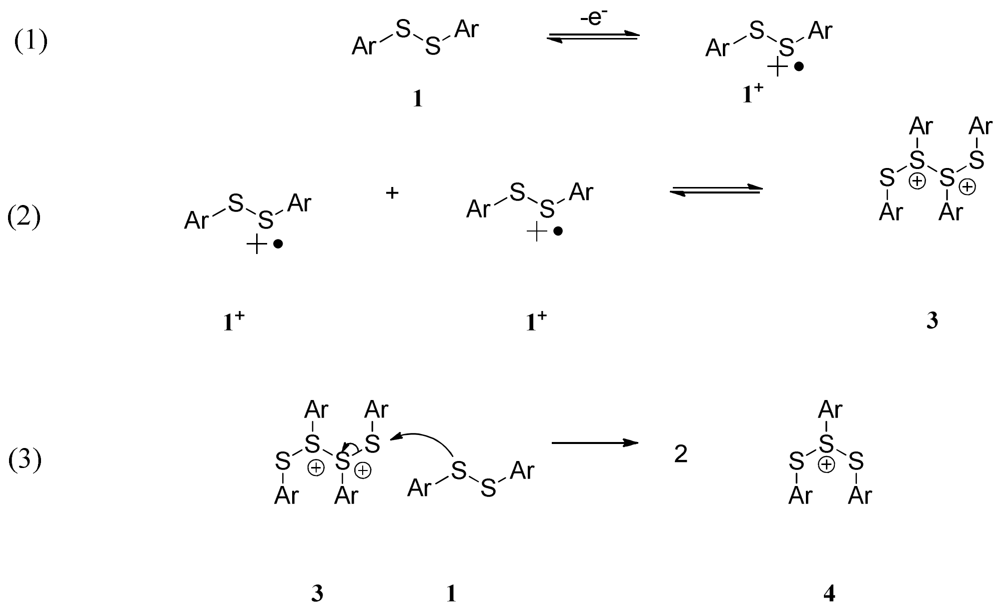
long-term (bulk electrolysis time scale) product is, in fact, the expected trisulfide $[R_3S_3]^+$. However, some degree of chemical reversibility of the parent 0/+ couple was observed in each case for CV scans at modest scan rates, giving the first definitive voltammetric evidence for the radical cations of these compounds, and allowing a more detailed discussion of the mechanism of anodically-induced formation of the trisulfide.

Results and Discussion

The literature paper most relevant to our study is the communication by Matsumoto *et al.* in which catalytic amounts of $[Ar_3S_3]^+$ were shown to initiate stereoselective addition of Ar_2S_2 to dienes.[14] The authors generated the trisulfide cation *in-situ* by bulk electrolysis of Ar_2S_2 in CH_2Cl_2/0.1 M $[NBu_4][B(C_6F_5)_4]$, essentially the same medium as used in the present work. An important difference, however, is that the published work was carried out at low temperature (195 K), a factor that has an important effect on the ability to detect the primary radical cation $[Ar_2S_2]^+$, $\mathbf{1}^+$. Although voltammograms of Ar_2S_2 were not shown or referred to in reference 14, CV scans of the diaryldisulfides under these low-temperature conditions are not likely to show any chemical reversibility for the $[Ar_2S_2]^{0/+}$ couple (see below).

The present study focuses on three *para*-substituted arene derivatives, **1a**-**1c**, and the bis-*ortho*-substituted arene derivatives **2a** and **2b**. Measurements were also made on dimethyldisulfide. Results on **1a**-**1c** suggested that the overall anodic process proceeds by the mechanism given in Scheme 1, a key component being the dimer dication, $[Ar_4S_4]^{2+}$, **3**. Subsequent preparation and electrochemical testing of the more sterically-encumbered compounds **2a** and **2b** confirmed expectations based on this scheme.

Scheme 1. Proposed mechanism for anodic oxidation of diaryldisulfides



Oxidation of *para*-substituted arene disulfides, **1a**-**1c**

At room temperature, all three of this group of disulfides displayed some degree of chemical reversibility with a CV scan rate of 0.2 V s^{-1} in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$, permitting assignment of the $E_{1/2}$ values of their one-electron oxidations (Table 1). 1 mM solutions of **1a** and **1c** showed scan-rate dependent chemical reversibility similar to that shown in Figure 1, i_c/i_a ratios going from about 0.5 to 0.75 when scan rates were increased from 0.2 V s^{-1} to 2 V s^{-1}. At a given concentration, anodic peak currents increased with the square root of scan rate, confirming a diffusion-controlled anodic process. A diffusion coefficient of 1.73 x 10^{-5} cm^2s^{-1} was measured for **1a** by chronoamperometry on a 0.025 mM solution at 298 K. No matter what the degree of chemical reversibility of the **1**$^{0/+}$ process, there were never more than two cathodic features: either that coupled to reduction of the radical cation at the appropriate E_{pc}, or a totally irreversible peak (lacking a coupled anodic feature) appearing about one volt or more negative of the $E_{1/2}$ of the **1**$^{0/+}$ couple. The potential of the irreversible wave varies with scan rate (v), appearing at the E_{pc} values given in Table 1 when v = 0.2 V s^{-1}. The *para*-substituted aryl derivatives will be discussed somewhat interchangeably owing to their similar overall anodic behavior.

Table 1. Potentials in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$. E_{pc} was recorded at a scan rate of 0.2 V s^{-1}.

Entry	Compound	$E_{1/2}$ (V *vs* FcH)	E_{pc} (V) of trisulfide product **4**
1	(*p*-$MeC_6H_4)_2S_2$, **1a**	1.04	-0.03
2	(*p*-$FC_6H_4)_2S_2$, **1b**	1.21	0.02
3	(*p*-$OMeC_6H_4)_2S_2$, **1c**	0.92	-0.05
4	**2a**	1.01	-0.14
5	**2b**	0.98	Not formed
6	Me_2S_2	1.10	-0.43

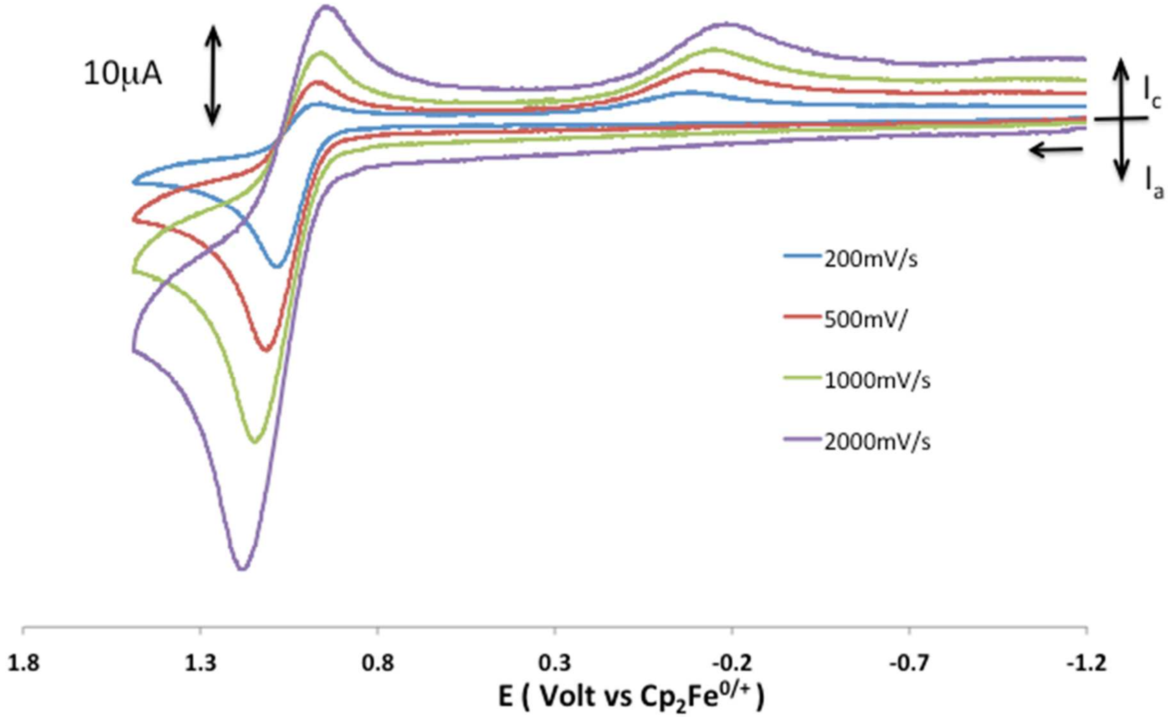


Figure 1. CV of **1a** (1.05mM) in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$ at different scan rates, 25°C, 2 mm glassy carbon electrode.

A somewhat increased degree of chemical reversibility was observed for oxidation of the *p*-fluoroaryl derivative **1b** (solid line in Figure 2). In that case, there is only scant evidence of the follow-up product at $E_{pc} \approx 0$ V. There are important variations that arise with changes in temperature and analyte concentration that will be described later. At this point, however, we bring attention to the complete *loss of reversibility* for **1b**$^{0/+}$ if the electrolyte anion is $[PF_6]^-$ rather than $[B(C_6F_5)_4]^-$ (dashed line *vs* solid line in Figure 2). The fact that almost all of the earlier papers reporting voltammetry of diaryldisulfides[5-12] were carried out using electrolytes having the traditional smaller anions such as $[PF_6]^-$ or $[BF_4]^-$ accounts in great part for the absence of CV detection of $[Ar_2S_2]^+$ in the previous literature. It is also important to note that the follow-up product, identified as the trisulfide $[(p\text{-}FC_6H_4)_3S_3]^+$ (see below), is still observed in the $[PF_6]^-$ - containing medium ($E_{pc} \approx 0.25$ V).

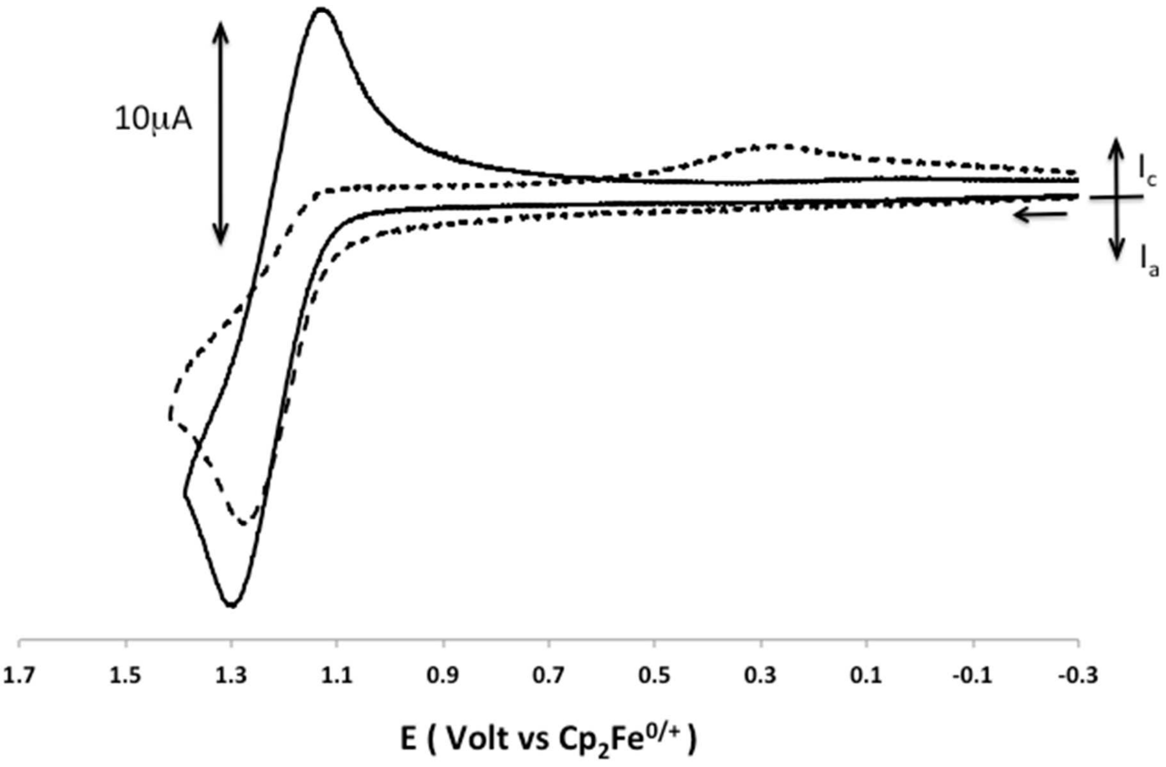


Figure 2. CV of **1b** (1.34mM) in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$ (solid line) and in CH_2Cl_2/0.05M $NBu_4][PF_6]$ (dashed line), scan rate 0.2 V/s, 25°C, 2mm glassy carbon electrode.

That the final oxidation product is the same in both $[PF_6]^-$ and $[B(C_6F_5)_4]^-$ electrolytes was confirmed by bulk anodic electrolysis of **1b** in $CH_2Cl_2/[NBu_4][B(C_6F_5)_4]$ at E_{appl} = 1.38 V. This reaction passed 1.03 F and gave a single electroactive product with E_{pc} = - 0.03 V (Figure 3). Re-electrolysis negative of the product wave (E_{appl} = - 0.70 V) consumed only 0.79 F and resulted in *quantitative* regeneration of the starting material (see comparative CVs in Figure S1 of Supplementary Material). In a number of previous papers, including the electrolysis of Ar_2S_2 in a $[B(C_6F_5)_4]^-$ electrolyte,[14] the main product of the oxidation of Ar_2S_2 has been shown to be the trisulfide $[Ar_3S_3]^+$, **4**.[5,10,11] This was confirmed in the present case by testing the voltammetric behavior of an authentic sample of $[Ar_3S_3]^+$ generated *in situ* by the reaction of **1a** with an equivalent of $SbCl_5$.[19] The resulting solution had an irreversible reduction wave near the E_{pc}

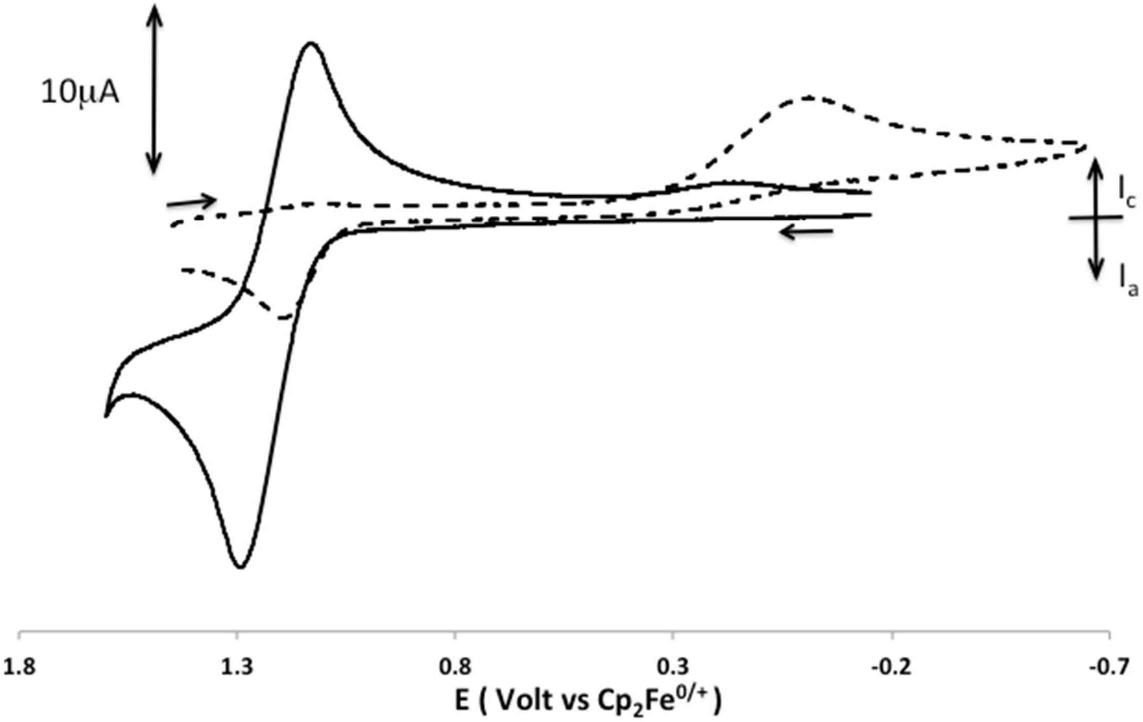


Figure 3. CV of **1b** (1.91mM) in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$ before bulk electrolysis (solid line) and after bulk electrolysis at 1.38V (dashed line), scan rate 0.2 V/s, 25°C, 2 mm glassy carbon electrode.

value of -0.03 V observed after the bulk oxidation of **1a**. Consistent with this assignment, **1a** itself was formed when $[(p\text{-MeC}_6H_4)_3S_3]^+$ was reduced, either in CV scans or by bulk cathodic electrolysis. Although Eq 4 therefore describes the *gross* redox reaction, it is not informative about the mechanism of this chemically reversible process, especially on the nature of the

$$(4) \qquad 3\ Ar_2S_2\ -\ 2\ e^- \rightleftharpoons 2\ [Ar_3S_3]^+$$

follow-up reactions beginning with the putative radical cation $[Ar_2S_2]^+$, $\mathbf{1}^+$. Molecular orbital theory predicts a relatively strong S-S bond in the radical cation $[R_2S_2]^+$, lowering the likelihood of simple S-S cleavage playing a role in the reaction.[20]

Earlier work by Jouikov *et al.* reported a second-order dependence to the follow-up reactions of diaryldisulfide oxidations.[21] Our increased ability to observe the disulfide radical cation allowed a more direct voltammetric study of analyte concentration effects, which are typified for **1a**-**1c** in Figure 4. At higher concentrations of **1a**, three important effects are seen: (i) the oxidation of **1a** becomes less chemically reversible (ii) the cathodic wave of the trisulfide product $[(p\text{-MeC}_6H_4)_3S_3]^+$ increases and (iii) the concentration-normalized anodic peak current of **1a** decreases . As will be discussed, Scheme 1 is consistent with these experimental findings. A key element in the scheme is inclusion of the dimer dication, $[Ar_4S_4]^{2+}$, **3**, formed by radical-radical dimerization of $\mathbf{1}^+$ (Eq 2). Nucleophilic attack on **3** by another mole of neutral **1** (Eq 3) gives the final trisufide **4** in a net 2/3 e^- process.

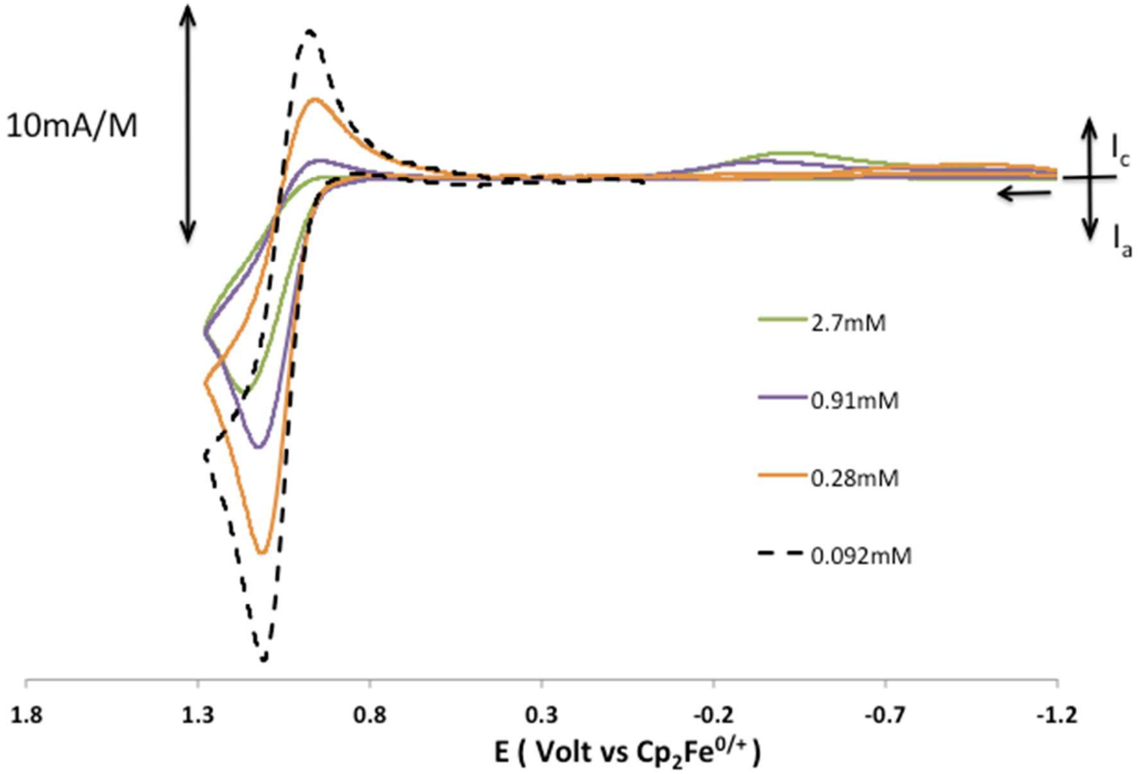
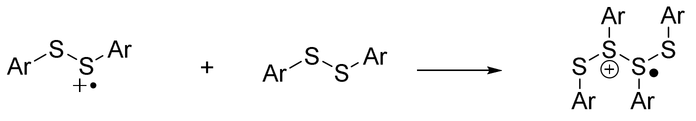


Figure 4. Background subtracted CV of **1a** at different concentrations in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$, scan rate 0.2 V/s, 25°C, 2 mm glassy carbon electrode. Note that the ordinate has units of milliamp/molar.

At low concentrations, the one-electron oxidation of **1** dominates (Eq 1), accounting for the close-to-reversible CV behavior at or below approximately 10^{-4} M concentrations of **1**. If the only effect of higher concentrations of analyte were to favor the dimer dication in the chemically reversible process of Eq 2, the measured $E_{1/2}$ would simply shift negative without changing the chemical reversibility of the anodic reaction. A further follow-up reaction must be invoked to account for the observed loss of reversibility (point (i) in the preceding paragraph) and the appearance of the cathodic wave for reduction of **4** (point (ii)).

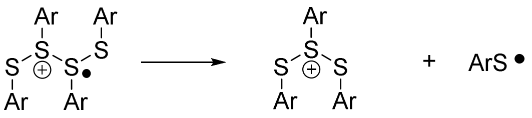
In principle, the additional follow-up reaction could be of neutral **1** with either the monomer radical cation $[Ar_2S_2]^+$ (Eq 5) or the dimer dication $[Ar_4S_4]^{2+}$ (Eq 3). Although the radical-substrate reaction of Eq 5 cannot be ruled out, since subsequent S-S cleavage would give the observed trisulfide $[Ar_3S_3]^+$ and a reactive sulfide radical (Eq 6), we consider it a less likely path

(5)



1^+ **1** **3'**

(6)



3' **4**

than that of reaction 3. Except in rare cases, radical-substrate cations of the type in Eq 5 are thermodynamically unstable with respect to their oxidation to the corresponding dication.[22] Furthermore, in this scenario one would have to account for the fate of the reactive ArS· radical. Thus, the nucleophilic attack of **1** on **3** rather than on **1**$^+$ is the mechanistically simpler route to the observed product.

Still to be addressed is point (iii) above, namely the decrease of the concentration-normalized anodic peak current of **1a** as its concentration is increased. This effect is tied to the fact that the oxidation of **1** is a one-electron process (Eq 1) in the low-concentration limit and a 2/3 e$^-$ process (Eq 3) in the high-concentration limit. Furthermore, introduction of the fast second-order reaction of Eq 3 causes the anodic wave shape to take on irreversible character, being broader and having a lower peak current than its reversible counterpart.[23] At concentrations of 2-3 mM, the width and height of the anodic wave are close to those expected for an irreversible oxidation process (β transfer coefficient = 0.48) of 2/3 e$^-$ stoichiometry.[24]

It was mentioned above that bulk electrolysis of **1b** at room temperature gave an n_{app} value of 1.0. When this electrolysis was repeated at 253 K, a coulometry count of 0.66 F was obtained as predicted by Scheme 1. It is likely that the somewhat higher electron count for **1b** at room temperature arises from slow catalytic regeneration of **1b** by the reaction of **1b**$^+$ with adventitious reductants in the medium. This would not be unusual for strong oxidants such as **1b**$^+$. Strengthening this interpretation is the fact that back-electrolysis of $[Ar_3S_3]^+$ required only 0.78 F while quantitatively regenerating the starting disulfide.

Another experimental finding to be considered is that at reduced temperatures, CV scans of group **1** compounds lose virtually all of the chemical reversibility for the **1**$^{0/+}$ process (see Figure

5 for **1a**). This is explicable in terms of the lower temperature favoring the dimer dication [(*p*-$MeC_6H_4)_4S_4]^{2+}$, thereby speeding conversion to the trisulfide [(*p*-$MeC_6H_4)_3S_3]^+$ by the reaction given in Eq 3. The temperature effect also accounts for the fact that Matsumoto *et al.*[14] apparently saw only totally irreversible CVs for Ar_2S_2 at 195 K.

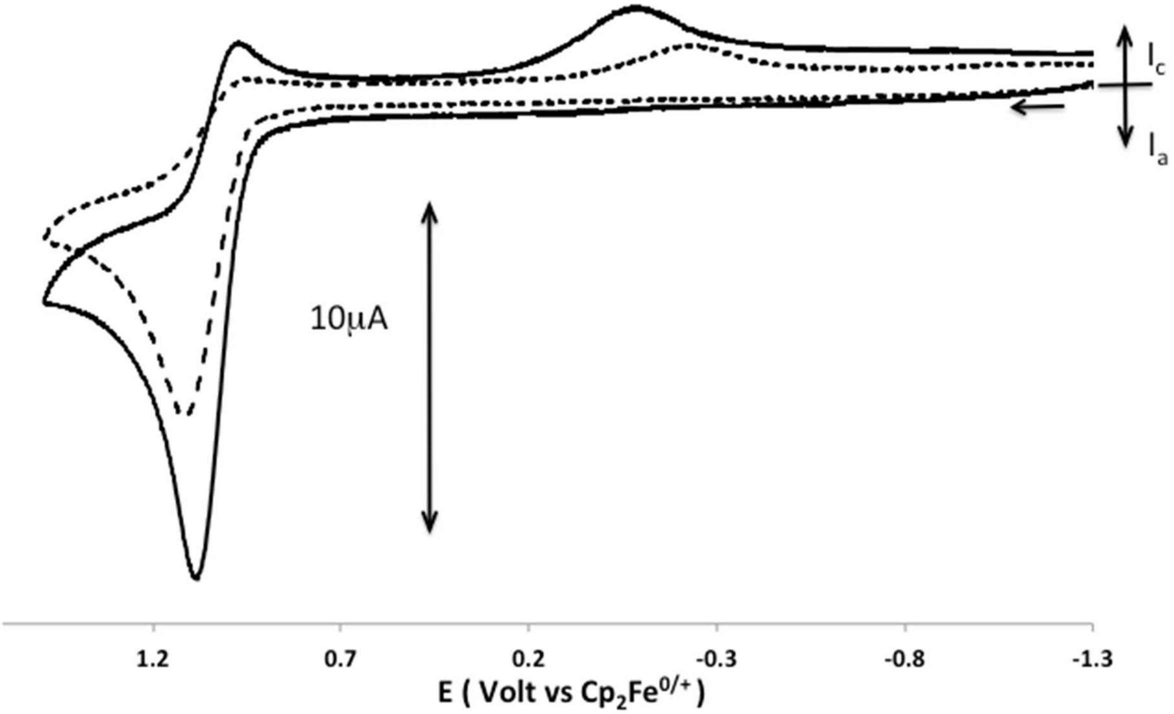


Figure 5. CV of **1a** (1.05mM) in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$ at 25°C (solid line) and at -20°C (dashed line), scan rate 0.2 V/s, 25°C, 2 mm glassy carbon electrode.

The role of the $[PF_6]^-$ anion in the reaction is now considered. It is well established that many cationic organometallics are subject to stronger ion-pairing[15,16,17,25] and increased nucleophilic attack[16,17,26] when generated in the presence of smaller anions such as $[PF_6]^-$ or $[BF_4]^-$ rather than weakly coordinating anions. CV scans of **1a-1c** in $[PF_6]^-$ - containing electrolytes do not diminish the apparent yield of the trisulfide product $[Ar_3S_3]^+$, as shown in

Figure 2 for **1b**. Thus, nucleophilic attack by $[PF_6]^-$, which often leads to decomposition of organometallic radical cations,[16,27-29] does not appear to be a factor in the present case, either on the CV or electrolysis time scale. Furthermore, bulk electrolysis of **1a** in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ followed the same reaction path as seen in solutions of $[B(C_6F_5)_4]^-$, albeit with slightly diminished yields. Thus, bulk oxidation of **1a** in the $[PF_6]^-$ electrolyte passed 0.71 F, giving a stable solution[30] of the trisulfide **4** (Ar = *p*-MeC_6H_4), bulk reduction of which regenerated **1a** in 80% yield. These findings support those reported earlier for the oxidation of diaryldisulfides in $[BF_4]^-$-based electrolytes.[6]

The $[PF_6]^-$ electrolyte effect is therefore to diminish the amount of the primary radical cation $\mathbf{1}^+$, while still allowing formation of the major trisulfide product. A reasonable explanation for this is the occurrence of increased ion-pairing between the dimer dication and the $[PF_6]^-$ ion. The accompanying thermodynamic effect would be to shift the monomer/dimer equilibrium in favor of the dimer, thereby speeding the formation of the trisulfide final product through Eq 3.

Oxidation of bis-*ortho*-substituted arene disulfides **2a** and **2b**

The preceding arguments suggests that restricting formation of the dimer dication $[Ar_4S_4]^{2+}$ should retard production of the trisulfide oxidation product and, in the absence of new reaction pathways, increase the lifetime of the primary radical cation $[Ar_2S_2]^+$. This postulate was tested by examination of two compounds, namely the dimesityldisulfide complex **2a** and the bis(2,4,6-triisopropylphenyl)disulfide complex **2b**, in which *ortho* substitution of the aryl groups introduces steric restraints to the formation of dimer dications,. As will be shown, the results gave strong support to the mechanistic model of Scheme 1 by bringing the $[Ar_2S_2]^{0/+}$ couple closer to a simple, chemically reversible, one-electron process.

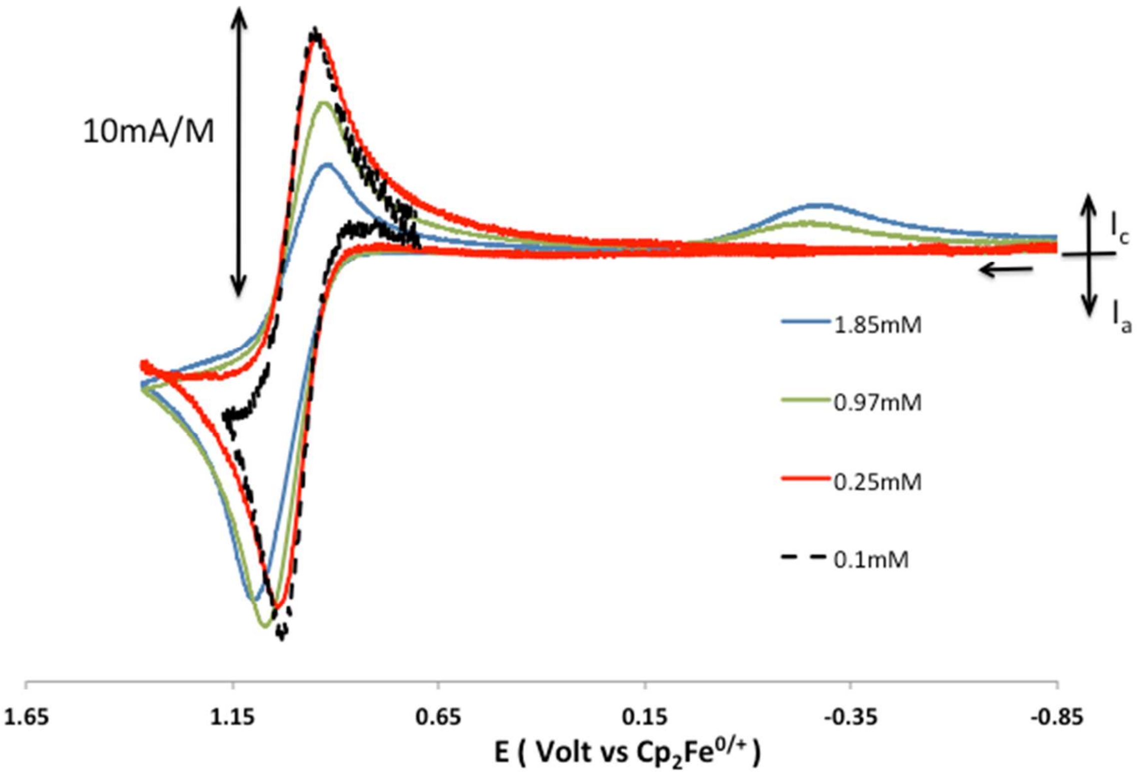


Figure 6. Background subtracted CV of **2a** at different concentrations in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$, scan rate 0.2 V/s, 25°C, 2 mm glassy carbon electrode. Note that the ordinate has units of milliamp/molar. A higher noise level restricted analysis in the range of -0.85 V to 0.65 V for 0.1 mM solution.

Figure 6 shows CVs for different concentrations of **2a** at room temperature. Below about 0.5 mM, the **2a**$^{0/+}$ process is very nearly reversible and there is little evidence of the trisulfide follow-up product, which only comes into play at higher concentrations. There is a much smaller change in the concentration-normalized anodic peak current for **2a** compared to the type-**1** disulfides (compare with Figure 4 for **1b**). It is also worth noting that, contrary to the behavior of the electronically similar **1a**, some chemical reversibility is seen for the $[Ar_2S_2]^{0/+}$ couple even when $[PF_6]^-$ is the electrolyte anion (Suppl Material Fig S4).

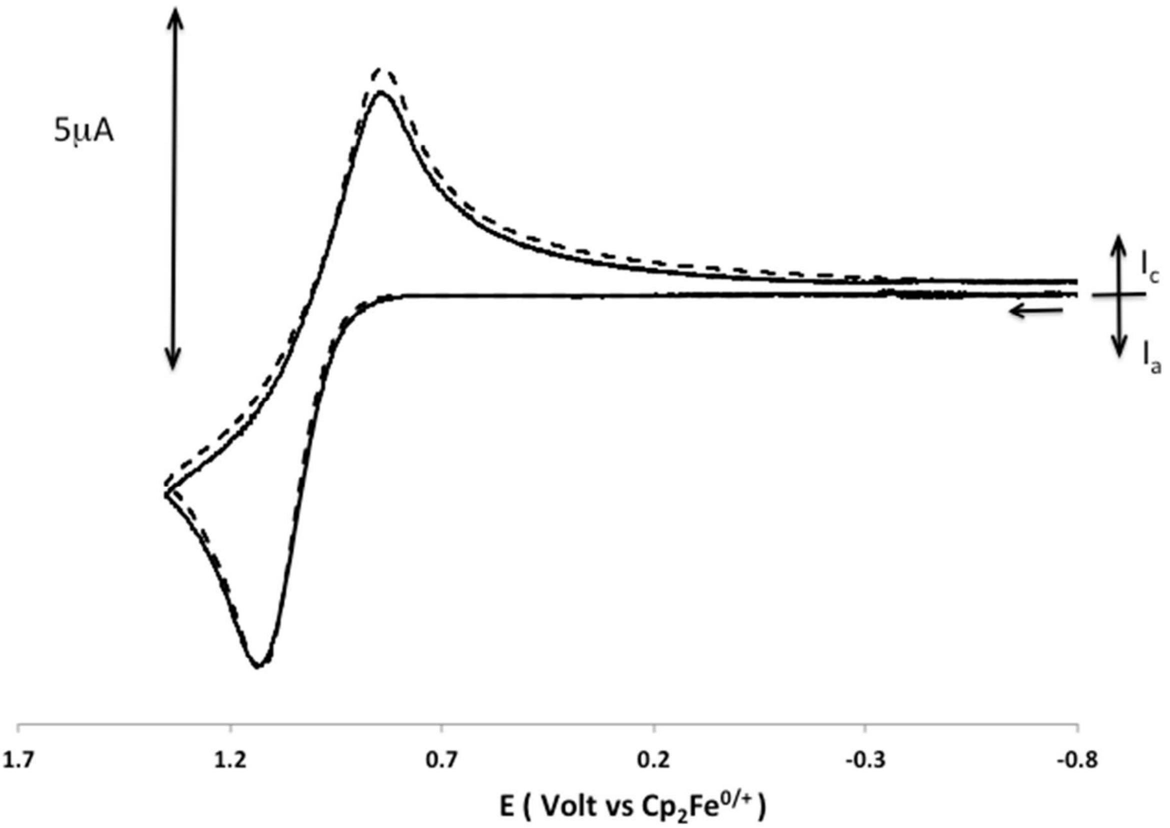


Figure 7. Background subtracted CV of **2b** (0.057mM) in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$ (solid line) and DigitalSimulation (dashed line), scan rate 0.2 V/s, 25°C, 2 mm glassy carbon electrode.

Formation of the dimer dication $[Ar_4S_4]^{2+}$ appears to be completely cut off when the very bulky triisopropyl-substituted compound **2b** is oxidized. In this case, no evidence for trisulfide product is observed either in CV scans or after bulk electrolysis, and concentration-normalized anodic currents do not change appreciably over the concentration range 0.26 mM to 1.89 mM. The unusually-shaped CV scans of **2b** (Figure 7) arise from slow heterogeneous electron transfer (ET) for the $\mathbf{2b}^{0/+}$ couple rather than from chemical follow-up reactions. Digital simulations (dashed line in Figure 7) confirm this, being consistent with a standard heterogeneous rate constant, k_s, of 7.4 x 10^{-4} cm s^{-1}. Whereas the reason(s) for the slow ET for this compound cannot be delineated without further study, we refer the interested reader to more in-depth studies on how steric effects may influence k_s values for other organic redox couples.[31]

Oxidation of Dimethyldisulfide. CV scans of 1.5 mM Me_2S_2 showed only the barest of evidence for the radical cation $[Me_2S_2]^+$ at scan rates of 1 V s^{-1} or less (Figure SM5). This is consistent with our model in which a second-order follow-up reaction occurs more readily when dimerization of the radical cation is favored. The major product for the oxidation of Me_2S_2, responsible for a cathodic wave near -0.43 V, is almost certainly the trisulfide $[Me_3S_3]^+$.

Reactivity of the trisulfide cation

A number of authors have investigated the reactivities of trisulfide cations, $[R_3S_3]^+$, with olefins,[5,14] alkynes,[9] and compounds with other functional groups.[6,10,32,33] We thought it useful to carry out similar reactions between the trisulfides $[Ar_3S_3]^+$ and a weak nucleophile such as an olefin in the present $[B(C_6F_5)_4]^-$ - containing medium. As expected, addition of olefin led to decrease in the chemical reversibility of the $[Ar_2S_2]^{0/+}$ couple and disappearance of the trisulfide reduction peak (see Figure 8 for **1a** in the presence of cyclohexene). Although a reaction between the radical-cation $[Ar_2S_2]^+$ and the olefin cannot be ruled out, it seems more likely that the trisulfide cation is undergoing a rapid reaction with the olefin.

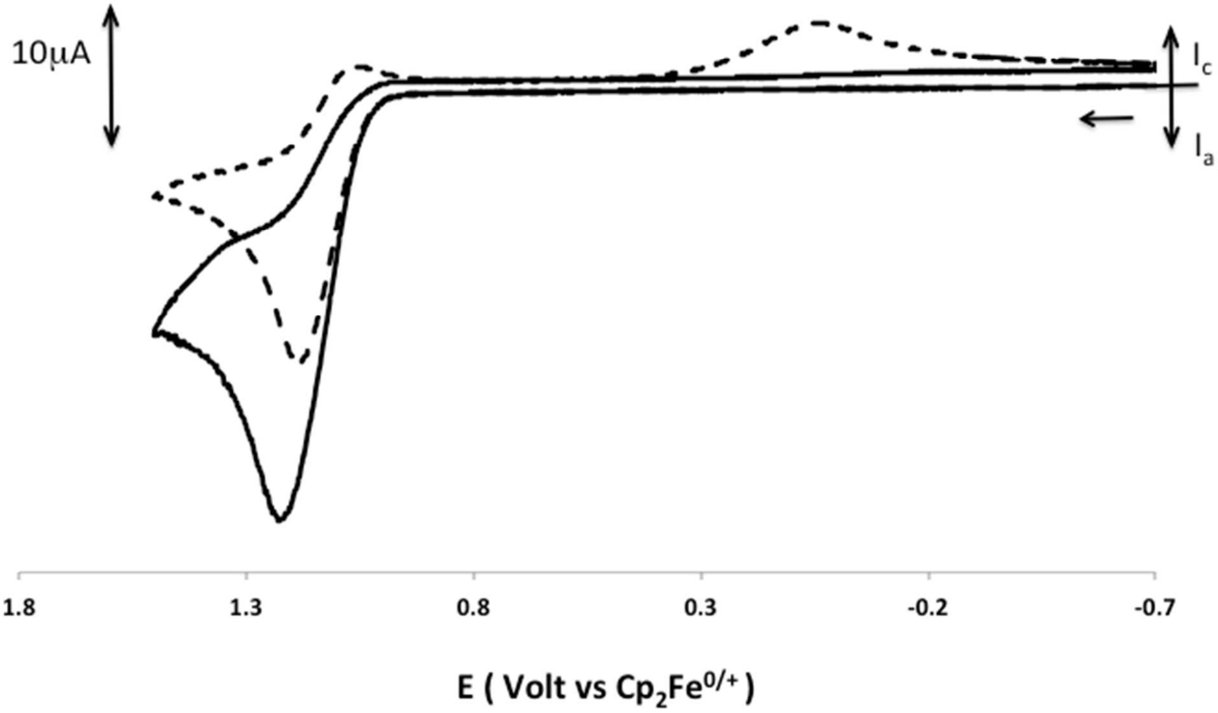


Figure 8. Cyclic voltammogram of **1a** (1.05mM) in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$, scan rate 0.2 V/s, 2mm diam. glassy carbon electrode, 25°C, without cyclohexene (dashed line) and with 1 equivalent of cyclohexene (solid line).

Bulk electrolysis at room temperature in the presence of one equivalent of olefin led to rapid consumption of the disulfide after only 0.21 F per olefin, indicative of an electrocatalytic mechanism leading to the formation of the corresponding vicinal disulfide (Eq 7) in high yield, consistent with previous literature.[14] To the best of our knowledge, only aromatic disulfides have been reported to undergo a catalytic addition to olefin under oxidative conditions.[34] In the present case, however, as denoted in Table 2, electron-rich and electron-poor aromatic disulfides as well as aliphatic disulfides are compatible with the reaction conditions. Moreover, the reaction could be performed at room temperature rather than at -78°C. When $[NBu_4][B(C_6F_5)_4]$ was replaced by $[NBu_4][PF_6]$, only traces of the corresponding 1,2-disulfide were observed.[35] Scheme 2 accounts for the disulfurization reaction.

(7)

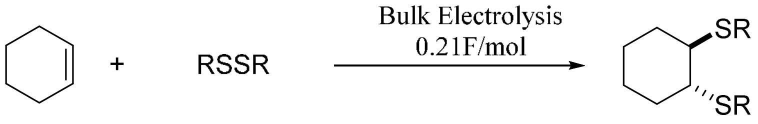
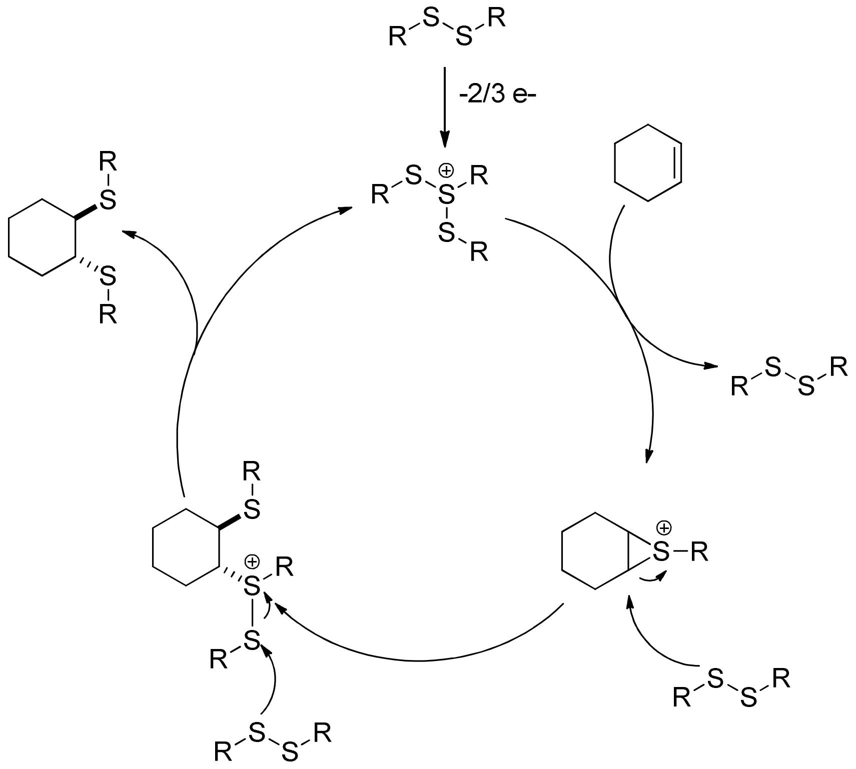


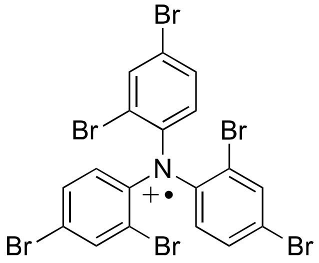
Table 2. Electrochemical disulfurization at room temperature in CH_2Cl_2/0.05M $[NBu_4][B(C_6F_5)_4]$.

Entry	Disulfide	1,2-disulfide yield (%)
1	$(p\text{-}MeC_6H_4)_2S_2$, **1a**	97, **7a**
2	$(p\text{-}FC_6H_4)_2S_2$, **1b**	91, **7b**
3	$(p\text{-}OMeC_6H_4)_2S_2$, **1c**	78, **7c**
4	Me_2S_2	94, **8**

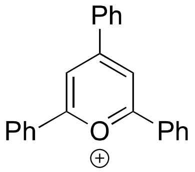
Scheme 2. Proposed mechanism for the anodically-initiated disulfurization of cyclohexene.



Finally, the chemical and photochemical oxidation of disulfides, at room temperature, in presence of one equivalent of olefin and a catalytic amount of either [(2,4-$Br_2C_6H_3)_3N][B(C_6F_5)_4]$ (**5**) (Magic Green) or 2,4,6-triphenylpyrrilium $[B(C_6F_5)_4]$ (**6**) and UV light led smoothly, within less than 15 minutes, to the formation of the expected 1,2-disulfide in high yield (Eq 8). This would be a versatile alternative to the low temperature electrolysis, and in some cases might have practical advantages. See Table 3 for yields.



5



6

(8)

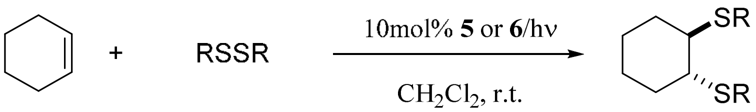


Table 3. Chemical and photochemical disulfurization at room temperature

Entry	Disulfide	[Cat][B(C_6F_5)$_4$]	1,2-disulfide yield (%) [(a)]
1	(p-MeC_6H_4)$_2S_2$, **1a**	**5**	99, **7a**
2	(p-FC_6H_4)$_2S_2$, **1b**	**5**	92, **7b**
3	(p-OMeC_6H_4)$_2S_2$, **1c**	**5**	75, **7c**
4	Me_2S_2	**5**	95, **8**
5	(p-MeC_6H_4)$_2S_2$, **1a**	**6**	91, **7a**
6	(p-FC_6H_4)$_2S_2$, **1b**	**6**	79, **7b**
7	(p-OMeC_6H_4)$_2S_2$, **1c**	**6**	61, **7c**
8	Me_2S_2	**6**	90, **8**

(a) Yields are reported for isolated pure compounds

Summary and Conclusions

The anodic oxidation of five different diaryldisulfides has been studied in a dichloromethane/[NBu_4][B(C_6F_5)$_4$] electrolyte. With one exception, namely the sterically-encumbered bis-ortho substituted triisopropyl compound **2b**, bulk oxidation furnishes a quantitative yield of the triaryltrisulfide [Ar_3S_3]$^+$, in agreement with previous literature.[5,10,11,14] By controlling the concentration of the disulfide, new cyclic voltammetry evidence has emerged, providing the first verification of the radical cation $[Ar_2S_2]^+$ and allowing a more detailed mechanistic analysis than previously possible.

If the aryl groups contain only a para-substituent, the chemical reversibility of the $[Ar_2S_2]^{0/+}$ couple is rather modest at CV scan rates of 0.2 to 0.5 V s^{-1}, with only minor changes occurring with alterations in the para-substituent. The reversibility of $\mathbf{1}^{0/+}$ is increasingly *disfavored* at higher concentrations of disulfide and at lower temperatures, conditions which favor a second-order follow-up reaction of the radical cation $[Ar_2S_2]^+$, almost certainly forming the dimer dication $[Ar_4S_4]^{2+}$. A further follow-up reaction must then occur, most likely between $[Ar_4S_4]^{2+}$ and the neutral starting material, to provide the trisulfide final product, $[Ar_3S_3]^+$. Under conditions favoring the follow-up reactions, the anodic electron-transfer stoichiometry is reduced from the one electron needed for formation of $[Ar_2S_2]^+$ to the two-thirds electron needed to form the trisulfide $[Ar_3S_3]^+$. Replacement of the $[PF_6]^-$ supporting electrolyte anion by the weakly coordinating $[B(C_6F_5)_4]^-$ anion is key to permitting detection of the radical cations. It is likely that weaker ion-pairing between the dimer dication and $[B(C_6F_5)_4]^-$ imparts thermodynamic stability to the monomeric radical cation, thereby disfavoring the follow-up reactions required to obtain the long-term electrolysis product $[Ar_3S_3]^+$.

Efficient disulfurization is observed when the oxidation of Ar_2S_2 is carried out in the presence of cyclohexene. Initiation of the disulfurization can be carried out either anodically or by use of a catalytic amount of a sufficiently strong one-electron oxidizing agent.

Finally, we note that the anodic behavior of diphenyldiselenide, Ph_2Se_2, was briefly investigated. CV scans between 0.2 and 1 V s^{-1} for 0.88 mM Ph_2Se_2 in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$ showed only a chemically irreversible anodic wave at $E_{pa} \approx 1.05$ V and a single cathodic product wave near -0.1 V.

Experimental

Electrochemical procedures were carried out under dry nitrogen, using either Schlenck techniques or a drybox maintained at 1-3 ppm oxygen. Solvents were dried and distilled as previously described.[36] Ditolyldisulfide and dimethyldisulfide were obtained commercially. Di-*p*-fluorophenyldisulfide, di-*p*-methoxyphenyldisulfide, dimesityldisulfide and di(2,4,6-triisopropylphenyl)disulfide were prepared by reduction of the corresponding sulfonyl chloride with triphenylphosphine.[37] $[NBu_4][PF_6]$ (Tokyo Chemical Industry) was recrystallized from absolute ethanol and vacuum dried for at least 24 h at 100º C. $[NBu_4][B(C_6F_5)_4]$ was prepared as described earlier[38] and also vacuum dried at 100º C. A full description of the electrochemical procedures is available.[36] Among the most important features is that a traditional three-electrode cell setup was employed for voltammetry, with the reference electrode separated by a fine frit from the working electrode solution. For bulk electrolyses, a fine frit was also used to separate the working and auxiliary compartments. The working electrodes were 2 mm glassy carbon disks for voltammetry and platinum gauze for bulk electrolyses. The experimental reference electrode was a homemade Ag/AgCl wire, but all potentials in this paper are referred to the ferrocene/ferrocenium potential[39], obtained using the *in-situ* method[39(b)] to track the experimental potential *vs* ferrocene. NMR data were obtained using a 500 MHz instrument.

Preparation of $[N(2,4\text{-}C_6H_3Br_2)_3][B(C_6F_5)_4]$, [**5**][TFAB]: [**5**]$[SbCl_6]$[40] (15g, 14.2 mmol) and K[TFAB] (Boulder Scientific Co.) (11.3 g, 15.7 mmol) were dissolved in 700 mL of dry dichloroethane and stirred at room temperature for 30 min. The reaction was cooled at -20°C for 45 minutes and then filtered. The solvent was removed under reduced pressure and the resulting green solid was dissolved in 700 mL of dry dichloromethane. The solution was filtered again to remove residual $K[SbCl_6]$. The filtrate was concentrated to 100 mL and then added to 700 mL of dry hexane, leaving a green amorphous solid. The liquid was decanted off, another 100 mL of dichloromethane was added, and the resulting solution was again added to 700 mL of hexanes (the redissolving process gave a purer final product). After cooling the solution to -20°C for 30 min, followed by filtration and overnight vacuum drying of the deep green precipitate, 19.9 g (85%) of the desired product were obtained as a deep green powder. Anal. Calcd for $C_{42}H_9BBr_6F_{20}N$: C, 36.09; H, 0.65; N, 1.00. Found: C, 35.79; H, 0.79; N 1.13

Preparation of [2,4,6-triphenylpyrrilium]$[B(C_6F_5)_4]$, [**6**][TFAB]: [**6**]$[BF_4]$ (1.2g, 3.04 mmol) and K[TFAB] (Boulder Scientific Co.) (2.18 g, 3.04 mmol) were suspended in 60 mL of dry diethylether and stirred at room temperature for 12 hours. The solution was then filtered and the solvent removed under reduced pressure. 2.82g (94%) of the desired product were obtained as a bright yellow powder. ^1H NMR (500 MHz, $CDCl_3$) : 7.70-7.77 (m, 6H), 7.8 (qt, 3H, J= 7.5Hz, 1.2Hz), 7.98-8.00 (m, 2H), 7.20-7.22 (m, 4H), 8.38 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) :

114.3, 128.0, 128.2, 128.8, 130.7, 130.9, 132.3, 136.5, 136.6. ^{19}F NMR (470 MHz, CDCl$_3$) : -166.7, -162.8, -132.6. IR (neat) υ_{max}/cm^{-1}: 660, 681, 767, 975, 1081, 1458, 1620. Anal. Calcd for $C_{47}H_{17}BF_{20}O$: C, 57.11; H, 1.73. Found: C, 57.24; H, 2.01.

General procedure for oxidatively-catalyzed desulfurization of olefins. Cyclohexene (58 µL, 0.57 mmol) and the disulphide (0.57 mmol) were dissolved in 0.6mL of dry dichloromethane. Then [**5**][TFAB] or [**6**][TFAB] (0.057 mmol) was added and the solution was stirred (and photolyzed when [**6**][TFAB] was used) for 15 minutes at room temperature after what 0.2 mL of triethylamine were added to quench the reaction. The solvent was removed under reduced pressure and the crude product was then purified by chromatography over silica gel using diethyl ether/ hexane (1/9) as eluent.

1,2-bis(*p*-tolylthio)cyclohexane **7a**. ^{1}H NMR (500 MHz, CDCl3) : 1.45-1.48 (m, 2H), 1.67-1.76 (m, 4H), 2.29-2.34 (m, 2H), 2.41 (s, 6H), 3.26-3.29 (m, 2H), 7.14 (d, 4H, J=8.09Hz), 7.34 (d, 4H, J=8.11Hz). ^{13}C NMR (125 MHz, CDCl3) : 20.9, 23.4, 29.8, 49.8, 129.4, 130.7, 132.8, 136.9. IR (neat) υ_{max}/cm^{-1}: 810, 1018, 1090, 1445, 1491, 2856, 2932, 3019. MSEI+ *m/z* (%) : 329.3 (0.4) (MH$^+$), 328.1 (1), 327.2 (5), 205.5 (16), 204.8 (100). HRMSESI+ for $C_{20}H_{25}S_2$: calculated = 329.13922, found = 329.13922.

1,2-bis((4-fluorophenyl)thio)cyclohexane **7b**. ^{1}H NMR (500 MHz, CDCl3) : 1.35-1.39 (m, 2H), 1.54-1.60 (m, 2H), 1.63-1.68 (m, 2H), 2.16-2.20 (m, 2H), 3.05-3.08 (m, 2H), 6.96-6.99 (m, 4H), 7.34-7.37 (m, 4H). ^{13}C NMR (125 MHz, CDCl3) : 23.7, 30.4, 50.6, 115.9 (d, J=21.7Hz), 129.2 (d, J=3.4Hz), 135.3 (d, J=8.1Hz), 162.3 (d, J=247.9). ^{19}F NMR (470 MHz, CDCl$_3$) : -113.9. IR (neat) υ_{max}/cm^{-1}: 635, 830, 1013, 1155, 1225, 1489, 1589, 2858, 2934. MSEI+ *m/z* (%): 336.2 (1) (MH$^+$), 335.2 (5), 210.5 (5), 209.5 (13), 208.7 (100), 81.1 (10). HRMSESI+ for $C_{18}H_{18}F_2S_2Na$: calculated = 359.07102, found = 359.07102.

1,2-bis((4-methoxy)thio)cyclohexane **7c**. ^{1}H NMR (500 MHz, CDCl3) : 1.31-1.35 (m, 2H), 1.52-1.55 (m, 2H), 1.63-1.66 (m, 2H), 3.80 (s, 6H), 6.81 (d, 4H, J=8.75Hz), 7.34 (d, 4H, J=8.75Hz). ^{13}C NMR (125 MHz, CDCl$_3$) : 23.9, 50.7, 55.2, 114.3, 124.5, 135.5, 159.3. IR (neat) υ_{max}/cm^{-1}: 827, 1031, 1171, 1245, 1284, 1492, 1591, 2836, 2931. MSEI+ *m/z* (%) : 361.2 (1) (MH$^+$), 360.7 (1), 359.1 (5), 223.0 (6), 222.0(15), 221.0 (100),, 139.0 (1). HRMSESI+ for $C_{20}H_{24}O_2S_2Na$: calculated = 383.11099, found = 383.11096.

1,2-bis(methylthio)cyclohexane **8**. ^{1}H NMR (500 MHz, CDCl$_3$) : 1.28-1.32 (m, 2H), 1.44-1.49 (m, 2H), 1.66-1.70 (m, 2H), 2.08 (s, 6H), 2.09-2.16 (m, 2H), 2.58-2.61 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) : 13.9, 24.5, 31.6, 49.1. IR (neat) υ_{max}/cm^{-1}: 737, 905, 1008, 1201, 1439, 2834, 2931, 2974. MSEI+ *m/z* (%) : 177.5 (5) (MH$^+$), 176.5 (6), 175.5 (58), 174.6 (9), 129.8 (10), 128.8 (100), 127.8 (10), 81.0 (3). HRMSESI+ for $C_8H_{16}S_2Na$: calculated = 199.05856, found = 199.0586.

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Supporting information: 15 pages of cyclic voltammograms, an analysis of the dependence of anodic peak current as a function of analyte concentration, and NMR spectra. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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Graphical Abstract