Different mechanisms for the reaction of disubstituted aromatic esters and thioic *S*-esters with electrochemically generated superoxide

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Dialkyl pyridine and benzene dicarboxylates and dicarbothioates (dithioic *S,S'*-diesters) react with electrochemically generated superoxide to form the monocarboxylate anions in almost 100% yield (step 1) before being converted to the dicarboxylate dianions (step 2). This result indicates that the rate of reaction with superoxide to form the anion (rate constant k_1) is considerably faster than the rate to form the dianion (rate constant k_2) ($k_1 \gg k_2$). However, the number of moles/equivalent of superoxide needed to bring about the conversion of the diesters to the carboxylate anions is 2.0 ± 0.1 for each step, while for the dithioic *S*-esters only 1.7 ± 0.2 moles/equivalent are needed for each step. The reason for this difference between the diesters and dithioic *S*-esters is most likely due, in the case of the dithioic *S,S'*-diesters, to homolytic rather than heterolytic bond cleavage occurring, where the C(O)–S bond is cleaved to form the thiyl radical (˙SPr), which either dimerises to form PrSSPr or further reacts with $O_2^{\cdot-}$ to form ⁻SPr. Previously postulated mechanisms do not account for the difference between esters and thioic *S*-esters. From a synthetic perspective, this work provides a useful route for the preparation of mixed carboxylates–thioic *S*-esters from dithioic *S*-esters.

Introduction

Oxygen can be electrochemically reduced to the superoxide anion $O_2^{\cdot-}$, a powerful reductant, in aprotic solvents containing tetraalkylammonium salts, with a half-life of several minutes to hours depending on the solvent and supporting electrolyte.[1–3] There have been several reports describing the reaction of esters[4–7] with $O_2^{\cdot-}$ in aprotic solvents to form the corresponding carboxylic acid anion and alkoxide moiety. The reaction has been proposed to occur *via* initial nucleophilic addition of superoxide at the carbonyl carbon of the ester followed by elimination of an alkoxide anion *via* a net two electron reduction. One study[5] reported complete retention of configuration in the alcohol moiety from the optically active ester upon reaction with superoxide thus suggesting that carbonyl–oxygen scission occurs.

Although the reaction of aromatic esters with $O_2^{\cdot-}$ have been studied, almost all the reported cases involve monocarboxylates [–C(O)O–][4,6] with one example of a thioic *S*-ester [–C(O)S–].[6] In this paper, studies on the reaction of $O_2^{\cdot-}$ with a range of disubstituted pyridine and benzene alkyl diesters (**1**) and dithioic *S,S'*-diesters (**2**) have been conducted and the results compared with the previously reported monocarboxylates.

Ar = pyridine or benzene, R = Me, Et or Pr

One of the problems with studying the reaction quantitatively with chemical sources of $O_2^{\cdot-}$ is the difficulty of handling the reagents. In this study we electrochemically generated $O_2^{\cdot-}$ coulometrically in acetonitrile at a glassy carbon electrode so that the exact number of moles available at each stage of the reaction was accurately known. In addition to coulometry experiments, NMR spectroscopy, TLC and cyclic voltammetry experiments were used to identify the products and yields of the reactions of compounds **1** and **2** with $O_2^{\cdot-}$.

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Experimental

Instrumentation and reagents

The diesters were prepared by standard methods,[8] either by refluxing the carboxylic acid in thionyl chloride to make the acid chloride and then in the corresponding alcohol to make the ester or by refluxing the carboxylic acid directly in alcohol with conc. H_2SO_4. The dithioic *S,S'*-diesters were prepared by refluxing the aromatic acid chloride in dichloromethane with the correct molar equivalent of propane thiol.[9] *S,S'*-Dipropyl pyridine-2,6-dicarbothioate, the only starting material which was a solid at room temperature, was recrystallised from methanol–water to yield white crystals with an identical mp to the literature value (mp 40–42 °C).[9] The remaining compounds were purified by radial chromatography on silica gel with diethyl ether–light petroleum (bp 60–90 °C) as the eluent to yield colourless oils. Only one spot was obtained for these purified oils using TLC and a variety of different solvents as the eluent indicating the compounds were of high purity. NMR spectroscopy and mass spectrometry confirmed the identity of the compounds and also indicated that they were of high purity. Propyl disulfide (Aldrich, 98%) was used as received. HPLC grade acetonitrile was purified immediately prior to use by passing through a column of activated neutral alumina or by distillation over calcium hydride.[10] Other analytical grade solvents were used as received and laboratory grade solvents were distilled prior to use. Electrochemical grade tetraethylammonium hexafluorophosphate (Et_4NPF_6) (Southwestern Analytical) which was used as the supporting electrolyte was dried *in vacuo* prior to use.

Cyclic voltammetry (CV) measurements were conducted with a BAS 100A (Bioanalytical Systems) Electrochemical Analyser or an Oxford Electrodes potentiostat using a three electrode arrangement. Glassy carbon (GC) working electrodes were of macro-dimensions (1–3 mm diameter) and an Ag/Ag⁺ (0.05 M AgNO₃) reference electrode was used. The bulk electrolysis experiments at a glassy carbon electrode were performed in a 5 ml volume controlled potential electrolysis cell which has been described elsewhere.[11] ¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 spectrometer with CDCl₃ or [(CD)₃SO] and referenced to the solvent. TLC analysis were

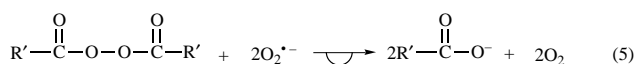performed on Merck SiO$_2$ 60 F$_{254}$ precoated aluminium sheets and visualised with UV light.
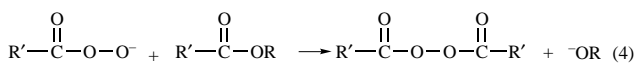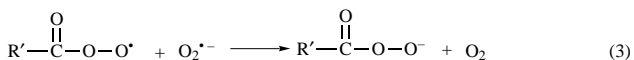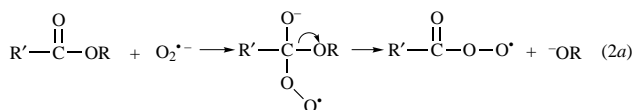
Procedure

The reactions with O$_2$·$^-$ were carried out at high (*ca.* 100 mM) and low (*ca.* 10 mM) concentration of **1** and **2** by bubbling high purity O$_2$ through an acetonitrile solution containing the compound and supporting electrolyte and applying a potential that was sufficiently negative to reduce the O$_2$ but not to reduce the compound. (All of the type **1** and **2** compounds described in this paper can be reduced, but at potentials at least 400 mV more negative than the reduction potential of O$_2$.[12]) The number of moles of superoxide that were generated electrochemically was calculated *via* Faraday's law, eqn. (1), where N = no. of

$$N = Q/nF \qquad (1)$$

moles, Q = charge (coulombs), n = no. of electrons and F = Faraday's constant. The reaction was stopped at various values of the moles/equivalent of superoxide, the solution degassed for 2–3 min with N$_2$ to remove O$_2$ and a cyclic voltammogram recorded (superoxide itself is non-volatile in MeCN with 0.1 M Et$_4$NPF$_6$). The term 'moles/equivalent' refers to the total number of moles of superoxide generated compared to the total number of moles of compounds **1** or **2**. For the high concentration (100 mM) samples, at various stages in the reaction with O$_2$·$^-$, a sample was taken, methylated with MeI (the methylation reaction of carboxylates in the presence of quaternary ammonium cations is quantitative and rapid[13,14]), the solvent removed and the electrolyte–products examined by ^{1}H NMR spectroscopy and TLC to determine which products had been formed.

Results and discussion

Recently, workers have reported that oxygen is electrochemically reversibly reduced to superoxide in acetonitrile containing Bu$_4$NClO$_4$ as the supporting electrolyte.[3] However, our data suggest that in acetonitrile with 0.1 M Bu$_4$NClO$_4$ (or Et$_4$NPF$_6$) the reduction process is quasi-reversible at a glassy carbon electrode, since CV experiments at a scan rate of 100 mV s^{-1} show the separation between the anodic and cathodic peaks to be *ca.* 200 mV (Fig. 1). This value is considerably greater than the theoretical separation of 56 mV for a one electron electrochemically reversible reduction. Superoxide is further reduced (irreversibly) at a more negative potential to form the peroxide anion. Irrespective of the electrochemical reversibility, the reduction of oxygen to superoxide occurs by one electron to form a moderately stable anion radical in acetonitrile.
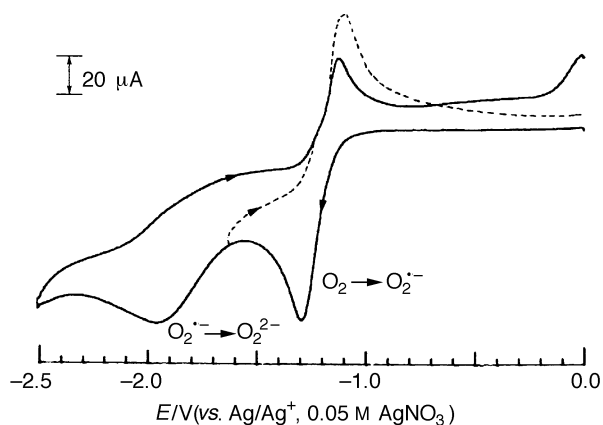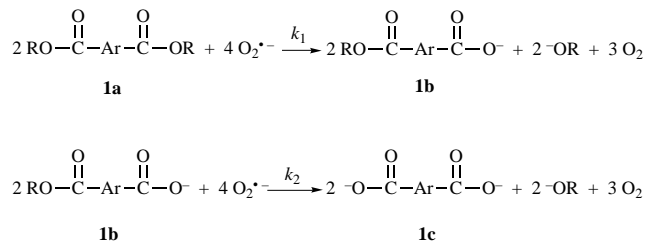
$$O_2 \; + \; e^- \; \rightleftharpoons \; O_2^{\cdot -} \qquad (1)$$

$$R'-\overset{O}{\overset{\|}{C}}-OR \; + \; O_2^{\cdot -} \longrightarrow R'-\overset{O^-}{\underset{\underset{O^\cdot}{\overset{|}{O}}}{\overset{|}{C}}}-OR \longrightarrow R'-\overset{O}{\overset{\|}{C}}-O-O^\cdot \; + \; {}^-OR \qquad (2a)$$

$$R'-\overset{O}{\overset{\|}{C}}-O-O^\cdot \; + \; O_2^{\cdot -} \longrightarrow R'-\overset{O}{\overset{\|}{C}}-O-O^- \; + \; O_2 \qquad (3)$$

$$R'-\overset{O}{\overset{\|}{C}}-O-O^- \; + \; R'-\overset{O}{\overset{\|}{C}}-OR \longrightarrow R'-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R' \; + \; {}^-OR \qquad (4)$$

$$R'-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R' \; + \; 2O_2^{\cdot -} \longrightarrow 2R'-\overset{O}{\overset{\|}{C}}-O^- \; + \; 2O_2 \qquad (5)$$

Scheme 1

Fig. 1 Cyclic voltammogram in MeCN (Et$_4$NPF$_6$) showing the reduction of oxygen at a GC electrode at a scan rate of 100 mV s^{-1}

Diesters

The mechanism previously proposed[7] to account for the reaction of esters with O$_2$·$^-$ is given in Scheme 1. Overall, two O$_2$·$^-$ radicals react with one ester group to form a carboxylate anion and alkoxide. An alternative mechanism has been proposed for diketones[15] which involves superoxide first reducing the diketone to an anion radical and then another superoxide molecule reacting *via* nucleophilic attack on the reduced diketone at the carbonyl. This mechanism is only thermodynamically possible if the diketone has a less negative reduction potential than oxygen. Since the diesters studied in this paper are all reduced at a more negative potential than oxygen, the alternative mechanism can be discounted.

For diesters, a variation of the mechanism depicted in Scheme 1 needs to be introduced, with the precise details of the reaction being determined by the rate of reaction of the diester with O$_2$·$^-$ (Scheme 2). In Scheme 2, the rate of reaction of a
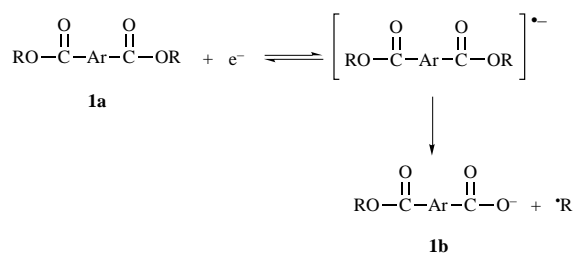
$$2\,RO-\overset{O}{\overset{\|}{C}}-Ar-\overset{O}{\overset{\|}{C}}-OR \; + \; 4\,O_2^{\cdot -} \xrightarrow{k_1} 2\,RO-\overset{O}{\overset{\|}{C}}-Ar-\overset{O}{\overset{\|}{C}}-O^- \; + \; 2\,{}^-OR \; + \; 3\,O_2$$

$$\mathbf{1a} \hspace{6cm} \mathbf{1b}$$

$$2\,RO-\overset{O}{\overset{\|}{C}}-Ar-\overset{O}{\overset{\|}{C}}-O^- \; + \; 4\,O_2^{\cdot -} \xrightarrow{k_2} 2\,{}^-O-\overset{O}{\overset{\|}{C}}-Ar-\overset{O}{\overset{\|}{C}}-O^- \; + \; 2\,{}^-OR \; + \; 3\,O_2$$

$$\mathbf{1b} \hspace{6cm} \mathbf{1c}$$

Scheme 2

diester with O$_2$·$^-$ to form a mixed ester–carboxylate anion can be defined by the rate constant k_1. The further reaction of the ester–carboxylate anion with O$_2$·$^-$ to form the dicarboxylate dianion can be defined by the rate constant k_2.

Three possible reaction scenarios may be associated with Scheme 2 which depend on the k_1/k_2 ratio. If $k_1 \gg k_2$, then after the reaction of **1a** with 2 moles/equivalent of O$_2$·$^-$ there will exist in solution only **1b** and no detectable **1a** or **1c**. If $k_1 \approx k_2$, then after the reaction of **1a** with 2 moles/equivalent of O$_2$·$^-$ there will exist a mixture of **1a**, **1b** and **1c**. Finally, if $k_1 \ll k_2$, after the reaction of **1a** with 2 moles/equivalent of O$_2$·$^-$ there will exist **1a** and **1c**. The reaction of **1a** with 4 moles/equivalent of superoxide will in all cases lead to **1c** only. Experiments were conducted to measure which scenarios apply to the diesters. Dipropyl pyridine-2,6-dicarboxylate, dipropyl pyridine-2,5-dicarboxylate, dipropyl benzene-1,3-dicarboxylate and dipropyl benzene-1,4-dicarboxylate were examined.

We previously reported[11,12,14] that the bulk electrochemical one electron reduction of diesters in acetonitrile (neither O$_2$ or O$_2$·$^-$ present) with the reduction potential held at the $E_{\frac{1}{2}}$ value of the diester produced anion radicals which were unstable on the synthetic timescale. The anion radicals, which may be

detected on the much shorter voltammetric timescale, rapidly decomposed with loss of the alkyl fragment as a radical to leave the ester–carboxylate anion in high yield (*ca.* 70–100%) (Scheme 3).

$$RO-\overset{\overset{\displaystyle O}{\|}}{C}-Ar-\overset{\overset{\displaystyle O}{\|}}{C}-OR \;+\; e^- \;\rightleftharpoons\; \left[RO-\overset{\overset{\displaystyle O}{\|}}{C}-Ar-\overset{\overset{\displaystyle O}{\|}}{C}-OR \right]^{\bullet-}$$

1a

$$\downarrow$$

$$RO-\overset{\overset{\displaystyle O}{\|}}{C}-Ar-\overset{\overset{\displaystyle O}{\|}}{C}-O^- \;+\; {}^{\bullet}R$$

1b

Scheme 3

Although the reactions shown in Schemes 1 and 2 are different from the reaction in Scheme 3, the mixed ester–carboxylate anion products (**1b** in Schemes 2 and 3) are chemically equivalent. Characteristically, **1b** is in all cases harder to reduce than the starting material (**1a**) by 200–300 mV. Therefore, any compound **1b** formed during the reaction of **1a** with $O_2^{\bullet-}$ could be detected voltammetrically at negative potentials. The analytical and spectroscopic data from authentic samples of the methylated forms of **1b** have been published elsewhere.[11,14]

The 2 moles/equivalent reaction of $O_2^{\bullet-}$ with dipropyl pyridine-2,6-dicarboxylate at high and low concentration formed the ester–carboxylate anion (**1b**) in very high yield indicating that $k_1 \gg k_2$ for this compound. Furthermore, this result implies that the overall reaction is independent of concentration. The identity of the product was confirmed by both TLC and NMR experiments (after methylation) of the high 100 mM concentration reaction mixture, and by monitoring the voltammetric response during the course of experiments on the low 10 mM concentration samples. The TLC and NMR data provided no evidence for formation of **1c** (or more accurately the methylated form of **1c**).

Fig. 2(*a*) shows a voltammogram of a type **1a** compound. Fig. 2(*b*) displays a cyclic voltammogram obtained during the course of the reaction of 10 mM **1a** with $O_2^{\bullet-}$. Comparison of Figs. 2(*a*) and 2(*b*) shows that the ester–carboxylate anion product of the reaction of dipropyl pyridine-2,6-dicarboxylate with $O_2^{\bullet-}$ is harder to reduce than the starting material by *ca.* 250 mV. (The methylated form of **1b** has nearly identical voltammetry to the parent dipropyl dicarboxylate, **1a**).[11,12,14] When the course of the reaction was monitored by cyclic voltammetry, immediately after the generation of 2 moles/equivalent of $O_2^{\bullet-}$ virtually no superoxide was detected in solution [Fig. 2(*b*)]. This result indicated that the first step of the reaction of the diester with superoxide is fast, *i.e.* k_1 is large. Voltammetric monitoring showed the second step in the reaction (defined by k_2) to form the dicarboxylate dianion (**1c**) is much slower than the first step, which was expected since only **1b** was obtained at the 2 moles/equivalent reaction stage. Thus, when a cyclic voltammogram was recorded on the solution immediately after the generation of 4 moles/equivalent of superoxide (the electrolysis of oxygen was stopped and the solution briefly purged with N_2 before the voltammogram was recorded), a significant amount of superoxide was still detected in the solution as well as unreacted ester (**1b**) [Fig. 2(*c*)]. The voltammetry of superoxide is easily distinguished from that of O_2 from the sign of the current. For example, if only O_2 is present in solution, the current at potentials more positive than -1.0 V (*vs.* Ag/Ag$^+$) is zero. However, if superoxide is present in solution there will be a positive current flowing at potentials more positive than -1.0 V (*vs.* Ag/Ag$^+$) resulting from the reoxidation of superoxide back to oxygen as occurs under the conditions of Fig. 2(*c*) and Fig. 3(*b*).

The second pyridine ester examined, dipropyl pyridine-2,5-dicarboxylate, reacted in a very similar fashion to dipropyl
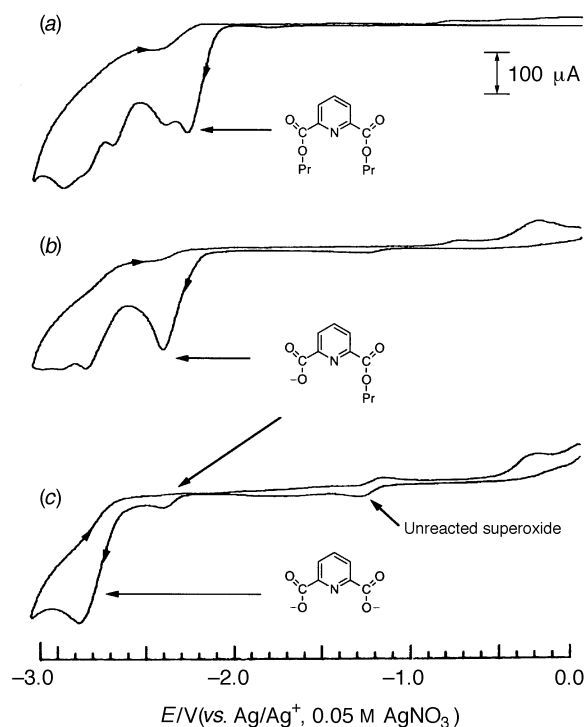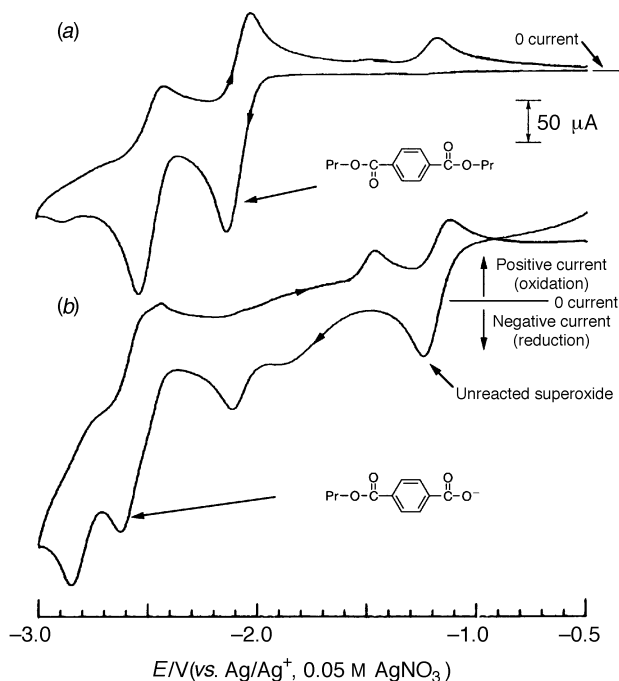

Fig. 2 Cyclic voltammograms obtained at a scan rate of 100 mV s^{-1} using a GC electrode in a N_2 purged solution of MeCN (0.1 M Et$_4$NPF$_6$) showing the reaction of dipropyl pyridine-2,6-dicarboxylate (10 mM) with electrochemically generated superoxide (*a*) before the reaction has commenced, (*b*) after the electrochemical generation of 2 moles/equivalent of superoxide, (*c*) after the electrochemical generation of 4 moles/equivalent of superoxide

pyridine-2,6-dicarboxylate. With both the benzene esters, dipropyl benzene-1,3-dicarboxylate and dipropyl benzene-1,4-dicarboxylate, again only one anionic product was obtained after the generation of 2 moles/equivalent of superoxide, also indicating that $k_1 \gg k_2$ for these compounds. However, the rate of reaction of the benzene esters with superoxide was much slower, particularly for dipropyl benzene-1,4-dicarboxylate. As shown in Fig. 3, halting the reduction of O_2 even prior to the 2 mole/equivalent stage, degassing, then recording a voltammogram indicated that a large quantity of superoxide remained which had not reacted with the ester (**1a**) on the timescale of the experiment (*t ca.* 10 min). A comparison of results with the benzene esters indicates that it is not only the quality of the leaving group (the O−Pr chain) that determines the rate of reaction of the ester with superoxide. The pyridine esters clearly react more rapidly with $O_2^{\bullet-}$ than the benzene esters, with dipropyl benzene-1,4-dicarboxylate exhibiting the slowest rate of reaction.

Dithioic *S,S′*-diesters

The products of the reaction of the dithioic *S,S′*-diesters with $O_2^{\bullet-}$ were analogous to those formed with the diesters. However, the total number of moles of $O_2^{\bullet-}$ necessary to bring about the conversion of the thioic *S*-ester groups to the carboxylate anions was less than 2 indicating that a different mechanism must operate. Fig. 4(*a–d*) contains cyclic voltammograms obtained at various stages in the reaction of *S,S′*-dipropyl pyridine-2,6-dicarbothioate (**2a**) with $O_2^{\bullet-}$. Fig. 4(*a*) shows a cyclic voltammogram of **2a** with no oxygen present. The cyclic voltammogram recorded in the presence of a small amount of O_2 shown in Fig. 4(*b*) is considerably different to that in Fig. 4(*a*) and illustrates in the 3–4 s time (at a scan rate of 100 mV s^{-1}) taken to sweep the potential from the reduction potential of O_2 to the reduction potential of **2a**, that a significant amount of **2a** has reacted with $O_2^{\bullet-}$ to form the thioic *S*-ester–carboxylate anion. This conclusion is reached by noting
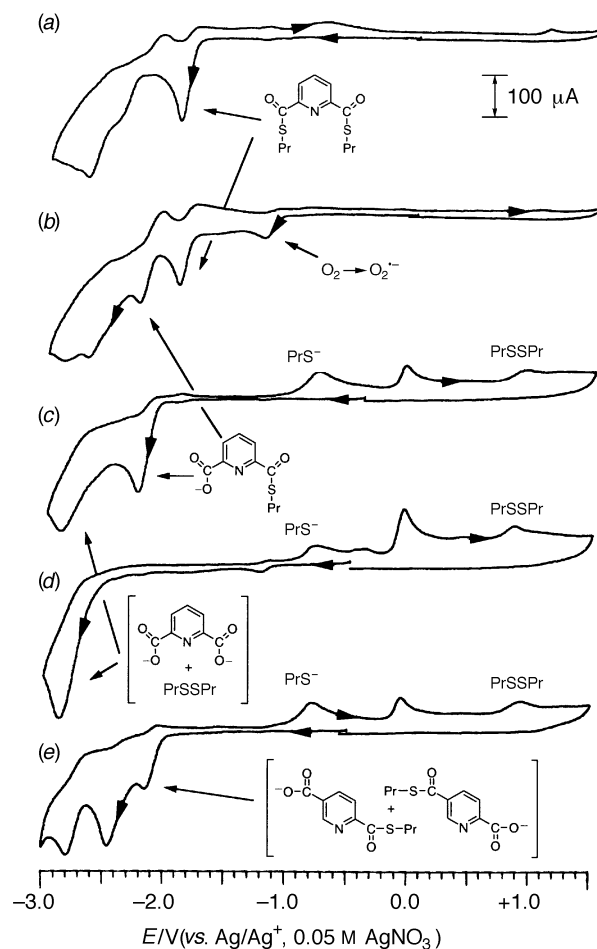
Fig. 3 Cyclic voltammograms obtained at a scan rate of 100 mV s^{-1} using a GC electrode in a N$_2$ purged solution of MeCN (0.1 M Et$_4$NPF$_6$) showing the reaction of dipropyl benzene-1,4-dicarboxylate (9.4 mM) with electrochemically generated superoxide (*a*) before the reaction has commenced, (*b*) after the electrochemical generation of 1.55 moles/equivalent of superoxide

that the peak current for the reduction of **2a** decreases when O$_2$ is present and concomitantly a new peak associated with the reduction of the thioic *S*-ester–carboxylate anion appears. Fig. 4(*c*) represents a cyclic voltammogram of the products of the reaction of **2a** with 1.7 (±0.2) moles/equivalent of superoxide and shows that the mixed thioic *S*-ester–carboxylate anion is formed in 100% yield. Reaction with a total of 3.4 (±0.3) moles/equivalent of superoxide leads to the quantitative formation of the dicarboxylate dianion [Fig. 4(*d*)].

S,S'-Dipropyl pyridine-2,5-dicarbothioate and *S,S'*-dipropyl benzene-1,3-dicarbothioate also were found to react rapidly with 1.7 (±0.2) moles/equivalent of superoxide to form the mixed carboxylate anion, carbothioate esters in 100% yield. In this context, the expression 'rapidly' means that in the time required to halt the electrolysis of O$_2$, degas the solution of residual O$_2$ and record a voltammogram (2–4 min), all of the superoxide had completely reacted. That is, O$_2$˙$^-$ could not be detected voltammetrically. For *S,S'*-dipropyl pyridine-2,5-dicarbothioate both thioic *S*-ester–carboxylate isomers were formed which are illustrated in Fig. 4(*e*). These isomeric products were identified by a comparison of the ¹H and ¹³C NMR spectra and R_f values obtained from TLC experiments of authentic samples of the methylated forms of these isomers which had been prepared previously.[14] Two isomers were also detected as products during the reaction of the analogous diester, dipropyl pyridine-2,5-dicarboxylate, with O$_2$˙$^-$.

The difference in the number of moles/equivalent of superoxide required to convert the thioic *S*-ester groups [*ca.* 1.7 (±0.2) moles/equivalent] and esters [2.0 (±0.1) moles/equivalent] to the carboxylate anions can be explained by modifying step (2*a*) in Scheme 1 to include a homolytic rather than heterolytic bond cleavage pathway. This modification to the reaction scheme is illustrated in Scheme 4 as step (2*b*).

The occurrence of step (2*b*) would cancel the necessity of step (3) in Scheme 1 and only steps (1, 2*b*, 4 and 5) would be needed to convert the thioic *S*-ester groups into carboxylate anions. Consequently, only 1.5 moles/equivalent of superoxide would be necessary to convert the thioic *S*-ester groups into carboxylate anions. Step (2*b*) requires the formation of the thio-

Fig. 4 Cyclic voltammograms obtained at a scan rate of 100 mV s^{-1} using a GC electrode in a N$_2$ purged solution of MeCN (0.1 M Et$_4$NPF$_6$) for (*a*) 10 mM *S,S'*-dipropyl pyridine-2,6-dicarbothioate, (*b*) 10 mM *S,S'*-dipropyl pyridine-2,6-dicarbothioate with *ca.* 5 mM O$_2$, (*c*) 10 mM *S,S'*-dipropyl pyridine-2,6-dicarbothioate after the electrochemical generation of 1.7 moles/equivalent of superoxide, (*d*) 10 mM *S,S'*-dipropyl pyridine-2,6-dicarbothioate after the electrochemical generation of 3.4 moles/equivalent of superoxide, (*e*) 9.6 mM *S,S'*-dipropyl pyridine-2,5-dicarbothioate after the electrochemical generation of 1.7 moles/equivalent of superoxide
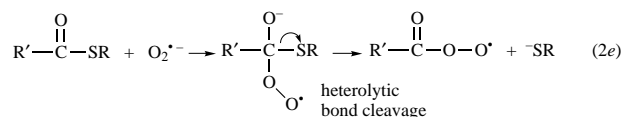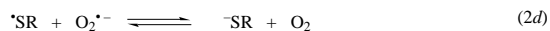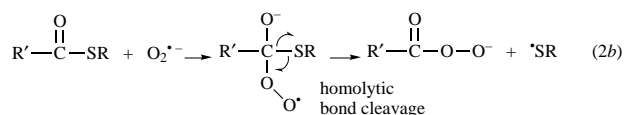
Scheme 4

thiyl radical (˙SR) which would be expected to either rapidly dimerise to form propyl disulfide (PrSSPr) [Scheme 4 (2*c*)], or further react with O$_2$˙$^-$ *via* electron exchange to form O$_2$ and the thiolate anion ($^-$SR) [Scheme 4 (2*d*)]. The occurrence of step (2*d*) would also result in the apparent number of moles/equivalent of O$_2$˙$^-$ needed to convert the thioic *S*-ester groups into carboxylate groups to appear to be >1.5 due to the competing reaction of O$_2$˙$^-$ with ˙SR.

Further evidence for the presence of steps 2*b*–2*d* is ob-

tained by more detailed analysis of the voltammetry. A cyclic voltammogram of an authentic sample of PrSSPr is provided in Fig. 5 and shows that PrSSPr can be reduced irreversibly at very negative potentials by two electrons to form thiolate anions (⁻SPr). The oxidation response at *ca.* −0.8 V on the reverse sweep of the cyclic voltammogram in Fig. 5 is only observed if PrSSPr is first reduced and is therefore due to the oxidation of a product of the reduction of PrSSPr. This has been assigned as the oxidation of the thiolate anion by comparison with similar systems.[16,17] PrSSPr in the bulk solution can also be oxidised by one electron at relatively positive potentials (*ca.* +1.0 V).

On the basis of knowledge obtained from the data obtained in Fig. 5, voltammetric peaks corresponding to the reduction and oxidation of PrSSPr, and the oxidation of ⁻SPr can be recognised as being present in Fig. 4(*c–e*). The response for reduction of PrSSPr is difficult to detect in Fig. 4(*c* and *d*) because the process occurs at a very similar potential to the dicarboxylate dianion. However, this overlap of voltammetric responses explains why the peak current for the reduction of the dicarboxylate dianion appears to be considerably larger than the peak current for the reduction of the starting material in the absence of $O_2{}^{\cdot-}$ (both processes are one-electron steps).

The thiolate anion is readily detected voltammetrically in the experiments depicted in Fig. 4(*c–e*) by starting the potential sweep at negative potentials (*ca.* −1.5 V) and scanning in the positive potential direction only. This experiment confirms that the thiolate ion is present in the bulk solution along with PrSSPr after the reaction of the thioic *S*-ester with $O_2{}^{\cdot-}$ has commenced. Therefore, detailed analysis of the voltammetry illustrated in Fig. 4 proves that both PrSSPr and ⁻SPr are formed during the reaction of the thioic *S*-esters with $O_2{}^{\cdot-}$, which is consistent with the mechanism following the route that is illustrated in Scheme 4 (*2b–2d*). An additional, although perhaps less likely, mechanism is also possible where a mixture of both homolytic and heterolytic bond cleavage occur [*i.e.* steps (*2b*) and (*2e*)]. This would also result in both the PrSSPr and ⁻SPr species being formed, and would have the net result of between 1.5–2.0 moles/equivalent of $O_2{}^{\cdot-}$ being necessary to convert the thioic *S*-ester groups into carboxylate anions.

Conclusion

Dialkyl pyridine and benzene dicarboxylates and dicarbothioates react with $O_2{}^{\cdot-}$ to form the carboxylate anions in very high yield before further reacting with $O_2{}^{\cdot-}$ to form the dicarboxylate dianions. This observation is consistent with the rate of reaction to form the carboxylate anion (k_1) being considerably faster than the rate of formation of the dicarboxylate dianion (k_2). In agreement with previously postulated mechanisms, it was found that 2.0 moles/equivalent of $O_2{}^{\cdot-}$ are needed to convert an ester group into a carboxylate anion. However, only approximately 1.7 moles/equivalent of $O_2{}^{\cdot-}$ are necessary to convert a thioic *S*-ester into a carboxylate anion. This difference is most likely a result of homolytic rather than heterolytic cleavage where the C(O)−SPr bond is cleaved to form ·SPr,
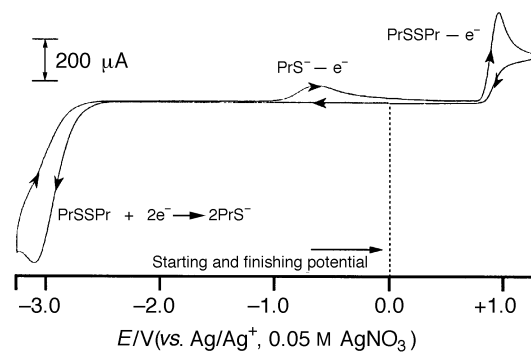
which either dimerises to form PrSSPr or further reacts with $O_2{}^{\cdot-}$ to form ⁻SPr. Both the ⁻SPr and PrSSPr species were voltammetrically detected to form during the reaction of thioic *S*-esters with $O_2{}^{\cdot-}$ which is supportive evidence of this mechanism.

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