

Investigation of the Direct and Indirect Reduction Processes of Some Disulfides by Electrochemical Means

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The free energy relationship for the reaction between aromatic radical anions $A^{\cdot-}$ having about the same intrinsic barrier and three disulfides RSSR (diphenyl disulfide, dimethyl disulfide and di-*tert*-butyl disulfide) in *N,N*-dimethylformamide has been obtained. For each RSSR second-order rate constants were measured electrochemically in the interval 10^{-3} – 10^5 $M^{-1} s^{-1}$ by changing the nature of $A^{\cdot-}$ and thereby the driving force. In the case of diphenyl disulfide the standard potential $E_{RSSR/RSSR^{\cdot-}}^{\circ}$ and the self-exchange reorganization energy $\lambda(0)$ of the RSSR/RSSR $^{\cdot-}$ couple could be extracted from the free energy relationship to values of $-1.4 (\pm 0.1)$ V vs. SCE and 65 kcal mol $^{-1}$, respectively. This knowledge may be combined with the kinetic features of the heterogeneous reduction process of diphenyl disulfide to obtain, among other parameters, the standard heterogeneous rate constant. The cleavage rate constant k_c of the corresponding radical anion was estimated from kinetic measurements to be about 5×10^8 s $^{-1}$. No such information was accessible for the aliphatic disulfides due to a high self-exchange energy of the RSSR/RSSR $^{\cdot-}$ couple but still a maximum value of k_c could be determined at 2×10^8 s $^{-1}$. The minimum values of $E_{RSSR/RSSR^{\cdot-}}^{\circ}$ and $\lambda(0)$ were estimated to be -1.9 V vs. SCE and 75 kcal mol $^{-1}$ and -2.2 V vs. SCE and 75 kcal mol $^{-1}$ for dimethyl disulfide and di-*tert*-butyl disulfide, respectively.

In this paper rate constants of the electron transfer (ET) reaction, k_{ET} , between different aromatic radical anions $A^{\cdot-}$ and three disulfides RSSR in *N,N*-dimethylformamide (DMF) are reported. For each RSSR the results obtained are depicted in plots showing $\log k_{ET}$ versus the standard potential E_A° of the $A/A^{\cdot-}$ couple. Part of the study was devoted to the clarification of whether the radical anion of RSSR existed in DMF and a determination of the standard potential $E_{RSSR/RSSR^{\cdot-}}^{\circ}$ was possible or if the reaction could be better described as a dissociative ET with bond breakage concerted with the electron transfer step. The three substrates chosen for investigation in this paper are diphenyl disulfide, dimethyl disulfide and the sterically hindered di-*tert*-butyl disulfide, all three selected primarily because of the availability of their thermodynamic data in the literature.

The electrochemical properties of disulfides have been studied in detail in a number of solvent systems.^{1–6} In aprotic solvents the reduction process of RSSR is, in general, characterized by an irreversible two-electron wave giving rise to the corresponding thiolate ion RS $^{\cdot-}$ [eqn. (1)].



An example of a cyclic voltammogram recorded in DMF of diphenyl disulfide at a gold electrode is shown in Fig. 1. The peak potential of the reduction wave, E_p^{red} , at a scan rate v of 1 V s $^{-1}$ is -1.60 V vs. SCE and is appreciably less negative than the corresponding values of the aliphatic disulfides. For instance, E_p^{red} of di-*tert*-butyl disulfide is -2.71 V vs. SCE. The thiolate ion RS $^{\cdot-}$ produced in the reduction process may be oxidised on the reverse scan at a potential close to 0 V vs. SCE [E_p^{ox} (thiophenoxide) = 0.00 V, E_p^{ox} (methanethiolate) = -0.40 V and E_p^{ox} (2-methyl-2-propanethiolate) = -0.13 V vs. SCE]. By this process RS $^{\cdot-}$ is generated and dimerises in a fast reaction to regenerate the disulfide in an overall EC mechanism and the couple RSSR/RS $^{\cdot-}$ thereby constitutes a redox pair.^{5,6} The cyclic voltammogram is significantly affected by the nature of the electrode material; at glassy carbon and platinum the peak potential of the reduction wave of diphenyl disulfide is shifted in a negative direction by about 100 and 400 mV, respectively, at a scan rate of 1 V s $^{-1}$. This feature, which has been noticed elsewhere,⁴ indicates a somewhat smaller standard heterogeneous rate constant at platinum compared with the other two

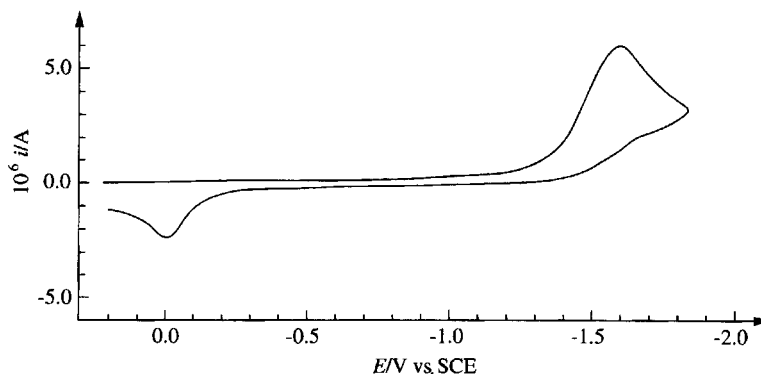


Fig. 1. Cyclic voltammogram obtained of 2 mM diphenyl disulfide in 0.1 M TBABF₄-DMF at a scan rate of 1 V s⁻¹ at a gold electrode.

electrode materials. The electrochemical behaviour of diphenyl disulfide was further investigated by fast cyclic voltammetry (CV) using a gold ultra-microelectrode (diameter 30 μm). The overall appearance of the cyclic voltammogram neglecting the shift in peak potentials was found to be relatively independent of scan rate. Even at $\nu = 20\text{--}40$ kV s⁻¹ the oxidation peak of thiophenoxide was recognizable and there was no sign of reversibility or quasi-reversibility corresponding to an RSSR/RSSR^{•-} couple. An upper limit of 10⁻⁴ s can thus safely be put on the lifetime of the radical anion of diphenyl disulfide.

The cathodic transfer coefficient α_c was determined from eqns. (2) and (3) by measuring the position of the peak potential E_p^{red} and the peak-width, $E_{p/2}^{\text{red}} - E_p^{\text{red}}$, during linear sweep voltammetry (LSV).⁷

$$\partial E_p^{\text{red}} / \partial (\ln \nu) = -RT/2\alpha_c F \quad (2)$$

$$E_{p/2}^{\text{red}} - E_p^{\text{red}} = 1.857 RT/\alpha_c F \quad (3)$$

For diphenyl disulfide α_c is 0.33 (± 0.04) and 0.36 (± 0.03) at a platinum and glassy carbon electrode, respectively, while $\alpha_c = 0.34$ (± 0.03) at platinum for di-*tert*-butyl disulfide. These values are somewhat smaller than the one obtained previously from a Tafel plot of diphenyl disulfide at a platinum electrode.⁶ Within the framework of the Marcus-Hush model, a value of α_c of less than 0.5 could be interpreted⁸ to suggest that the rate-determining step of the reduction process is a dissociative electron transfer process generating RS[•] and RS⁻ at the electrode surface without the intermediacy of the radical anion RSSR^{•-}. The radical RS[•] would then immediately be further reduced to the thiolate ion RS⁻, this being the origin of the overall two-electron stoichiometry observed for process (1). An alternative and probably more likely interpretation in this case⁹ is that the process initially involves an intrinsically slow electron transfer step to produce RSSR^{•-}, which in a fast reaction decays to RS⁻ and RS[•]. Depending on the rate of cleavage the latter species would then be further reduced via an ECE or DISPI mechanism.

In order to obtain more information about the electrochemical features of the disulfides the indirect reduction

of these compounds was considered. The analysis of the heterogeneous reduction behaviour of RSSR would suggest that the homogeneous reaction between electrochemically generated aromatic radical anions A^{•-} and RSSR follows the reaction scheme given below [eqns. (4)–(7)]



as long as A^{•-} is a sufficiently strong electron donor capable of reducing RS[•] to the corresponding thiolate ion [eqn. (7)]. The weakest electron donor used in the study of diphenyl disulfide, dimethyl disulfide and di-*tert*-butyl disulfide is the radical anion of 1,2-benzanthraquinone ($E_A^\circ = -0.672$ V vs. SCE), phenazine ($E_A^\circ = -1.090$ V vs. SCE) and 1,4-dicyanobenzene ($E_A^\circ = -1.485$ V vs. SCE), respectively. Taking into account the magnitude of the oxidation potential of RS⁻ the rate constant of reaction (7) would therefore be expected to be at the diffusion-controlled limit and competing processes such as a dimerisation of RS[•] or a coupling reaction between A^{•-} and RS[•] can be neglected. For the most exergonic cases reaction (7) might result in electrochemiluminescence.⁹ However, this phenomenon should not influence the determination of the rate constant of the forward reaction (5) and no further attention was paid to such a process in this study. It should be emphasized that even though the radical anion of RSSR is included in the scheme given above, the possibility of a dissociative electron transfer process, i.e., step (6) being concerted with the forward ET step (5), cannot be excluded at this point. Reversible behaviour of reaction (6) should also be considered even though some investigations have suggested the reverse reaction to be unlikely to occur.⁵

The validity of the proposed mechanism was substantiated by preparative and analytical experiments (see also

the Experimental). In the former kind of measurement, controlled potential reductions of the mediator were carried out in the presence of an excess of RSSR. The disulfides were converted completely into the corresponding thiols after acidic work-up with an electron consumption of about two electrons per RSSR. The mediator A could be isolated either unchanged or as the dihydro derivative AH_2 probably formed at the end of the preparative reduction owing to a slow protonation of the radical anion followed by further reduction and protonation. In the analytical experiments using LSV,¹⁰ chronoamperometry¹¹ and a steady-state technique¹² the catalytic efficiency of the process was found to be close to 100% as deduced from a comparison with simulated curves and the changes in the steady-state currents of the $A/A^{\cdot-}$ couple. The simulations were based on the assumption of kinetic control by the forward ET reaction (5), which is valid when k_{ET} is small and k_c is higher than $k_{-ET}[A]$.

In order to resolve rigorously the kinetic situation for reactions (5) and (6) the redox catalysis method¹³⁻¹⁶ was applied in a couple of cases, namely the reactions between isoquinoline radical anion and di-*tert*-butyl disulfide and azobenzene radical anion and diphenyl disulfide. On the assumption of kinetic control by the forward ET step (5), rate constants were determined by LSV and CV¹⁰ at different concentrations of the mediator and the thiophenoxide ion in the interval from 1 to 20 mM. Thiophenoxide was generated electrochemically from a reduction of diphenyl disulfide. As can be seen in Table 1, k_{ET} is found to be relatively independent of $[A]$ and $[RS^{\cdot-}]$ and any deviation present is within the uncertainty on the measurements ($\pm 10\%$); the backward reactions

of (5) and (6) can thus safely be neglected in the kinetic scheme in these specific cases. However, it should be mentioned that problems due to adsorption of, especially, diphenyl disulfide at the electrode surface were encountered in some of the measurements. These problems could be overcome by cleaning the surface using multi-scans just before the actual experiment. It was also noted that even small amounts of thiophenoxide seemed to have a pronounced effect on the reproducibility of the experiments. The small but consistent decrease in the rate constants observed in the presence of thiophenoxide in Table 1b can probably be ascribed to this phenomenon.

The LSV and CV method cannot be applied when the rate constants are below $10 M^{-1} s^{-1}$ but a kinetic analysis can still be carried out by employing a potentiostatic technique which previously has been used for determining rate constants of simple pseudo-first-order reactions.¹⁷ In this method the aromatic radical anion $A^{\cdot-}$ is first generated electrochemically from the aromatic compound A and the decay of the limiting oxidation current of $A^{\cdot-}$ (being proportional to the concentration of $A^{\cdot-}$) at a rotating disk electrode is then followed as a function of time after addition of an excess of disulfide to the solution. According to the overall reaction scheme [eqns. (5)–(7)] the differential equation for species $A^{\cdot-}$ can be expressed as eqn. (8) when the backward reaction of (6) has been neglected and the steady-state assumption has been applied to the RSSR $^{\cdot-}$ and $RS^{\cdot-}$ species. In the two limiting cases characterized by the conditions $k_c \gg k_{-ET}[A]$ and $k_c \ll k_{-ET}[A]$, eqn. (8) simplifies to eqns. (9) and (10), respectively.

$$d[A^{\cdot-}]/dt = - \frac{2k_c k_{ET}[RSSR]}{k_c + k_{-ET}[A]} [A^{\cdot-}] \quad (8)$$

$$d[A^{\cdot-}]/dt = -2k_{ET}[RSSR][A^{\cdot-}] \quad (9)$$

$$d[A^{\cdot-}]/dt = - \frac{2k_c k_{ET}[RSSR]}{k_{-ET}[A]} [A^{\cdot-}] \quad (10)$$

According to eqn. (8) the change in the concentration of $A^{\cdot-}$ is, in general, predicted to follow a simple pseudo-first-order decay if the concentrations of the substrate RSSR and the aromatic compound A are kept high. In the present investigation with the disulfides this situation was indeed observed in some cases. For instance, in the reaction between fluoranthene radical anion and di-*tert*-butyl disulfide the kinetics followed a pseudo-first-order decay regardless of the values of $[A]$ and $[RS^{\cdot-}]$ and even initial concentrations of 20 and 10 mM, respectively, had no influence on the reaction rate. The same behaviour was observed for the reaction between 1,4-diacetylbenzene radical anion and dimethyl disulfide thus allowing in these specific cases the backward reactions of eqns. (5) and (6) to be excluded from the kinetic analysis. For most of the other radical anions investigated by the potentiostatic method the kinetic picture was more complicated; the decay of $A^{\cdot-}$ was not confined to a pure pseudo-first-order reaction but dependent on the concentration of A as well as of $RS^{\cdot-}$. The importance of the

Table 1. Rate constants k_{ET} obtained for the reaction between some aromatic radical anions and RSSR by LSV and CV as a function of the mediator concentration $[A]$ in 0.2 M TBABF₄-DMF at 25 °C.

(a) Mediator: isoquinoline, RSSR: di-*tert*-butyl disulfide^a

	[A]/mM				
	1	2	5	10	20
$k_{ET}(LSV)/M^{-1} s^{-1}$	915	855	895	820	760
$k_{ET}(CV)/M^{-1} s^{-1}$	980	925	960	955	815

^a The excess factor of di-*tert*-butyl disulfide was kept constant at 2.

(b) Mediator: azobenzene, RSSR: diphenyl disulfide^a

	[A]/mM				
	1	2	5	10	20
$k_{ET}(LSV)/M^{-1} s^{-1}$	3820	3720	3600	3650	3160
$k_{ET}(CV)/M^{-1} s^{-1}$	3750	3540	3370	3720	3300
$k_{ET}(CV)/M^{-1} s^{-1b}$	3100	3130	2930	2950	2840

^a The excess factor of diphenyl disulfide was kept constant at 2. ^b Thiophenoxide was present in 8 mM concentration.

backward reaction of eqn. (6) was especially pronounced in the case of diphenyl disulfide whereas it could hardly be detected for di-*tert*-butyl disulfide and dimethyl disulfide. For instance in the reaction between anthraquinone radical anion ($[A^{\cdot-}]_{\text{init}} = 1 \text{ mM}$, $[A]_{\text{init}} = 5 \text{ mM}$) and diphenyl disulfide, the presence of 50 mM thiophenoxide slowed down the reaction kinetics considerably. However, the rather complicated kinetic picture could be simplified somewhat by taking less than the first half-life of the reaction into account in the kinetic analysis. By doing so the rate expression (8) should be an adequate description since the fast follow-up reaction (7) is expected to outrun the backward reaction of eqn. (6) in most cases as long as $[A^{\cdot-}] > [RS^{\cdot-}]$. Furthermore, with diphenyl disulfide as the substrate the simplification to the pseudo-first-order case could be accomplished chemically simply by scavenging thiophenoxide generated during the reaction with methyl *p*-toluenesulfonate to give the unreactive methyl phenyl sulfide. Use of the latter procedure is based on the conditions that the electron transfer reaction between the radical anion and methyl *p*-toluenesulfonate is too slow to influence process (5) and that the S_N2 reaction between thiophenoxide and methyl *p*-toluenesulfonate is able to remove thiophenoxide continuously. For the radical anions of 1,2-benzanthraquinone, 2,3-dimethylnaphthoquinone, 9,10-dicyanoanthracene, anthraquinone, (*E*)-1,2-dibenzoyl-ethylene and 1-methoxyanthraquinone the first condition was clearly fulfilled as deduced by recording and comparing the oxidation current of $A^{\cdot-}$ in the presence of methyl *p*-toluenesulfonate alone and in the presence of a mixture of methyl *p*-toluenesulfonate and diphenyl disulfide. As concerns the second condition, a comparison with simulations of a cyclic voltammetric study of the reaction between methyl *p*-toluenesulfonate and thiophenoxide generated from the reduction of diphenyl disulfide on the forward scan gave a rate constant of about $100 \text{ M}^{-1} \text{ s}^{-1}$. This high value will indeed allow the concentration of thiophenoxide to be kept low throughout the whole course of the reactions investigated by the potentiostatic technique and prevent the backward reaction of (6) from coming into play. Moreover, the rate constant obtained by this procedure for the reaction between anthraquinone radical anion and diphenyl disulfide was in agreement with the one obtained from a kinetic treatment of the first half-life of the same reaction in the absence of methyl *p*-toluenesulfonate.

A number of reactions were subjected to the kind of redox catalysis analysis described above, namely the reaction between perylene radical anion and di-*tert*-butyl disulfide, quinoxaline radical anion and di-*tert*-butyl disulfide, anthraquinone radical anion and diphenyl disulfide, and 2,3-dimethylnaphthoquinone radical anion and diphenyl disulfide. The initial concentration of the mediator was, in general, varied between 0 and 100 mM but with perylene and anthraquinone it could not be increased above 10 mM owing to the rather low solubility in DMF. The results obtained are listed in Table 2 in

which the parameter β in the term $\gamma = \beta/2[\text{RSSR}]$ denotes the numerical value of the slope in a plot of $\ln[A^{\cdot-}]$ vs. time. The first important point to note is that γ attains a constant value for all four reactions investigated at small concentrations of the mediator. This indicates kinetic control by the forward electron transfer (5) and according to rate expression (9), γ is then simply equal to the rate constant k_{ET} . At the higher mediator concentrations the reaction is slowed down and γ decreases as a function of $[A]$. The reaction has now moved into the mixed kinetic region described by expression (8), i.e., $\gamma = k_c k_{\text{ET}} / (k_c + k_{-\text{ET}}[A])$, and by inserting the known values of k_{ET} and $[A]$ the ratio $k_c/k_{-\text{ET}} = \gamma[A] / (k_{\text{ET}} - \gamma)$ can be obtained for each mediator the exception being anthraquinone. Alternatively k_{ET} and $k_c/k_{-\text{ET}}$ may be determined by a non-linear fit. In none of the reactions could full kinetic control by the cleavage reaction corresponding to eqn. (10) be achieved.

If the backward reaction of (5) is assumed to be diffusion-controlled ($k_{-\text{ET}} = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$)* the results obtained by redox catalysis can be used to estimate the rate constant k_c of the cleavage reaction. As will become clear later on from plots of $\log k_{\text{ET}}$ vs. $-E_A^{\cdot}$ this assumption is not totally correct and can only reasonably be justified for the reaction between diphenyl disulfide radical anion and anthraquinone or 2,3-dimethylnaphthoquinone. For the two reactions in Table 1 investigated by LSV and CV, $k_{-\text{ET}}$ is expected to be substantially smaller than $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and the weak tendency towards a decrease in the rate constant k_{ET} observed at the highest concentration of mediator used cannot therefore be ascribed to mixed kinetic control by reactions (5) and (6). The results obtained in Table 2 are of more interest since the mixed kinetic zone could actually be observed by the potentiostatic method. In this respect the latter method has a couple of advantages over the 'normal' redox catalysis analysis using LSV. The first one is the enhanced possibility of a situation in which the backward electron transfer is under diffusion control even for ET reactions considerably slowed down by a large reorganization energy; rate constants k_{ET} as low as $10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ may, in most cases, be measured by the potentiostatic method. The second advantage is that a value of $[A]$ of the order of 100–500 mM can easily be utilized as long as limitations due to impurities and insolubility do not arise. The determination of cleavage rate constants of about $5 \times 10^9 \text{ s}^{-1}$ should therefore, in optimal situations, be within reach of this method. In the present investigation the ratio $k_c/k_{-\text{ET}}$ for diphenyl disulfide was found to be ca. 0.05 M, as calculated and shown in Table 2(d) or obtained directly by a non-linear fit to all the data points. If $k_{-\text{ET}}$ is assumed to be close to the diffusion-controlled rate

* According to the Stokes–Einstein equation the value of the diffusion-controlled rate constant in DMF depends on the viscosity of the solvent and the radii of the reactants involved. For the kinds of system investigated in this paper the use of a value of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ seems to be satisfactory.^{15,18}

Table 2. The parameter $\gamma = \beta/2[\text{RSSR}]$ and $k_c/k_{-ET} = \gamma [A]/(k_{ET} - \gamma)$ obtained for the reaction between some aromatic radical anions and RSSR by a potentiostatic method as a function of the initial mediator concentration $[A]_{\text{init}}$ in 0.1 M TBABF₄-DMF at 25 °C. The initial concentration of A^{•-} was 1 mM.

(a) Mediator: perylene, RSSR: di-*tert*-butyl disulfide

	$[A]_{\text{init}}/\text{mM}$			
	0	1	5	10
$\gamma/\text{M}^{-1} \text{ s}^{-1}$	0.044	0.047	0.040	0.037
$(k_c/k_{-ET})/\text{M}$			0.038	0.045

^a The concentration of di-*tert*-butyl disulfide was in the range 50–100 mM and γ was obtained from the first half-life of the reaction.

(b) Mediator: quinoxaline, RSSR: di-*tert*-butyl disulfide^a

	$[A]_{\text{init}}/\text{mM}$						
	0	1	5	10	30	60	100
$\gamma/\text{M}^{-1} \text{ s}^{-1}$	0.042	0.041	0.030	0.023	0.013	9.2×10^{-3}	6.6×10^{-3}
$(k_c/k_{-ET})/\text{M}$			0.013	0.012	0.014	0.017	0.019

^a The concentration of di-*tert*-butyl disulfide was in the range 30–100 mM and γ was obtained from the first half-life of the reaction.

(c) Mediator: anthraquinone, RSSR: diphenyl disulfide^a

	$[A]_{\text{init}}/\text{mM}$		
	1	5	10
$\gamma/\text{M}^{-1} \text{ s}^{-1}$	0.18	0.21	0.22

^a Measured by both the potentiostatic method and stopped-flow UV spectroscopy at a wavelength of 555 nm. The concentration of diphenyl disulfide was in the range 20–50 mM. The solution also contained 3 mM methyl *p*-toluenesulfonate.

(d) Mediator: 2,3-dimethylnaphthoquinone, RSSR: diphenyl disulfide^a

	$[A]_{\text{init}}/\text{mM}$						
	0	1	5	10	30	60	100
$\gamma/\text{M}^{-1} \text{ s}^{-1}$	0.11	0.10	0.12	0.11	0.072	0.048	0.032
$(k_c/k_{-ET})/\text{M}$					0.058	0.047	0.041

^a The concentration of diphenyl disulfide was in the range 20–50 mM. The solution also contained 3 mM methyl *p*-toluenesulfonate.

constant of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, a cleavage rate constant k_c of about $5 \times 10^8 \text{ s}^{-1}$ for the radical anion of diphenyl disulfide thus follows.

For di-*tert*-butyl disulfide the situation is a bit more subtle since the backward electron transfer is not under total diffusion control in the two cases investigated. Variation in the ratio k_c/k_{-ET} determined for the reactions with perylene ($k_c/k_{-ET} \approx 0.04 \text{ M}$) and quinoxaline ($k_c/k_{-ET} \approx 0.015 \text{ M}$) are probably due to variations in the magnitude of k_{-ET} , although the high uncertainty in the measurements with perylene should be emphasized; the concentration of perylene could not be raised much above 10 mM in DMF. On the other hand, such a variation does not seem unreasonable from a kinetic point of view. According to the expression of the ratio k_{ET}/k_{-ET} given in eqn. (11) a ratio of about 2.3 between $k_{ET}/k_{-ET} = \exp[F/RT(E_{\text{RSSR}}^{\circ}/\text{RSSR}^{\cdot-} - E_A^{\circ})]$ (11)

the k_{-ET} values of quinoxaline and perylene is to be expected when the known values of k_{ET} and E_A° ($k_{ET} = 0.042$ and $0.046 \text{ M}^{-1} \text{ s}^{-1}$ and $E_A^{\circ} = -1.589$ and -1.613 V vs. SCE for quinoxaline and perylene, respectively) are inserted. Quite surprisingly, the k_c/k_{-ET} ratio did not seem to decrease further as the mediator 1,4-dicyanobenzene ($E_A^{\circ} = -1.485 \text{ V}$ vs. SCE) was employed. Even though the reactions were too slow in this case to allow the determination of reliable rate constants, a tentative value of k_c/k_{-ET} could be estimated at about 0.03 M. At this point we do not have any explanation of this result but the fact that the kinetic region characterized by diffusion control of the backward reaction is approached for the mediators in question may play a certain role. All things considered a maximum value of the cleavage rate constant can therefore be settled at about $2 \times 10^8 \text{ s}^{-1}$ for di-*tert*-butyl disulfide

radical anion. A similar determination of k_c for dimethyl disulfide radical anion was omitted since the rate constants, in general, were harder to reproduce.

In relation to the above discussion it should also be mentioned that radical anions of some aliphatic disulfides have been generated and observed directly in pulse radiolysis studies in aqueous media.¹⁹ The cleavage rate constants for $\text{RSSR}^{\cdot-}$ were found to be of the order of 10^6 s^{-1} , close to our result in DMF taking into consideration the possible influence of solvation effects.²⁰ In general the stability of the radical anions of disulfides is much higher than that of the radical anions of peroxides and most alkyl halides which cleave in a concerted manner. The origin of this phenomenon is probably ascribable to the ability of sulfur to accommodate more than eight outer-valence electrons; PM3 calculations of the charge density do indicate that most of the negative charge in the radical anion will be localized on the two sulfur atoms.[†] The higher stability of the radical anions of the aliphatic disulfides compared with diphenyl disulfide can be attributed to the somewhat stronger S-S bond in the former cases.

Based on the reaction scheme [eqns. (4)–(7)] with the forward ET step (5) being rate-determining, second-order rate constants k_{ET} were measured for the reaction between a number of aromatic radical anions and RSSR by cyclic voltammetry¹⁰ and the homogeneous kinetic method using a rotating disk electrode or ultraviolet (UV) spectroscopy for detection of $\text{A}^{\cdot-}$.¹⁷ The exact life-time of $\text{RSSR}^{\cdot-}$ has no effect on the determination of the rate constant as long as k_c is higher than $k_{-\text{ET}}[\text{A}]$. This condition is valid in all cases when $[\text{A}]$ is kept low. The influence of the thiolate ion in the slow reactions was overcome by scavenging with methyl *p*-toluenesulfonate or by taking less than the first half-life of the reaction into account in the kinetic analysis. The results obtained are presented in Tables 3–5 and as ($\log k_{\text{ET}}$ vs. $-E_{\text{A}}^\circ$) plots in Figs. 2–4. As can be seen the figures clearly suggest a correlation between the activation Gibbs energy, ΔG^\ddagger , and the driving force (proportional to $-FE_{\text{A}}^\circ$) of the electron transfer process. In favourable cases thermodynamic information such as the standard potential and self-exchange reorganization energy of the $\text{RSSR}/\text{RSSR}^{\cdot-}$ couple may be extracted from the experimentally derived free-energy relationships, since the $\text{A}/\text{A}^{\cdot-}$ couples are all characterized by having about the same small intrinsic barrier. While the plots of dimethyl disulfide and di-*tert*-butyl disulfide exhibit a single straight line with slopes of 1/126 mV and 1/117 mV, respectively, determined by linear least-squares analysis, two straight lines with an intermediate region can be resolved from the plot of diphenyl disulfide. This latter feature is an indication of a transition from activation-

controlled electron transfer at high driving force, to a region characterized by equilibrium at low driving force, thus being strong evidence of the existence of the radical anion of diphenyl disulfide.^{14–16} This result is also in accordance with the conclusion obtained from the measurements of the ratio $k_c/k_{-\text{ET}}$.

The two lines drawn in the figure of diphenyl disulfide are based on theoretical slopes of 1/59 mV and 1/118 mV and the fit to the experimental results is satisfactory, although the points corresponding to the slowest reactions show some scattered behaviour. In principle the relationship in the activation-controlled region should be parabolic according to the Marcus theory but as long as E_{A}° is close to the standard potential of the disulfide, $E_{\text{RSSR}/\text{RSSR}^{\cdot-}}^\circ$, the transfer coefficient of the homogeneous reaction can be considered to be independent of the driving force and close to 0.5, and a linear approximation will be valid. If the two points in the intermediate region corresponding to (*E*)-1,2-dibenzoyl ethylene and 1-methoxyanthraquinone as mediators are omitted in a linear least-squares analysis, the best straight line obtained in the activation-controlled region would have a slope of 1/126 mV, corresponding to a transfer coefficient of 0.47. These values are slightly smaller than expected but this circumstance does not effect the determination of the standard potential of diphenyl disulfide which can be extrapolated from the plot simply by extending the lower line to the diffusion-controlled limit ($= 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The value of $E_{\text{RSSR}/\text{RSSR}^{\cdot-}}^\circ$, is thereby found to be $-1.4 (\pm 0.1) \text{ V}$ vs. SCE. It should be emphasized that the procedure, might be somewhat hampered if the cleavage reaction is very fast ($k_c > 10^{10} \text{ s}^{-1}$) and hence occurring within the solvent cage.¹⁶ However, in the present case with a k_c of about $5 \times 10^8 \text{ s}^{-1}$ such a complication can be disregarded.

The rate constant corresponding to $E_{\text{RSSR}/\text{RSSR}^{\cdot-}}^\circ$ (and zero driving force), $k^{\circ, \text{hom}}$, can be interpolated from the activation-controlled region in Fig. 2 to a value of $50\,000 \text{ M}^{-1} \text{ s}^{-1}$; whether the best straight line as obtained by linear least-squares analysis or the theoretical line is used in this estimation influences the magnitude of $k^{\circ, \text{hom}}$ only slightly. Furthermore, by combining the Marcus and the Eyring equations [eqn. (12)],²¹ where Z is the

$$\lambda = (\log Z - \log k^{\circ, \text{hom}}) 4RT \ln 10 \quad (12)$$

pre-exponential factor ($= 3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$), the reorganization energy λ of the reaction ($\approx 37 \text{ kcal mol}^{-1}$) is obtained. Since the self-exchange reorganization energy, $\lambda(0)$, of the $\text{A}/\text{A}^{\cdot-}$ couple is known to be ca. 10 kcal mol^{-1} as measured by EPR spectroscopy,²² $\lambda(0)$ of the $\text{RSSR}/\text{RSSR}^{\cdot-}$ couple can finally be estimated to be about 65 kcal mol^{-1} according to Marcus cross-relation.²³

With the knowledge of $E_{\text{RSSR}/\text{RSSR}^{\cdot-}}^\circ$ and α_c a determination of the standard heterogeneous rate constant $k^{\circ, \text{het}}$ of the reduction process for diphenyl disulfide (not corrected for double-layer effects) can be obtained from

[†] The PM3 calculations were carried out on a Macintosh Quadra 700 using the program package MOPAC written by James J. P. Stewart. Prof. K. A. Jørgensen and Dr. E. R. Møller are thanked for providing the facilities for the theoretical calculations.

Table 3. Rate constants k_{ET} obtained for the reaction between different aromatic radical anions and diphenyl disulfide in 0.1 M TBABF₄-DMF at 25 °C.

Mediator	$-E_A^\circ/V$ vs. SCE	$k_{ET}/M^{-1} s^{-1}$
1,2-Benzanthraquinone ^a	0.672	2.4×10^{-3}
2,3-Dimethylnaphthoquinone ^a	0.740	0.11
9,10-Dicyanoanthracene ^a	0.773	0.034
Anthraquinone ^{a,b}	0.800	0.20
(<i>E</i>)-1,2-Dibenzoyl ethylene ^a	0.830	0.40
1-Methoxyanthraquinone ^a	0.880	1.1
2-Chlorophenazine ^c	0.957	8.0
4-Methoxycarbonylazobenzene ^c	1.015	14
Phenazine ^c	1.090	150
3-Chloroazobenzene ^c	1.135	390
4-Chloroazobenzene ^c	1.183	930
Azobenzene ^c	1.279	3370
2,4'-Dimethoxyazobenzene ^c	1.416	29000
4-Dimethylaminoazobenzene ^c	1.464	91000

^a Measured by a potentiostatic method in the presence of 3 mM methyl *p*-toluenesulfonate. ^b Measured by stopped-flow UV spectroscopy at 555 nm in the presence of 3 mM methyl *p*-toluenesulfonate. ^c Measured by cyclic voltammetry.

Table 4. Rate constants k_{ET} obtained for the reaction between different aromatic radical anions and dimethyl disulfide in 0.1 M TBABF₄-DMF at 25 °C.

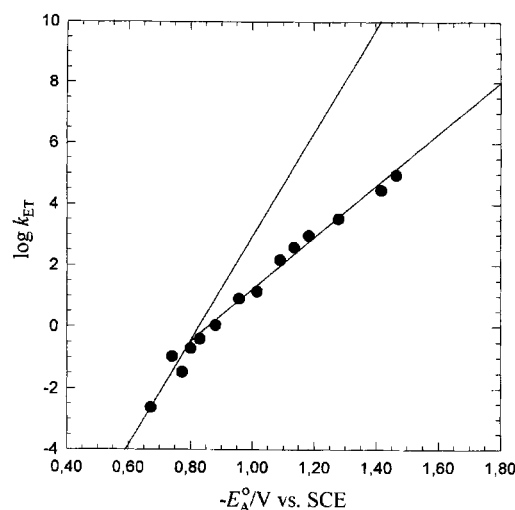
Mediator	$-E_A^\circ/V$ vs. SCE	$k_{ET}/M^{-1} s^{-1}$
Phenazine ^a	1.090	7.5×10^{-4}
4-Chloroazobenzene ^a	1.183	0.038
Azobenzene ^a	1.279	0.20
1,4-Diacetylbenzene ^a	1.406	0.62
1,4-Dicyanobenzene ^a	1.485	5.4
Perylene ^b	1.613	25
Fluoranthene ^b	1.688	130
9,10-Diphenylanthracene ^b	1.794	1270
Anthracene ^b	1.890	7900
Pyrene ^b	2.018	46000

^a Measured by a potentiostatic method in which the rate constant k_{ET} was calculated from the first half-life of the reaction. ^b Measured by cyclic voltammetry.

Table 5. Rate constants k_{ET} obtained for the reaction between different aromatic radical anions and di-*tert*-butyl disulfide in 0.1 M TBABF₄-DMF at 25 °C.

Mediator	$-E_A^\circ/V$ vs. SCE	$k_{ET}/M^{-1} s^{-1}$
1,4-Dicyanobenzene ^a	1.485	3.6×10^{-3}
Tetracene ^a	1.505	4.3×10^{-3}
Quinoxaline ^a	1.589	0.042
Perylene ^a	1.613	0.046
Fluoranthene ^a	1.688	0.16
9,10-Diphenylanthracene ^a	1.794	0.83
Anthracene ^b	1.890	8.9
Pyrene ^b	2.018	88
Isoquinoline ^b	2.131	890
Chrysene ^b	2.182	3600
Benzonitrile ^b	2.230	11000
<i>p</i> -Tolunitrile ^b	2.337	62000

^a Measured by a potentiostatic method in which the rate constant k_{ET} was calculated from the first half-life of the reaction. ^b Measured by cyclic voltammetry.


Fig. 2. Plot of $\log k_{ET}$ vs. $-E_A^\circ$ for the electron transfer reaction between some electrochemically generated aromatic radical anions and diphenyl disulfide in 0.1 M TBABF₄-DMF at 25 °C.

eqn. (13).⁷

$$E_p^{\text{red}} = E_{\text{RSSR}/\text{RSSR}}^\circ - \frac{RT}{\alpha_c F} \times \left[0.780 + \ln \left(\frac{D^\ddagger}{k^{\circ, \text{het}}} \right) + \ln \left(\frac{\alpha_c F v}{RT} \right)^\ddagger \right] \quad (13)$$

The diffusion coefficient D was measured to give $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ by comparing the two-electron wave of diphenyl disulfide with the one-electron wave of ferrocene ($D = 1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) at a rotating disk electrode. Inserting the relevant values then leads to $k^{\circ, \text{het}} = 2 \times 10^{-3} \text{ cm s}^{-1}$, $4 \times 10^{-4} \text{ cm s}^{-1}$ and $1 \times 10^{-5} \text{ cm s}^{-1}$ at a gold, glassy carbon and platinum electrode, respectively, thus illustrating the importance of the electrode material on the heterogeneous electron transfer process. Note also that the $k^{\circ, \text{het}}$ values obtained are

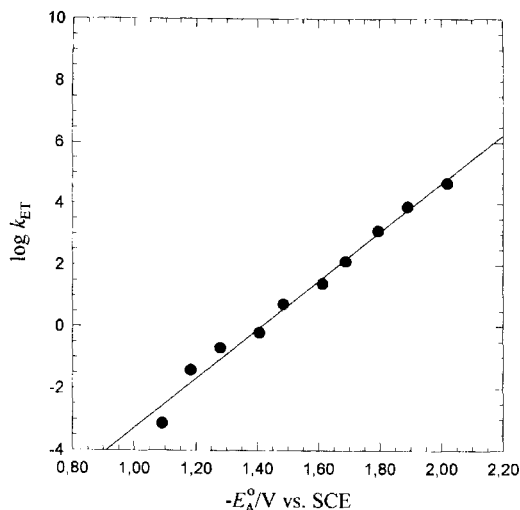


Fig. 3. Plot of $\log k_{\text{ET}}$ vs. $-E_{\text{A}}^{\circ}$ for the electron transfer reaction between some electrochemically generated aromatic radical anions and dimethyl disulfide in 0.1 M TBABF₄-DMF at 25 °C.

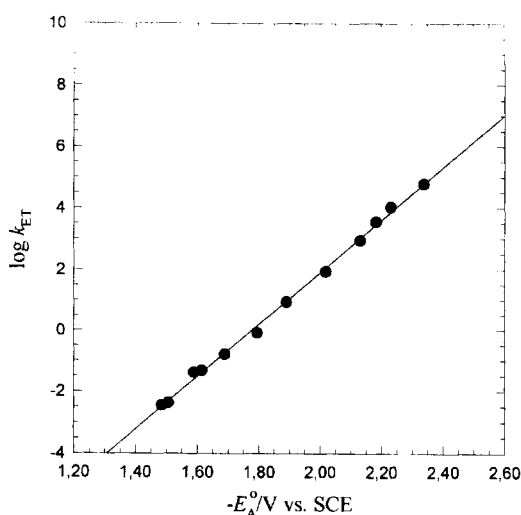


Fig. 4. Plot of $\log k_{\text{ET}}$ vs. $-E_{\text{A}}^{\circ}$ for the electron transfer reaction between some electrochemically generated aromatic radical anions and di-*tert*-butyl disulfide in 0.1 M TBABF₄-DMF at 25 °C.

sufficiently small to allow the process to be treated as the irreversible case.⁷

The most interesting feature of the two figures pertaining to dimethyl disulfide and di-*tert*-butyl disulfide is the lack of a region controlled by diffusion of the backward reaction. The $k_{\text{c}}/k_{-\text{ET}}$ values determined for di-*tert*-butyl disulfide would therefore not be expected to attain a constant value with the mediators used in this study. Actually it may be that this region is about to appear in the case of dimethyl disulfide for the two most endergonic reactions investigated but this tendency could not be confirmed by further measurements due to experimental limitations. The general behaviour observed for the aliphatic disulfides is most likely to be attributed to

an even higher self-exchange reorganization energy compared with diphenyl disulfide. PM3 calculations support this view since the charge in the corresponding radical anions is found to be localized more on the sulfur atoms in the former cases.

In principle the straight line showing an activation-controlled process for the two aliphatic disulfides might also be due to a dissociative electron transfer mechanism even though the $k_{\text{c}}/k_{-\text{ET}}$ measurements clearly did not point in this direction. However, in order to exclude this possibility rigorously from a theoretical point of view, the experimental results obtained for all three disulfides were compared with the predictions provided by theory for the dissociative electron transfer process.^{8,24} Such an analysis has previously been performed for a number of alkyl halides^{8,24-26} and di-*tert*-butyl peroxide²⁷ as electron acceptors. The extensive study of alkyl halides has in general shown agreement between experiment and theory especially when the alkyl halide is sterically hindered, even though reports have appeared indicating deviations at the extremes of the driving force interval.²⁸⁻³⁰ The experimental rate constants for di-*tert*-butyl peroxide were found to be appreciably lower than expected which was interpreted to suggest a non-adiabatic rather than an adiabatic electron transfer mechanism.

According to Ebersson²⁴ and Savéant⁸ the activation Gibbs energy ΔG^{\ddagger} for the dissociative electron transfer may be expressed as shown in eqn. (14).

$$\Delta G^{\ddagger} = \frac{\lambda_0 + \Delta G_{\text{BDE}}^{\circ}(\text{RSSR})}{4} \times \left(1 - \frac{F(E_{\text{RSSR}/\text{RS}^{\cdot-} + \text{RS}^-}^{\circ} - E_{\text{A}}^{\circ})}{\lambda_0 + \Delta G_{\text{BDE}}^{\circ}(\text{RSSR})} \right)^2 \quad (14)$$

The parameter $\Delta G_{\text{BDE}}^{\circ}(\text{RSSR})$ is the bond dissociation Gibbs energy of the S-S bond in the disulfide, λ_0 is the solvent reorganisation energy and $E_{\text{RSSR}/\text{RS}^{\cdot-} + \text{RS}^-}^{\circ}$ is defined as the standard potential of the reduction process $\text{RSSR} + \text{e} \rightleftharpoons \text{RS}^{\cdot-} + \text{RS}^-$. $\Delta G_{\text{BDE}}^{\circ}(\text{RSSR})$ can be extracted from the bond dissociation energy $\Delta H_{\text{BDE}}^{\circ}(\text{RSSR})$ by correcting for the entropy term. While the values of $\Delta H_{\text{BDE}}^{\circ}(\text{RSSR})$ for diphenyl disulfide and dialkyl disulfides are known and given as 51 and 72 kcal mol⁻¹, respectively,^{31,32} the entropy is unknown for the sulfur-centred radicals in question, the exception being methylthiyl. For dimethyl disulfide^{31,32} $\Delta G_{\text{BDE}}^{\circ}(\text{RSSR})$ is lower than $\Delta H_{\text{BDE}}^{\circ}(\text{RSSR})$ by 10 kcal mol⁻¹ and because of insufficient data this will also be assumed to be valid for the two other disulfides studied in this paper. In the case of di-*tert*-butyl disulfide this assumption is justified by the entropies, which can be estimated by use of Benson's additivity rules.³³ A similar calculation is impossible for diphenyl disulfide owing to the lack of a group contribution of the [C_B-S'] group. The solvent reorganisation energy λ_0 can, to within small variations, be estimated at 15 kcal mol⁻¹ for all three disulfides using the procedure described by Savéant^{8,34} and the standard

potential $E_{\text{RSSR}/\text{RS}^+ + \text{RS}^-}^\circ$ may be obtained from a simple thermochemical cycle incorporating the standard potential of the RS^+ species, $E_{\text{RS}^+/\text{RS}^-}^\circ$, and $\Delta G_{\text{BDE}}^\circ$ (RSSR) [eqn. (15)]. Even though the standard potential $E_{\text{RS}^+/\text{RS}^-}^\circ$

$$FE_{\text{RSSR}/\text{RS}^+ + \text{RS}^-}^\circ = FE_{\text{RS}^+/\text{RS}^-}^\circ - \Delta G_{\text{BDE}}^\circ (\text{RSSR}) \quad (15)$$

is not always accessible experimentally by direct measurement a reasonable estimate can often be obtainable through a thermochemical cycle incorporating, as shown in eqns. (16) and (17), the $\text{p}K_{\text{a}}$, the bond dissociation

$$FE_{\text{RS}^+/\text{RS}^-}^\circ = \Delta G_{\text{BDE}}^\circ (\text{RSH}) - 2.303RT\text{p}K_{\text{a}} + FE_{\text{H}^+/\text{H}^\cdot}^\circ \quad (16)$$

$$\Delta G_{\text{BDE}}^\circ (\text{RSH}) \approx \Delta H_{\text{BDE}}^\circ (\text{RSH}) + \Delta G_{\text{sol}}^\circ (\text{H}^\cdot) - TS^\circ (\text{H}^\cdot) \quad (17)$$

Gibbs energy of the S–H bond in RSH, $\Delta G_{\text{BDE}}^\circ$ (RSH), and the standard potential of the $\text{H}^+/\text{H}^\cdot$ couple, $E_{\text{H}^+/\text{H}^\cdot}^\circ$ ($= -2.69$ V vs. SCE in DMF).³⁵ $\Delta G_{\text{BDE}}^\circ$ (RSH) is approximated by the bond dissociation energy in the gas phase, $\Delta H_{\text{BDE}}^\circ$ (RSH), plus a contribution from the solvation energy of H^\cdot in DMF, $\Delta G_{\text{sol}}^\circ (\text{H}^\cdot) = 3.4$ kcal mol⁻¹, and the entropy of the hydrogen atom in the gas phase, $S^\circ (\text{H}^\cdot) = 27.4$ cal mol⁻¹ K⁻¹. The differences in the solvation and entropy terms of RSH and RS^+ are assumed to be negligible.

Let us first consider the estimation of $E_{\text{RS}^+/\text{RS}^-}^\circ$ and $E_{\text{RSSR}/\text{RS}^+ + \text{RS}^-}^\circ$ for RSSR being equal to diphenyl disulfide. The values of $\text{p}K_{\text{a}}$ and $\Delta H_{\text{BDE}}^\circ$ (RSH) of thiophenol are given as 10.7 in DMF and 83.3 kcal mol⁻¹,^{36,31} respectively, leading immediately to $E_{\text{RS}^+/\text{RS}^-}^\circ = 0.08$ V vs. SCE as calculated from eqns. (16) and (17). However, in the present case $E_{\text{RS}^+/\text{RS}^-}^\circ$ may as well be estimated by a more direct approach using electrochemical data. The oxidation peak potential of a 1 mM solution of thiophenoxide generated from the electrochemical reduction of 0.5 mM diphenyl disulfide was found to be +0.05 V vs. SCE at a scan rate ν of 100 mV s⁻¹. For an $E_{\text{rev}}\text{C}$ mechanism in which the chemical step involves dimerisation of RS^+ , the relationship between the oxidation peak potential E_{p}^{ox} and the reversible potential $E_{\text{RS}^+/\text{RS}^-}^\circ$ has long been recognized [eqn. (18)].^{7,37}

$$E_{\text{p}}^{\text{ox}} = E_{\text{RS}^+/\text{RS}^-}^\circ + \frac{RT}{F} 0.902 - \frac{RT}{3F} \ln \left(\frac{2RTk_{\text{dim}}[\text{RS}^-]}{3F\nu} \right) \quad (18)$$

By assuming that the rate constant of dimerisation k_{dim} is 6×10^9 M⁻¹ s⁻¹ and that kinetic control is only by the follow-up chemical step³⁸ (at least at small scan rates where $E_{\text{p}}^{\text{ox}} - E_{\text{p}/2}^{\text{ox}}$ is not far from the theoretical value of 39 mV),³⁷ $E_{\text{RS}^+/\text{RS}^-}^\circ$ can be calculated at 0.15 V vs. SCE. This value is not only close to the one obtained above in the thermodynamic approach but also to a corresponding potential measured in acetonitrile (0.1 V vs. SCE) by applying fast cyclic voltammetry and taking into account the mixed kinetic control of the reaction by the oxidation step at the electrode and the chemical dimerisation step.³⁸ The standard potential $E_{\text{RS}^+/\text{RS}^-}^\circ$ in

DMF and acetonitrile would be expected to be of similar size since the anion-solvating abilities of these two solvents are known to be similar.³⁹ Inserting the average value of $E_{\text{RS}^+/\text{RS}^-}^\circ = 0.12$ V vs. SCE into eqn. (15) finally leads to $E_{\text{RSSR}/\text{RS}^+ + \text{RS}^-}^\circ = -1.7$ V vs. SCE for diphenyl disulfide. This value is of the same magnitude or even slightly negative relative to the reduction potential $E_{\text{p}}^{\text{red}}$ measured in cyclic voltammetry, an order of potentials that, as expected, hardly fits the concept of a dissociative ET mechanism. It may also be noted that the Gibbs energy of dissociation of $\text{RSSR}^{\cdot-}$, $\Delta G_{\text{RSSR}^{\cdot-}}^\circ$, corresponding to reaction (6) can be calculated from the potentials estimated above as $FE_{\text{RSSR}/\text{RSSR}^{\cdot-}}^\circ - FE_{\text{RSSR}/\text{RS}^+ + \text{RS}^-}^\circ \approx 7$ kcal mol⁻¹. This positive value of $\Delta G_{\text{RSSR}^{\cdot-}}^\circ$, which suggests the backward reaction of (6) to be feasible on thermodynamic grounds, is in line with the conclusion drawn on the basis of the kinetic measurements made in this study.

The determination of $E_{\text{RSSR}/\text{RS}^+ + \text{RS}^-}^\circ$ for dimethyl disulfide and di-*tert*-butyl disulfide is relatively uncertain since no thermodynamic information is directly available about the acidity of the corresponding thiols RSH in DMF and since the electrochemical oxidation process of the corresponding thiolate ions is characterized by slow charge transfer. The $\text{p}K_{\text{a}}$ value of 1-butanethiol is known in DMSO ($= 17$)³⁶ and this value may be extrapolated to DMF ($= 17.9$) without increasing the uncertainty appreciably.³⁹ The $\text{p}K_{\text{a}}$ of methanethiol and 2-methyl-2-propanethiol would be expected to be of the same magnitude or perhaps slightly higher for the latter species (probably about 20) if the trend in the thiol series is similar to that of the corresponding alcohols. For both thiols $\Delta H_{\text{BDE}}^\circ$ (RSH) can be put equal to 91 kcal mol⁻¹.³¹ The application of eqn. (16) followed by (15) then leads to $E_{\text{RS}^+/\text{RS}^-}^\circ \approx 0.0$ V and -0.1 V vs. SCE and $E_{\text{RSSR}/\text{RS}^+ + \text{RS}^-}^\circ \approx -2.7$ V and -2.8 V vs. SCE for dimethyl disulfide and di-*tert*-butyl disulfide, respectively. First of all it should be noted that the values of $E_{\text{RS}^+/\text{RS}^-}^\circ$ are in reasonable accordance with other thermochemical calculations with acetonitrile as solvent⁴⁰ but that some inconsistency is apparent when compared with the corresponding oxidation potentials E_{p}^{ox} obtained by cyclic voltammetry. While the difference between $E_{\text{RS}^+/\text{RS}^-}^\circ$ and E_{p}^{ox} is about 400 mV for the methanethiolate ion, the two sets of values are close to each other for the 2-methyl-2-propanethiolate ion. Whatever the reason may be for this different behaviour it does not effect the conclusion that the finding of $E_{\text{RSSR}/\text{RS}^+ + \text{RS}^-}^\circ$ values being close to the actual reduction potentials $E_{\text{p}}^{\text{red}}$ strongly suggests the dissociative ET mechanism also to be an unlikely reaction path in these two cases.

Finally, with the relevant parameters estimated, the non-dissociative character of the mechanisms can be confirmed theoretically by evaluating the free energy relationship based on eqn. (14) for all three disulfides in question. The theoretical rate constants may be calculated using a pre-exponential factor equal to 3×10^{11} M⁻¹ s⁻¹ and the most striking feature of such

values is that they are found to be as much as 10–20 orders of magnitude lower than the experimental ones. This deviation is so high that it can hardly be explained by anything other than a mismatch between experiment and model. Even though the uncertainty in the estimation of the parameters λ_0 and $E_{\text{RSSR}/\text{RS}^{\cdot-} + \text{RS}^-}$ is rather high it, at most, accounts for a deviation of three orders of magnitudes. There seems therefore to be no doubt from both an experimental and a theoretical point of view that the radical anions of dimethyl disulfide and di-*tert*-butyl disulfide do exist in DMF and that the absence of a region controlled by diffusion of the backward reaction in the free energy relation plot should indeed be attributed to a high value of the self-exchange reorganization energy $\lambda(0)$. With this knowledge Figs. 3 and 4 may be used to put a lower limit on the values of $E_{\text{RSSR}/\text{RSSR}^{\cdot-}}$ and $\lambda(0)$ for dimethyl disulfide and di-*tert*-butyl disulfide by extending a line of slope 1/59 mV from the point corresponding to the most endergonic reaction to the diffusion-controlled limit ($=10^{10} \text{ M}^{-1} \text{ s}^{-1}$). By this procedure the minimum values of $E_{\text{RSSR}/\text{RSSR}^{\cdot-}}$ and $\lambda(0)$ are found to be -1.9 V vs. SCE and 75 kcal mol^{-1} and -2.2 V vs. SCE and 75 kcal mol^{-1} for dimethyl disulfide and di-*tert*-butyl disulfide, respectively. As a consequence, the corresponding Gibbs energies of dissociation, $\Delta G_{\text{RSSR}^{\cdot-}}$, must be appreciably positive ($>15 \text{ kcal mol}^{-1}$) and the backward reaction of (6) should in principle be favourable.⁴¹ The kinetic measurements in DMF did not firmly confirm this conclusion.

In summary it may be concluded that the radical anions of the three disulfides investigated exist in DMF with a k_c of about $5 \times 10^8 \text{ s}^{-1}$ for diphenyl disulfide and less than $2 \times 10^8 \text{ s}^{-1}$ for di-*tert*-butyl disulfide and presumably dimethyl disulfide. These rate constants were estimated by kinetic measurements using a potentiostatic method. The cleavage of diphenyl disulfide radical anion is a reversible process and the reverse coupling process is fast and close to diffusion control. Whereas relevant parameters such as $E_{\text{RSSR}/\text{RSSR}^{\cdot-}} = -1.4 \text{ V vs. SCE}$ and $\lambda(0) = 65 \text{ kcal mol}^{-1}$ could be obtained for diphenyl disulfide from a plot of $\log k_{\text{ET}}$ against the driving force of the reaction, a similar determination was not possible for the two aliphatic disulfides, owing to a higher value of the self-exchange reorganization energy. However, minimum values of $E_{\text{RSSR}/\text{RSSR}^{\cdot-}}$ and $\lambda(0)$ were found to be -1.9 V vs. SCE and 75 kcal mol^{-1} and -2.2 V vs. SCE and 75 kcal mol^{-1} for dimethyl disulfide and di-*tert*-butyl disulfide, respectively. The compounds of most interest for further investigation seem therefore to be substituted diaryl disulfides. This work is in progress and preliminary results do indeed indicate that both thermodynamic and kinetic information will be accessible in most cases.

Experimental

Materials. Diphenyl disulfide, dimethyl disulfide, di-*tert*-butyl disulfide and methyl *p*-toluenesulfonate were com-

mercially available and distilled or recrystallised from ethanol. Furthermore it was found necessary to sublime diphenyl disulfide before use in the potentiostatic measurements. The solvent *N,N*-dimethylformamide (DMF) and the supporting electrolyte tetrabutylammonium tetrafluoroborate (TBABF₄) were purified according to standard procedures. The mediators were the same as used previously.

Instrumentation. Instrumentation and data treatment procedures have been described in detail elsewhere.¹⁰ The rotating disk electrode system used in the potentiostatic method (Metrohm 628–10, glassy carbon electrodes with $\text{Ø} = 3 \text{ mm}$) was commercially available. The working electrode in the CV measurements was homemade and a glassy carbon, platinum or gold electrode ($\text{Ø} = 30 \text{ }\mu\text{m}$, 0.5 mm or 1 mm) was used. The counter electrode was made of platinum and the reference electrode consisted of a silver wire in $0.1 \text{ M TBABF}_4\text{-DMF}$. The preparative reductions were carried out in an H-cell using a platinum net as the working electrode and the same reference electrode as just described. The counter electrode was a carbon rod positioned in the anodic compartment. The stopped-flow UV equipment consisted of a home built electrochemical flow cell combined with a Hewlett-Packard 8452A diode array spectrophotometer. The cell for UV detection had a path length of 0.2 or 1 cm . GC analyses were performed with a Hewlett-Packard 5890 gas chromatograph with an Hp-1 column: injector temperature $200 \text{ }^\circ\text{C}$; $60 \text{ }^\circ\text{C}$ for 5 min to $250 \text{ }^\circ\text{C}$ at $15 \text{ }^\circ\text{C min}^{-1}$.

Procedure. The rate constants k_{ET} were measured by cyclic voltammetry and linear sweep voltammetry for the faster reactions or by a potentiostatic method using a rotating disk electrode when $k_{\text{ET}} < 10 \text{ M}^{-1} \text{ s}^{-1}$. Both procedures have been described in detail elsewhere.^{10,17} Problems originating from adsorption in CV and LSV could be overcome in most cases by cleaning the electrode surface using multi-scans just before the actual experiment. In a few cases the rate constants were also measured by stopped-flow equipment with UV detection. The radical anions were generated in an electrochemical flow cell and subsequently mixed with a solution containing the disulfide. The decay of the radical anion due to reactions (5) and (7) was followed in the UV cell by recording the absorption spectrum of $\text{A}^{\cdot-}$ as a function of time and the kinetics were treated as described in Ref. 17. For the slower reactions measured by the potentiostatic method the rate constants were harder to reproduce especially in the case of dimethyl disulfide. The uncertainty in all rate constants was estimated to be $\pm 10\%$ but may be larger in the above-mentioned situation.

In the preparative reductions using an H-cell the procedure was as illustrated in the following example: 37 mg anthracene and 0.2 ml di-*tert*-butyl disulfide (fivefold excess) were dissolved in 40 ml $0.1 \text{ M TBABF}_4\text{-DMF}$ solution placed in the cathodic compart-

ment. The solution was deaerated for 15 min with argon before the electrolysis commenced at a controlled potential (-2.0 V vs. SCE) at a platinum net. When 190 C had passed (corresponding to 1.9 electrons per RSSR) the solution became blue due to the production of the radical anion of anthracene, and the electrolysis was stopped. Aqueous hydrochloric acid was added in order to protonate any generated thiolate ion and the products were extracted with diethyl ether. After drying, the diethyl ether was removed *in vacuo* and the products were identified by GC by comparison with authentic samples. The main product detected was 2-methyl-2-propanethiol accompanied by anthracene and small amounts of 9,10-dihydroanthracene. The total amount of anthracene and 9,10-dihydroanthracene corresponded to the amount of anthracene initially added to the electrolyte solution. In a similar reduction with anthraquinone and diphenyl disulfide at -0.8 V vs. SCE, the electron consumption was found to be 2.2 electrons per RSSR and the only product detected besides anthraquinone was thiophenol. If methyl *p*-toluenesulfonate was present in the solution in a concentration at least double the concentration of diphenyl disulfide, the generated thiophenoxide ion was converted completely into methyl phenyl sulfide.

Electroanalytical experiments applying LSV,¹⁰ chronoamperometry¹¹ and a steady-state technique¹² were used to confirm the reaction mechanism given in eqns. (4)–(7). In LSV the I_k/I_r ratio, where I_r is the reversible reduction peak current when only the mediator is present and I_k is the peak current after the substrate is added, was measured at different scan rates and compared with the theoretical behaviour determined from a simulation of the proposed reaction mechanism. Similarly in chronoamperometry I_k/I_r , where the two parameters now symbolize the diffusion-controlled current of the mediator with and without RSSR, was measured at a potential $E = E_A^\circ - 200$ mV for different step times and compared with theoretical curves. The agreement between experiment and theory was excellent in all cases investigated, i.e., the reactions between diphenyl disulfide and the mediators azobenzene, 4-chloroazobenzene and phenazine and the reactions between di-*tert*-butyl disulfide and the mediators isoquinoline, pyrene and anthracene. For a few of the slower reactions (perylene and di-*tert*-butyl disulfide, anthraquinone and diphenyl disulfide, and 1,2-benzanthraquinone and diphenyl disulfide) the catalytic efficiency of the mechanism was determined by a steady-state technique using a rotating disk electrode. By measuring the changes in the steady-state currents of A and A⁻ in the reaction with RSSR, A⁻ was found to be converted exclusively into A in accordance with the proposed mechanism.

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