A Comparative Evaluation of the Voltammetric Behaviour of Phenyl Methyl Sulfone, Phenyl Methyl Sulfide and Phenyl Methyl Sulfoxide in *N,N*-Dimethylformamide on a Glassy Carbon Electrode

Subbiah Chellammal, Michael Noel and Payyallar Narayanan Anantharaman
Central Electrochemical Research Institute, Karaikudi 623 006, India

Detailed voltammetric studies of $PhSO_2Me$, PhSOMe and PhSMe in DMF containing 0.1 mol dm^{-3} TBAP media on glassy carbon electrodes indicate significant weak adsorption of all three sulfur compounds. Weakly adsorbed species also get reduced in the same potential region where solution species are reduced. Comparative studies indicate a significantly higher apparent '*n*' value of 2.2 ± 0.2 for PhSOMe when compared to 1.7 ± 0.2 for the other two compounds. Formation of phenyl sulfinate at the same potential during PhSOMe reduction is confirmed by the oxidation wave in reverse sweep. A modified disproportionation reaction scheme involving $[PhSOMe]^{-}$ radical anion leading to the formation of $[PhSMe]^{2-}$ and $[PhSO_2Me]$ is proposed. Since the dianionic sulfide species undergoes fast, irreversible dissociation, the reduction peak due to this sulfide species is not observed at more negative potential. An interaction between PhS^{-} species and PhSOMe species is also indicated by the anodic voltammetric response.

Among sulfur compounds which are substituted by phenyl and methyl groups, phenyl methyl sulfone has received considerable attention in the electrochemical literature due to its relatively easy reduction at lower potentials in aqueous[1] and mixed aqueous solvents.[2] Although an earlier report suggested a 4e reduction of phenyl methyl sulfone to give phenyl methyl sulfide, subsequent studies unequivocally established that the electroreduction involves a 2e step leading to the formation of sulfinic acid.[3,4] [eqn. (1), where BH is the water molecule or any other solvent].

$$PhSO_2Me + 2e + BH \longrightarrow PhSO_2^- + MeH + B^- \quad (1)$$

The effect of the substituents in the aryl and alkyl groups on the position of S–C bond cleavage has remained as a major point of study using polarographic[5,6] and preparative electrolysis techniques.[7] Conversion of petroleum-based sulfur compounds into their sulfones and subsequent detection using polarography have been recommended.[8,9] In aprotic solvents, trapping of anion radicals[10] and reductive cleavage of other leaving groups in the aryl ring have been reported.[11]

In protic solvents, phenyl methyl sulfoxide is reduced to phenyl methyl sulfide.[2,12] Solvent and protonating agents have a significant effect on the polarographic behaviour.[12] In strongly acidic media, catalytic H_2 evolution is also observed.[13,14] In an interesting voltammetric study of diphenyl sulfoxide on Hg electrodes, disproportionation of the anion radical of diphenyl sulfoxide to the corresponding sulfide and sulfone was reported.[15] This effect has not yet been reported for phenyl methyl sulfoxide. In addition to the studies on the sulfones and sulfoxides cited above, a few reports on the polarographic reduction of phenyl methyl sulfide[16] and other sulfides[16,17] are also available.

The above literature survey, and a recent review[18] indicates that most of these reductions have been carried out on mercury electrodes and the behaviour of sulfoxides and sulfides have received less attention than that of sulfones. In this paper, voltammetry of the three parent compounds, phenyl methyl sulfone, sulfoxide and sulfide, was studied using a glassy carbon electrode. The role of adsorption, possible disproportionation[15] and the nature of radical anions formed were investigated.

Experimental

A 5 mm diameter, high purity Glassy Carbon rod (Tokai GC-A) embedded in a glass tube, was polished to a mirror finish using up to 5/0 emery, cleaned and used as the working electrode. No specific electrochemical activation of the electrode was required for use in the DMF media employed here. Pt counter electrode and Ag/AgCl reference electrode were used in a single compartment 25 cm^3 capacity glass cell.

AR Grade samples of phenyl methyl sulfone ($PhSO_2Me$), phenyl methyl sulfoxide (PhSOMe) and phenyl methyl sulfide (PhSMe) obtained from Aldrich (Germany) were used without further purification. AR Grade *tert*-butylammonium perchlorate (TBAP, Aldrich) was kept in a dessicator and used as received. AR Grade *N,N*-dimethylformamide (DMF, SISCO, India) was however refluxed with P_2O_5 and distilled twice before use. The second distillation, was carried out immediately prior to use.

Wenking potentiostat (Model 75 L FRG) Scan generator (VSG 72 FRG) and Rikadenki recorder (X-Y/t) were used for cyclic voltammetric experiments. All the experiments were carried out at 25 ± 0.5 °C.

Results and Discussion

Voltammetric Behaviour of Phenyl Methyl Sulfone.—Phenyl methyl sulfone ($PhSO_2Me$) gives a cathodic peak (i_{pc}) at about −2.2 V at a glassy carbon electrode (GCE) in DMF containing 0.1 mol dm^{-3} TBAP and on the reverse sweep an anodic peak (i_{pa}) at +0.5 V (Fig. 1). The peak potential of i_{pc} is shifted to more negative values by about 100 mV with a ten-fold increase in sweep rate and by about 250 mV with ten-fold increase in concentration of $PhSO_2Me$ (Table 1). Peak i_{pa} is much smaller than i_{pc} and the ratio $i_{pc}:i_{pa}$ increased with increasing V.

Cathodic peak i_{pc} is a linear function of the sulfone concentration, at least up to 6 mol dm^{-3} with a small positive intercept on the $i_{pc} = f(c)$ plot. Plots of $i_{pc} = f(V^{1/2})$ are linear but show a considerable positive intercept (Fig. 1, insert). Consequently, the values of $i_{pc}/V^{1/2}$ increase with decreasing rate of scanning [Fig. 2(*a*)].

All these observations may be explained by a weak adsorption of reactant,[19–21] similar to adsorption of other organic sulfur compounds in aqueous[22] and non-aqueous[23]

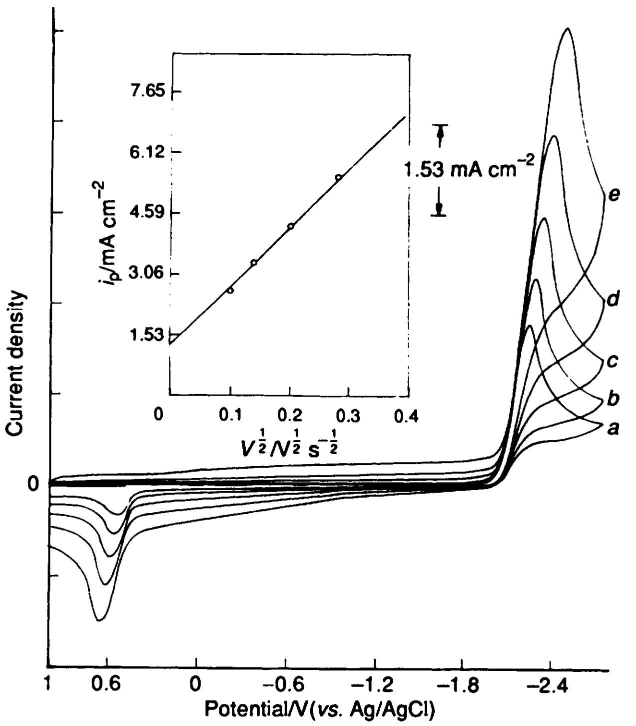


Fig. 1 Cyclic voltammograms for the reduction of PhSO$_2$Me on GCE in 0.1 mol dm^{-3} TBAP/DMF at various sweep rates. PhSO$_2$Me conc. 7.4 mmol dm^{-3}. (*a*) 40; (*b*) 80; (*c*) 160; (*d*) 320; (*e*) 640 mV s^{-1}.

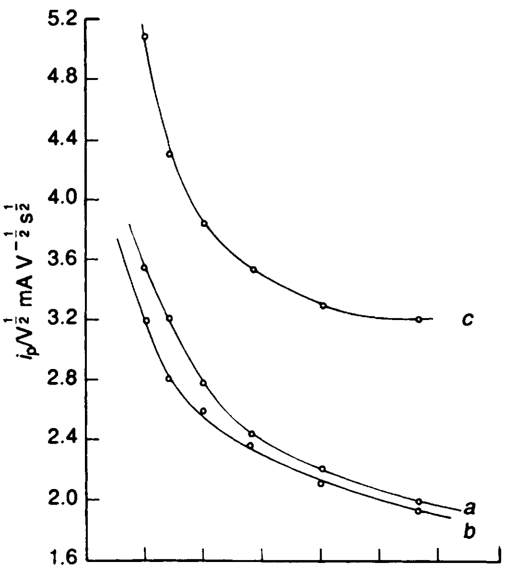


Fig. 2 Plot of $i_p/V^{1/2}$ *vs.* $V^{1/2}$ at concn. = 7.4 mmol dm^{-3}: (*a*) PhSO$_2$Me; (*b*) PhSMe; (*c*) PhSOMe

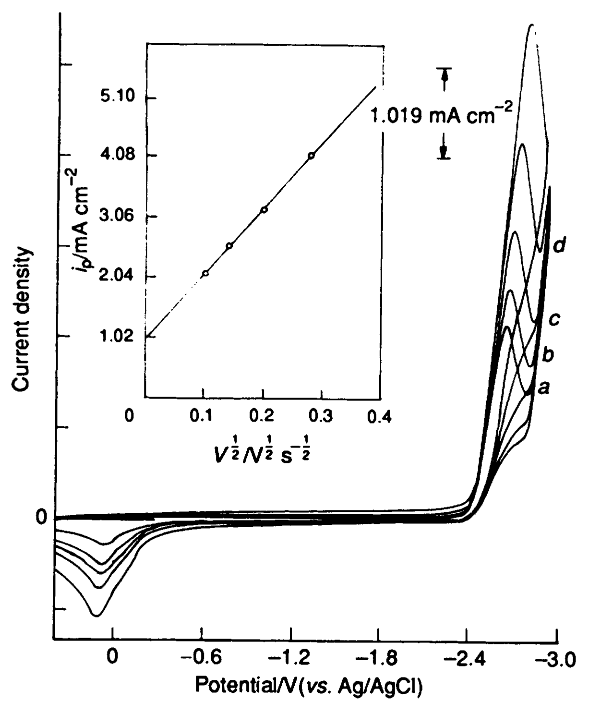


Fig. 3 Cyclic voltammograms of PhSMe reduction on GCE in 0.1 mol dm^{-3} TBAP/DMF at various sweep rates. PhSMe conc. 9 mmol dm^{-3}. (*a*) 10; (*b*) 20; (*c*) 40; (*d*) 80; (*e*) 160 mV S^{-1}.

media. Another possible cause for the positive intercepts in the i_p *vs.* $V^{1/2}$ and i_p *vs.* C plots may be the presence of a steady background current due to solvent-supporting electrolyte (SSE) decomposition. To verify whether this is due to an electrode effect or a solvent-supporting electrolyte effect a few cyclic voltammetric measurements were also made on HMDE. In these experiments similar positive intercepts were also noticed on the current axis, which confirms that these intercepts are due to the solvent-supporting electrolyte effect rather than a surface effect.

Assuming a minor contribution from such adsorption or SSE effect at high sweep rates and high concentations where values of $i_{pc}/CV^{1/2}$ remain reasonably constant, the '*n*' value of the overall EC$_i$ reaction was calculated from the peak current expression,[21] $i_p = 2.98 \times 10^5 \times n^{3/2} \times AC\,V^{1/2}\,D^{1/2}$. For these calculations, since accurate D values for PhSO$_2$Me in DMF are not available in the literature, it was assumed that the D value of PhSO$_2$Me would be close to the D value of 7.38×10^{-6} cm^2 s^{-1} obtained for PhSMe in DMF.[16] From these calculations the average '*n*' value was found to be 1.7 ± 0.2. The overall reduction can thus be represented by reaction (1), as obtained for the same reaction on mercury electrodes.

Voltammetric Behaviour of Phenyl Methyl Sulfide.—The voltammetric response of phenyl methyl sulfide (PhSMe) in 0.1 mol dm^{-3} TBAP/DMF on GCE is qualitatively quite similar to that of PhSO$_2$Me presented above. It gives a cathodic peak (i_{pc}) at about −2.6 V and on reverse scan a small anodic peak (i_{pa}) with a closely spaced prewave at 0.0 V. The peak potential is shifted to more negative values and the ratio $i_{pc}:i_{pa}$ increases with increasing sweep rate.

Plots of $i_{pc} = f\,(V^{1/2})$ are linear but show a considerable positive intercept (Fig. 3, insert). The decreasing $i_{pc}/V^{1/2}$ value with sweep rate for this compound is depicted in Fig. 2(*b*) which is quite similar to Fig. 2(*a*) for PhSO$_2$Me.

At high sweep rates and concentrations of PhSMe, where the values of $i_{pc}/CV^{1/2}$ remain fairly constant, efforts towards calculating the '*n*' value using the EC$_i$ reaction scheme were made. Using $D = 7.38 \times 10^{-6}$ cm^2 s^{-1} for this compound, available in the literature,[16] the '*n*' value was calculated to be 1.7 ± 0.2. The prewave appearing close to the anodic peak may be due to the oxidation of adsorbed PhS$^-$ species.[24] Based on this evidence, it may be concluded that the overall reduction for PhSMe in DMF on GCE may be represented as in eqn. (2).

$$\mathrm{PhSMe + 2e + BH \longrightarrow PhS^- + MeH + B^-} \qquad (2)$$

Voltammetric Behaviour of Phenyl Methyl Sulfoxide.—In voltammetry phenyl methyl sulfoxide (PhSOMe) in DMF containing 0.1 mol dm^{-3} TBAP on GCE displays a cathodic peak (i_{pc}) at about −2.4 V and two anodic peaks i_{pa1} and i_{pa2} at

Table 1 Comparison of the peak currents and peak potentials for the reduction of $PhSO_2Me$, PhSOMe and PhSMe on GCE in 0.1 mol dm^{-3} TBAP/DMF at various sweep rates and concentrations

Concentration/mmol dm^{-3}	Sweep rate/V s^{-1}	i_{pc}/mA			$-E_{pc}$/V		
		$PhSO_2Me$	PhSOMe	PhSMe	$PhSO_2Me$	PhSOMe	PhSMe
1.96	0.02	0.118	0.173	0.115	2.14	2.34	2.60
	0.04	0.158	0.223	0.160	2.16	2.36	2.62
	0.08	0.208	0.296	0.210	2.18	2.38	2.68
	0.16	0.281	0.403	0.280	2.20	2.40	2.70
3.8	0.02	0.220	0.345	0.226	2.17	2.38	2.63
	0.04	0.300	0.430	0.293	2.19	2.40	2.64
	0.08	0.385	0.565	0.383	2.22	2.42	2.67
	0.16	0.505	0.760	0.516	2.24	2.44	2.70
7.4	0.02	0.413	0.610	0.425	2.22	2.40	2.66
	0.04	0.520	0.770	0.535	2.24	2.42	2.70
	0.08	0.670	1.010	0.690	2.26	2.44	2.72
	0.16	0.850	1.320	0.915	2.32	2.48	2.76
9.1	0.02	0.520	0.760	0.506	2.24	2.42	2.66
	0.04	0.609	0.950	0.626	2.26	2.46	2.70
	0.08	0.795	1.220	0.813	2.28	2.48	2.72
	0.16	1.010	1.590	1.079	2.32	2.54	2.78

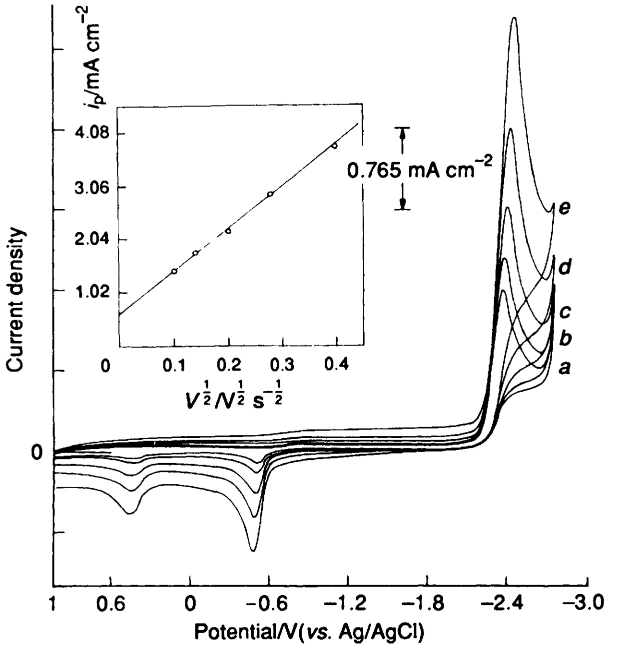


Fig. 4 Cyclic voltammograms for the reduction of PhSOMe on GCE in 0.1 mol dm^{-3} TBAP/DMF at various sweep rates. PhSOMe Conc. = 3.8 mmol dm^{-3}. (*a*) 10; (*b*) 20; (*c*) 40; (*d*) 80; (*e*) 160 mV s^{-1}.

−0.5 V and +0.5 V respectively. The peak potential of i_{pc} is shifted to more negative values by about 100 mV with a ten-fold increase in sweep rate (Table 1).

Cathodic peak i_{pc} is a linear function of concentration of the sulfoxide, at least up to 6 mmol dm^{-3}, with a small positive intercept on the $i_{pc} = f(c)$ plot. Plots of $i_{pc} = f(V^{1/2})$ are also linear with positive intercepts (Fig. 4, insert). In all these respects the voltammetric responses for PhSOMe are quite similar to those of $PhSO_2Me$ and PhSMe, except that the cathodic peak current (i_{pc}) values of PhSOMe are significantly higher than the above [Table 1, Fig. 2(*c*)].

Since the molecular dimensions of $PhSO_2Me$, PhSOMe and PhSMe are not likely to be substantially different, the major difference in the peak current values is not likely to be due to the difference in their diffusion coefficient. Using the peak current expression for the EC_i reaction mechanism and reasonably constant experimental $i_{pc}/CV^{1/2}$ values from Fig. 4, the '*n*' value for this compound was calculated to be around $n = 2.2 \pm 0.2$. This suggests that, on the voltammetric time scale itself, PhSOMe undergoes disproportionation producing $PhSO_2Me$ which can also get reduced simultaneously at that potential, giving rise to an '*n*' value significantly greater than 2. The observation of an anodic oxidation peak around +0.5 V in the present case (Fig. 4) as well as during $PhSO_2Me$ reduction (Fig. 1) lends further support to the above conclusion.

As mentioned in the introductory section, a similar disproportionation effect was first observed earlier for diphenyl sulfoxide.[15] The following mechanism was proposed (Scheme 1).

$$\text{Ph–SO–Ph} + e \rightleftharpoons [\text{Ph–SO–Ph}]^{\cdot -} \quad (3)$$

$$2[\text{Ph–SO–Ph}]^{\cdot -} \longrightarrow [\text{Ph–S–Ph, PhSO}_2\text{Ph}]^{2-} \quad (4)$$

$$\xrightarrow[\text{Protonation}]{\text{Slow}} \text{Ph–S–Ph} + \text{PhH} + \text{PhSO}_2^- \quad (5)$$

Scheme 1

The main evidence produced for the disproportionation mechanism presented in Scheme 1 in the earlier work[15] was the formation of the phenyl sulfinate ($PhSO_2^-$) during the coulometric experiments.

A major objection, however, can be levelled against the above reduction mechanism reaction (4) which leads to the formation of diphenyl sulfide. The corresponding reduction peak was not observed on the voltammetric time scale because of its slow generation during the disproportionation mechanism. Two experimental results presented above (Fig. 2) clearly show that, in the case of PhSOMe at least, the disproportionation reaction proceeds significantly within the voltammetric time scale itself. However no cathodic peak due to PhSMe is observed around −2.6 V in the absence of protonating agents.

In the present experiments, PhSMe formation could be confirmed only when protonating agents like H_2O were added; with the addition of increasing quantities of water, the i_{pc} peak due to PhSOMe decreases and simultaneously a new cathodic peak due to PhSMe reduction appears (Fig. 5).

In the presence of a stronger protonating agent like *o*-cresol

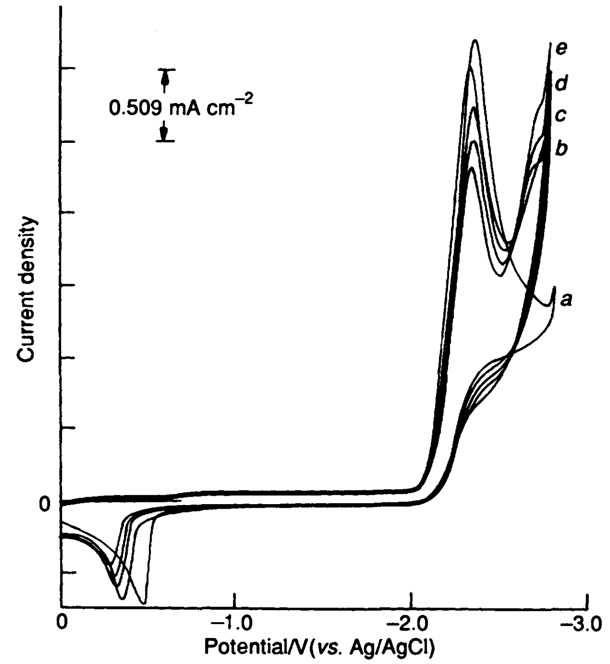


Fig. 5 Effect of water as proton donor on the reduction of PhSOMe on GCE in 0.1 mol dm^{-3} TBAP/DMF at 40 mV s^{-1}. (*a*) Ph SOMe conc. 5.7 mmol dm^{-3}; (*b*) *a* + 2 × 10^3 mmol dm^{-3} H_2O; (*c*) *a* + 5.6 × 10^3 mmol dm^{-3} H_2O

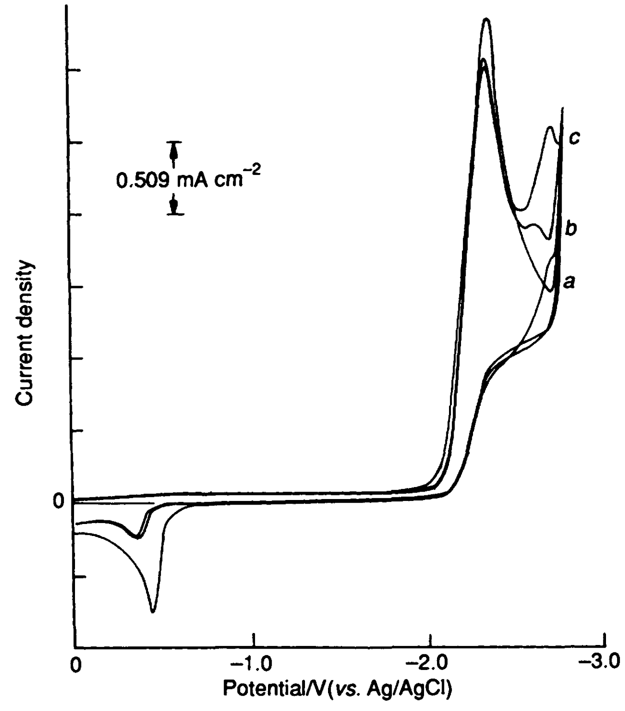


Fig. 6 Effect of *o*-cresol as proton donor on the reduction of PhSOMe on GCE in 0.1 mol dm^{-3} TBAP/DMF at 40 mV s^{-1}. (*a*) PhSOMe conc. 5.7 mmol dm^{-3}; (*b*) *a* + 7 mmol dm^{-3} *o*-Cresol; (*c*) *a* + 10 mmol dm^{-3} *o*-cresol

even millimolar concentrations lead to the formation and hence reduction of PhSMe (Fig. 6). In the earlier work on diphenyl sulfoxide also, in the presence of protonating agents, a reduction wave due to diphenyl sulfide could be observed.[15] Based on these observations, it may be concluded that PhSOMe is reduced to PhSMe only in the presence of protonating agents [eqn. (6)].

$$\mathrm{PhSOMe} + 2e + 2\,\mathrm{BH} \longrightarrow \mathrm{PhSMe} + \mathrm{H_2O} + 2\mathrm{B}^- \quad (6)$$

In the absence of protonating agent, a modified disproportionation reaction scheme, proposed in Scheme 2, would explain all the experimental observations presented above in a consistent manner.

$$\mathrm{Ph\text{-}SO\text{-}CH_3} + e \rightleftharpoons [\mathrm{Ph\text{-}SO\text{-}CH_3}]^{\bullet -} \quad (7)$$

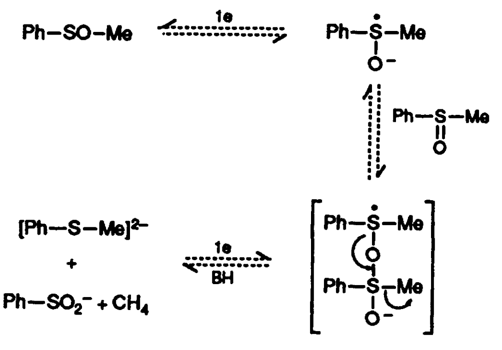
$$2[\mathrm{Ph\text{-}SO\text{-}CH_3}]^{\bullet -} \longrightarrow [\mathrm{Ph\text{-}S\text{-}CH_3}]^{2-} + [\mathrm{Ph\text{-}SO_2\text{-}CH_3}] \quad (8)$$

$$[\mathrm{Ph\text{-}S\text{-}CH}]^{2-} + \mathrm{BH} \xrightarrow{\text{fast}} \mathrm{PhS}^- + \mathrm{CH_4} + \mathrm{B}^- \quad (9)$$

$$\mathrm{Ph\text{-}SO_2\text{-}CH_3} + 2e + \mathrm{BH} \longrightarrow \mathrm{PhSO_2^-} + \mathrm{CH_4} + \mathrm{B}^- \quad (1)$$

Scheme 2

The crucial difference between the two reaction schemes (1 and 2) is that in Scheme 1 the dianionic species is proposed to be sulfone [reaction (4)] whereas in the present case the dianionic species is sulfide [reaction (8)]. Although the sulfone is more easily reducible (and hence formation of a sulfone dianion intermediate could be predicted) it appears that the oxygen transfer is facilitated by higher electron density on the S atom that releases the oxygen (Scheme 3).



Scheme 3

Since the PhSMe dianion thus produced would be highly unstable, it would immediately dissociate and hence no reduction wave for PhSMe would be obtained at more negative potentials. This mechanism probably also accounts for the voltammetric responses for diphenyl sulfide reported earlier.

One further question however can be raised regarding reaction Scheme 2 proposed above. If the reaction scheme is correct then the $\mathrm{PhS^-}$ anion should be generated during the reaction of PhSOMe as well [reaction (9)]. This should give rise to an oxidation peak around 0.0 V as noticed in Fig. 3. But in the CV curves of PhSOMe, this peak is not observed. Instead another oxidation peak is observed around −0.5 V. This new peak is probably due to the oxidation of some associated complex of $\mathrm{PhS^-}$ and PhSOMe species. Such complex species involving S–S linkages are not at all uncommon in sulfur chemistry[25] and such complexed species can certainly get oxidised at lower potentials. Evidence in favour of this conclusion is provided in Fig. 7. The voltammetric response of 3.7 mmol dm^{-3} PhSOMe is presented in Fig. 7(*a*). On adding 6.9 mmol dm^{-3} PhSMe to this solution the anodic peak current at −0.5 V increases significantly at the expense of the anodic peak around 0.0 V. This suggests that $\mathrm{PhS^-}$ generated during direct reduction of PhSMe also interacts preferably with PhSOMe and gets oxidised at lower potentials, Fig. 7(*b*). Further studies on this point, however would certainly be worthwhile.

Conclusions

The comparative investigation of electroreduction of $\mathrm{PhSO_2Me}$, PhSOMe and PhSMe in DMF containing 0.1 mol dm^{-3} TBAP

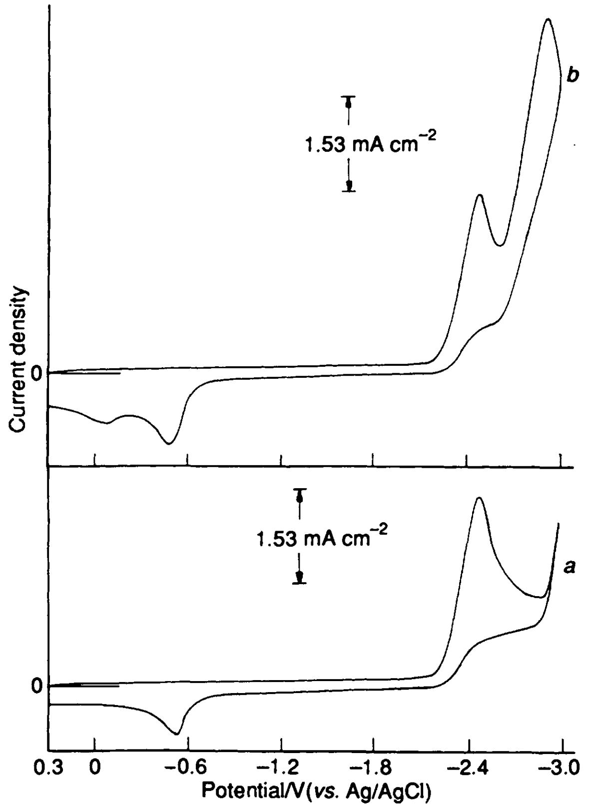


Fig. 7 Cyclic voltammograms for the reduction of (*a*) PhSOMe (conc. 3.7 mmol dm^{-3}); (*b*) *a* + 6.9 mmol dm^{-3} PhSMe on GCE in 0.1 mmol dm^{-3} TBAP/DMF; sweep rate 40 mV s^{-1}

solutions reveals that these compounds exhibit weak adsorption effects on GCE. The effects are predominantly seen at low concentrations and PhSMe from the bulk electrolyte medium on GCE. They are, however, quite similar to those reported in the literature on Hg electrode. The S–CH$_3$ bond cleavage occurs in both PhSO$_2$Me and PhSMe leading to the formation of PhSO$_2^-$ and PhS$^-$ ionic species. Some interesting effects due to the electrochemically induced disproportionation reaction noticed earlier for diphenyl sulfoxide on Hg were also noticed for PhSOMe in the present study, on the voltammetric time scale itself. A slightly modified reaction scheme involving unstable PhSMe dianion formation is proposed to interpret the present results. Efforts have also been made to identify the intermediates or products generated during the cathodic sweep and by the oxidation peaks generated during the anodic sweep. These predictions, however, require further confirmation.

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Paper 2/05253I
Received 30*th September* 1992
Accepted 26*th January* 1993