Voltammetric Behaviour of Mono- and Di- Nitro Aromatic Sulphides in N, N - Dimethyl formamide on a Glassy Carbon Electrode

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The heterogeneous reversible charge transfer rate constant (k_h) values for the one electron quasi-reverisble charge transfer process involved in electrochemical reduction of methyl p-nitro phenyl sulphide, p-nitro diphenyl sulphide and p, p-dinitro diphenyl sulphide were calculated. The slower charge transfer rate observed in the case of p,p'-dinitro diphenyl sulphide as compared to the two mono nitro compounds is probably related to a slight blocking type adsorption. In aprotic solvents, addition of poor protonating agents like water competes with the adsorption of these sulphides. A strong protonating agent like benzoic acid leads to a single four electron reduction in the first reduction potential region itself.

Detailed investigations on the voltammetric behaviour of many aromatic nitro compounds in different media are reported in the literature [1-3]. The substituent effect on the electro reduction of different nitro aryl sulphides have also received some attention [4-7]. The radical ion stability has also been established using ESR measurements [8,9]. These studies mainly concentrate on the first one electron reduction step on Hg and Pt electrodes. Subsequent reduction of the anion radical has received lesser attention. The electoreduction of these compounds on GCE and the effect of protonating agents and ion-pair forming agents on the electroreduction of these compounds have not been reported so far. Hence, a comparative evaluation of the electro-reduction of methyl p-nitro phenyl sulphide, p-nitro diphenyl sulphide and p, p-dinitro diphenyl sulphide in DMF medium on GCE is presented in this work. In addition to evaluating the voltammetric behaviour over a wide potential range, the effect of water and benzoic acid (weak and strong protanating agents) have also been studied.

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 carried out for use in the DMF media. Pt counter electrode and Ag/AgCl reference electrode were used in a single compartment 25 cm^3 capacity glass cell. AR grade sample of methyl p-nitrophenyl sulphide (Aldrich) was used in the study. P-nitro diphenyl sulphide [10] and dinitro diphenyl sulphide [11] were synthesised and used. AR grade tetra butyl ammonium perchlorate (TBAP, Aldrich) and benzoic acid were kept in a desiccator and used as received. AR grade N, N-dimethyl formamide (DMF, SISCO India) was further purified by refluxing with P_2O_5 and distilling twice before use. The second distillation was carried out immediately piror to use.

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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±0.2°C.

RESULTS AND DISCUSSION

Cyclic Voltammograms of Mononitro Compounds

Cyclic Voltammograms of methyl p-nitrophenyl sulphide and p-nitro diphenyl sulphide in the potential range of 0.0V to -1.3V (*vs* Ag/AgCl) at different scan rates were recorded. Typical curves are given in Fig.1. In this potential region, both these compounds give rise to a reversible redox peak suggesting the formation of stable anion redical (equn. 1).

$$ArNO_2 + e^- \longrightarrow ArNO_2^{\cdot-} \quad \ldots (1)$$

The i_{pc} increase linearly with $v^{1/2}$. The E_p values for the cathodic and anodic peaks shift with scan rates in the opposite directions. The ΔE_p therefore increases with scan rate suggesting quasi-reversible nature of the electron transfer process involved.

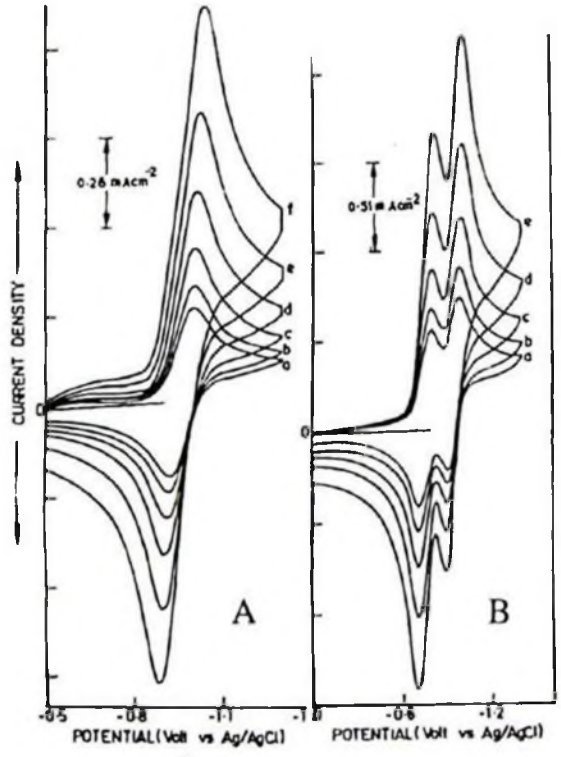


Fig.1 - Cyclic Voltammograms for the First Reduction Step on GCE
A p-$O_2NC_6H_4SMe$ (2 mM)
B p-$O_2NC_6H_4SC_6H_4NO_2$-p (4 mM)
Medium 0.1 M TBAP/DMF;
Scan Rates (a) 10 (b) 20 (c) 40 (d) 80 (e) 160 & (f) 320 (mVS^{-1})

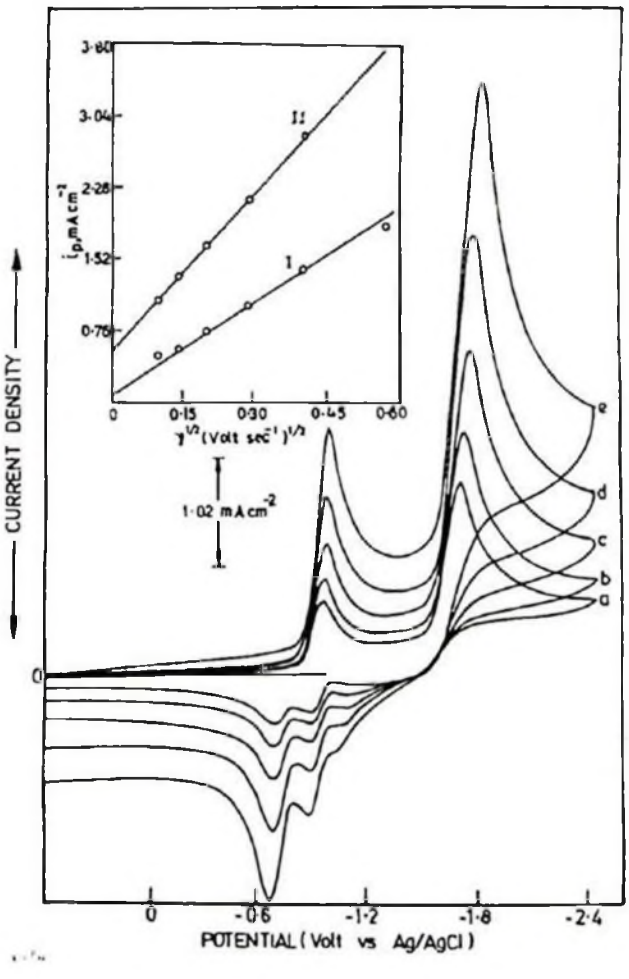


Fig.2 - Cyclic Voltammograms for Reduction on GCE in the Entire Potential Region

Depolariser 2 mM p-$O_2NC_6H_4SMe$
Medium 0.1 M TBAP/ DMF
Scan rates (a) 10 (b) 20 (c) 40 (d) 80 (e) 160 (mVS^{-1})

Typical cyclic voltammograms of 2 mM methyl p-nitrophenyl sulphide at different scan rate over a wider potential range of 0.0V to -2.5V are presented in Fig. 2. Both the i_{pc} value increase linearly with $v^{1/2}$ (inset). On the reverse sweep, three anodic peaks are noticed around -1.1V, -0.9V and -0.7V respectively. The p-nitro diphenyl sulphide also showed quite similar sweep rate dependence.

Reduction of Dinitro Compound

p, p-Dinitrodiphenyl sulphide however, gives rise to two closely spaced quasi-reversible single electron redox couples under identical conditions (Fig.1B). In this case also i_{pc} as well as ΔE_p increase with increasing scan rate for both redox process.

In a wider potential range p,p'-dinitro diphenyl sulphide gives an additional cathodic peak around -1.8V. All the three i_{pc} values increase linearly with increasing C and $v^{1/2}$ (Fig.3 inset).

On Hg [12] and Pt [12] electrodes, the redox process relating to the formation and re-oxidation of nitrobenzene anion radical has always been found to be quite reversible (ΔE_p values of 60 mV even at fairly higher scan rate). However, even at fairly slow scan rate employed here (10-160 mVs^{-1}) the ΔE_p values on GCE are significantly higher. This suggests that the electron transfer rate on GCE is generally slower as compared to mercury. This trend has already been noticed for a number of other redox processes as well [13-15].

In general, i_{pc} shows a linear increase with $v^{1/2}$ for dinitro compound as well. Assuming reversible diffusion controlled, one-electron charge transfer in this range and using the peak current expression [15] for reversible charge transfer, the diffusion coefficient value was calculated for all the three compounds. For the dinitro compound the i_{pc} for the first reduction peak was employed for these calculations (Table 1).

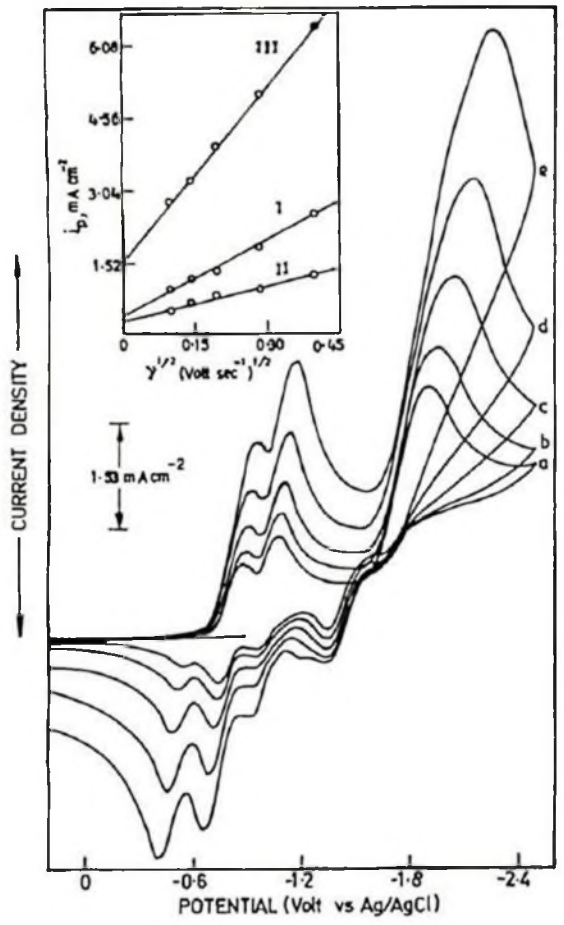


Fig.3 - Cyclic Voltammograms on GCE

10 mM $p\text{-}O_2NC_6H_4SC_6H_4.NO_2\text{-}p'$ in 0.1 M TBAP/DMF;
Scan Rates (a) 10 (b) 20 (c) 40 (d) 80 & (e) 160 (mVS^{-1})

Table 1

Heterogeneous Rate Constant for Electroreduction of Nitro sulphides on GCE

Medium 0.1 M TBAP/DMF

Compound	D cm^2/sec	k^o_h cm/sec
$p\text{-}O_2NC_6H_4SMe$	8×10^{-6}	3.48×10^{-3}
$p\text{-}O_2NC_6H_4SPh$	6.3×10^{-6}	2.29×10^{-3}
$p\text{-}O_2NC_6H_4SC_6H_4NO_2\text{-}p'$	6.07×10^{-6}	2.26×10^{-3}
Anion radical→dianion	2.55×10^{-3}	

Further Reduction of Nitro Compounds

In the case of mononitro compound on GCE, the second reduction peak is due to further reduction of the anion radical of the nitro compounds to the corresponding phenyl hydroxylamine (eq. 2) [1-3].

$$ArNO_2^{\cdot} + 3e^{-} + 4BH \longrightarrow ArNHOH + 4B^{\cdot} + H_2O \quad \ldots (2)$$

The i_{pc2} for mono nitro compounds and i_{pc3} for dinitro compound are around 2.5 to 3 times of i_{pc1} as in the case of Hg and Pt electrodes [12].

Using 'D' values obtained above and Nicholson's correlation function between ΔE_p values and heterogeneous charge transfer rate constant k^{o}_{h} [17], the k^{o}_{h} values for all the four one-electron, quasi-reversible, charge transfer processes were calculated. These values were found to be fairly constant over the sweep rate range employed. The coverage k^{o}_{h} values obtained were found to be in the order of 10^{-3} cm sec^{-1}. The rate constant for methyl p-nitro phenyl sulphide/anion radical redox process is slightly higher than all the other three redox processes involving diphenyl functions. The slower charge transfer rates in large molecular species (Table 1) is probably related to slight blocking type of adsorption. The formation of ArNHOH intermediate and its redox behaviour in this potential region was also confirmed by multi-sweep cyclic voltammetric experiment (eqn.3).

$$ArNO + 2e^{-} + 2H \longrightarrow ArNHOH \quad \ldots (3)$$

Effect of Water Addition

Addition of weak protonative species (water) to mono nitro compounds (namely methyl p-nitro phenyl sulphide and p-nitro diphenyl sulphide), both

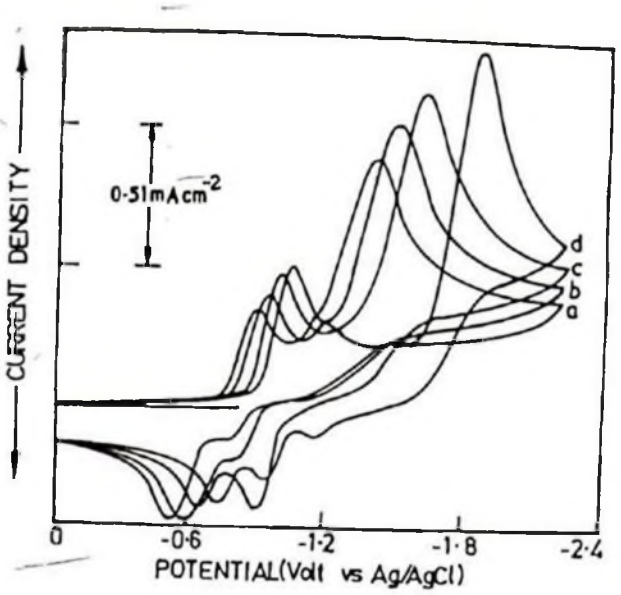


Fig.4 - Effect of Water on the Reduction on GCE

4 nM p-$O_2NC_6H_4SMe$ in 0.1 M TBAP/ DMF
Scan Rate = 80mVs^{-1}
Water Content (mM) (a) 0 (b) 4 (c) 6 (d) 9

the cathodic peak potentials shifted in the positive direction with the increasing addition of water. The anodic peak around -1.1V almost disappeared with the addition of water. The other two anodic peaks on the reverse scan also shifted in the positive direction. The shifts in the peak potentials mentioned above are associated with the prior protonation of the redox species (Fig.4 a typical case).

In general, the protonated species are more easily reducible and hence the reduction peak shifts in the positive direction. Quite similar effect of water addition was also noticed for p,p'-dinitro diphenyl sulphide and p-nitro diphenyl sulphide. The exact cause for this interesting behaviour, however, is not quite clear.

Addition of Benzoic Acid

Inclusion of benzoic acid in methyl p-nitro phenyl sulphide results in the positive shift of the first

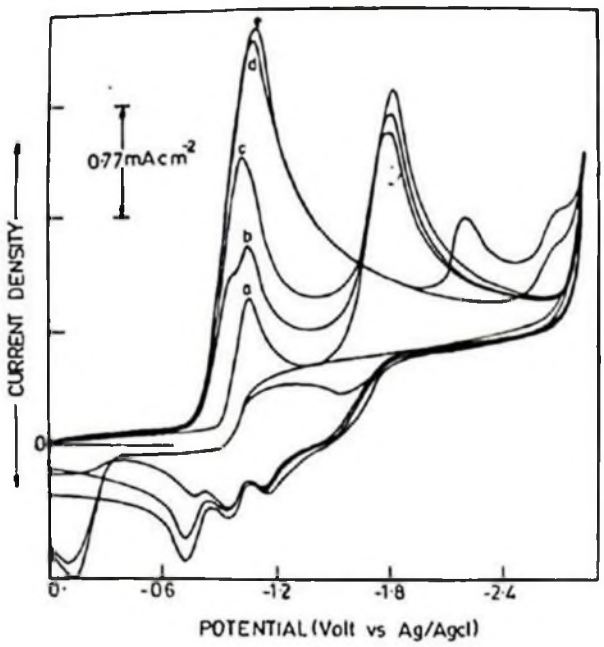


Fig.5-Effect of Benzoic acid on Reduction at GCE

4mM p-$O_2NC_6H_4SMe$ in 0.1 M TBAP/DMF
Scan Rate= 80 mVS^{-1}).
Benzoic acid (mM) (a) 0 (b) 4 (c) 8 (d) 16 & (e) 18

cathodic peak; this increases with benzoic acid concentration [18]. When benzoic acid concentration was four times that of the nitro compound, a single reduction peak was noticed in the first cathodic peak potential region, and the subsequent cathodic peaks get suppressed completely. This may be attributed to the consumption of four protons during the four electron electro reduction of $-NO_2$ to -NHOH in the first cathodic peak region itself.

When benzoic acid concentration exceeds four times the concentration of nitro compound, two new cathodic peaks appear around -2.2V and -2.6V respectively (Fig.5).

Pure benzoic acid alone also gives a typical diffusion controlled reduction peak around -2.2V in the absence of nitro compound, under otherwise identical experimental condition. This reduction peak (around this potential region) is noticed only in presence of benzoic acid and not in presence of benzoate anions. The cathodic peak observed around -2.2V in presence of nitro compound (Fig 5), may be attributed to the presence of excess undissociated benzoic acid in the medium. The exact cause for the cathodic peak around -2.6V is not clear. This process may either be due to discharge of H^+ species by catalytic H_2 evolution (promoted by the Ar-NHOH group produced during the cathodic reduction) or due to C-S bond cleavage.

In the case of p,p'-nitro dinitro diphenyl sulphide, as long as benzoic acid concentration does not exceed four times that of the dinitro compound, the first cathodic peak current alone increases significantly at the expense of the second and third cathodic peak currents (Table 2).

Table 2

Effect of Benzoic acid (BA) on the Reduction

BA (mM)	-	4	8	16	32
$-E_{pc1}$(V)	0.90	0.86	0.86	0.90	0.90
$-E_{pc2}$(V)	1.10	1.04	1.06	1.04	1.10
$-E_{pc3}$(V)	2.04	2.00	1.98	1.94	*
i_{pc1}(mA)	0.201	0.272	0.385	0.575	0.600
i_{pc2}(mA)	0.111	0.091	0.045	0.022	0.265
i_{pc3}(mA)	0.563	0.474	0.390	0.240	*

* Peak 3 is absent, but a new peak is observed around -2.6 V (0.1 mA)

Beyond this concentration level, the first cathodic peak current remains constant and the second cathodic peak current increases further with the complete suppresssion of the third cathodic peak current. At least in this case, it appears that each

nitro group reduction occurs in presense of benezoic acid in two distinct stages. The first stage leads to reduction of one -NO_2 to -NHOH. Once again, catalytic hydrogen evolution process around -2.6V is noticed when benzoic acid concentration exceeds eight times the concentration of the dinitro compound.

Constant potential electrolysis in different potential regions under these conditions might provide some further insight into these processes. However, in carrying out these experiments one should overcome the filming effects that are noticed in general on solid electrodes and especially on GCE. A particular form of film formation effect noticed during the electro reduction of these compounds in presence of lithium salts has already been reported from this laboratory [19].

CONCLUSIONS

In many respects, the voltammetric behaviour of nitro phenyl sulphides and dinitro diphenyl sulphide on GCE (presented here) is similar to the behaviour of other mono nitro and dinitro aromatic compounds on Hg and Pt electrodes reported in the literature. Slightly slower charge transfer rate is noticed on GCE for this process. This is probably associated with a weak blocking type of adsorption of these sulphur compounds on glassy carbon electrode surface. It appears that water in aprotic solvents competes with the adsorption of these sulphides. Benzoic acid addition leads to a single four electron reduction peak leading to the formation of -NHOH in the first cathodic potential region itself.

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