Electrochemical Behaviour of *NN'*-Thiobisamines. Cyclic Voltammetry in Dimethyl Sulphoxide with Low Water Content

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The electrochemical behaviour of *NN'*-thiobispiperidine and *NN'*-thiobismorpholine in dimethyl sulphoxide at low water content has been studied by cyclic voltammetry. Electro-oxidation in this medium, producing SO_2 at the electrode surface, parallels the process observed by adding a Brönsted acid in which acid catalysed hydrolysis generates an intermediate species which is followed by a disproportionation process.

NN'-Thiobisamines $(R_2N)_2S$ are known go be quite unreactive species. They are insoluble in water and most of them can be crystallized from alcohols.[1] Thiobisamines are also virtually unreactive towards metal ions under anhydrous conditions.[2] The radical cations $(R_2N)_2S^{\cdot+}$, obtained by both chemical and electrochemical methods, also show relatively high stability.[3,4] This low reactivity of *NN'*-thiobisamines has been frequently explained by the diminished nucleophilicity of the sulphur and nitrogen atoms arising from double-bond character in the S–N linkage. Partial delocalization along the S–N bond has been confirmed by n.m.r.[5,6] and i.r.[7] spectroscopic studies, as well as by *X*-ray structural determinations.[8–10] On the other hand, the reactivity of $(R_2N)_2S$ towards metal ions is notoriously enhanced by water, there being numerous redox processes in which the thiobisamine acts as a reducing agent or disproportionates in a similar way to that in aqueous acid media.[2]

In order to obtain further information about the chemistry of thiobisamines, especially about their reactivity in media containing water, we have studied the electrochemical behaviour of *NN'*-thiobismorpholine and *NN'*-thiobispiperidine in dimethyl sulphoxide solution with low water content.

Experimental

NN'-Thiobisamines were prepared and purified according to literature methods.[11] Dimethyl sulphoxide (DMSO), tetraethylammonium perchlorate (TEAP), and toluene-*p*-sulphonic acid were obtained commercially and purified by standard methods.[12,13] The water content was determined by Karl Fischer titrations.

Current potential data were obtained by cyclic voltammetry using a PARC model 370 electrochemistry system. All measurements were made in a specially designed three-electrode glass cell. The working electrode was a carbon glassy electrode, the counter-electrode a platinum wire, and the reference electrode an aqueous saturated calomel electrode (s.c.e.).

The reference electrode was kept in a glass tube ending in a Vycor tip immersed in a compartment filled with supporting electrolyte solution, which in turn was connected to the working cell through a Luggin capillary placed *ca.* 1 mm from the working electrode.

Controlled-potential electrolyses were carried out using a platinum gauze as anode. The counter-electrode was a platinum wire isolated from the working solution by a fritted glass disc.

^1H N.m.r. experiments were carried out at 35 °C in a Varian T-60 spectrometer using $[^2H_6]$dimethyl sulphoxide solutions.

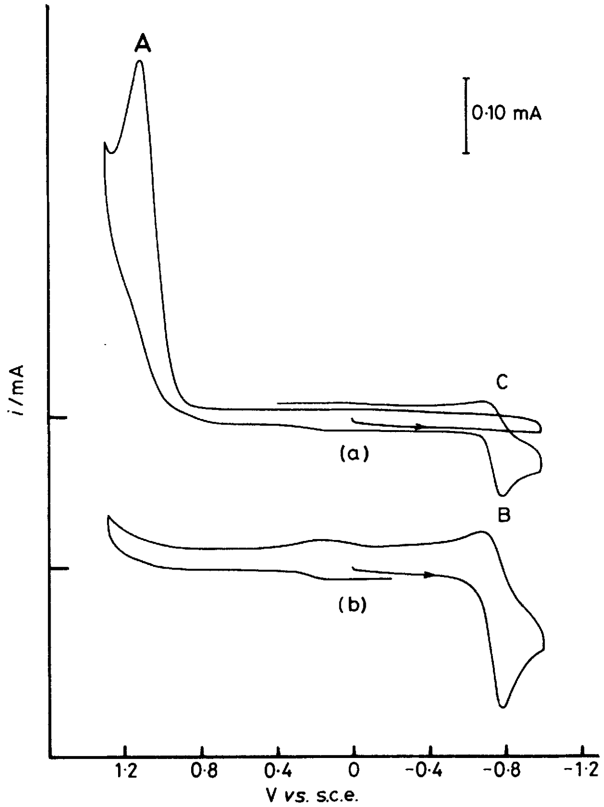


Figure 1. Cyclic voltammogram of (a) *NN'*-thiobismorpholine and (b) sulphur dioxide in DMSO (0.1M-TEAP); concentration of substrates *ca.* 2.80mM; voltage scan rate 300 mV s^{-1}

Results

The electrochemical behaviour of thiobismorpholine and thiobispiperidine in dimethyl sulphoxide with variable water content (10^{-3}—0.4M) and containing tetraethylammonium perchlorate (0.1M) as supporting electrolyte was studied at room temperature. As shown in Figure 1a *NN'*-thiobismorpholine is irreversibly oxidized at 1.12 V (peak A). One of the oxidation products formed at the electrode is then reversibly reduced at a potential (peak B at −0.8 V in Figure 1a) that coincides with that of the reduction of SO_2 in the same medium (Figure 1b). The peak currents of both peaks, A and B, increase linearly with the concentration of thiobisamines. Double-potential-step experiments carried out at +1.12 and

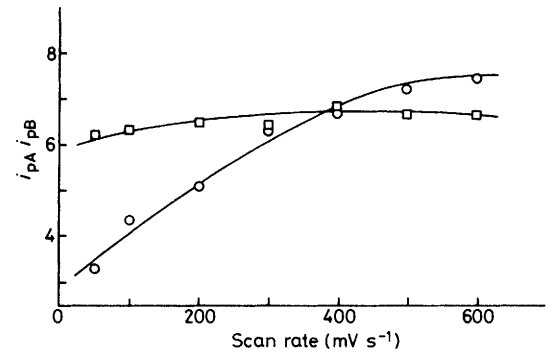


Figure 2. Dependence of i_{pA}/i_{pB} on the voltage scan rate for *NN'*-thiobismorpholine (*ca.* 1.4mM) in DMSO (0.1M-TEAP) at two different water contents: ○, 1 × 10^{-3}M and □, 0.4M

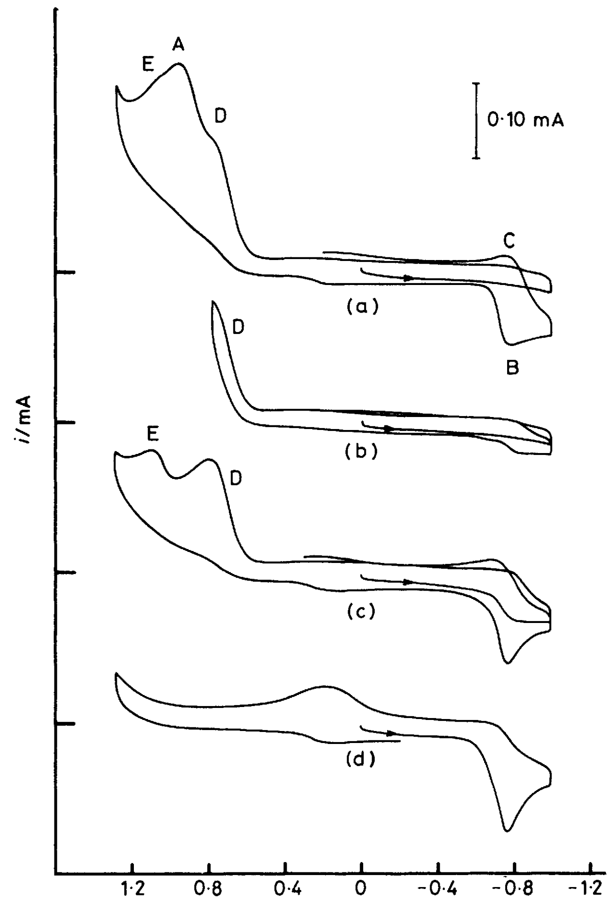


Figure 3. Cyclic voltammograms of *NN'*-thiobispiperidine (2 × 10^{-2} mmol) in DMSO (0.1M-TEAP) with increasing amounts of added toluene-*p*-sulphonic acid: (a) 1 × 10^{-2} mmol; (b) as (a) but clipped at +0.8V; (c) 2.5 mmol; and (d) 5 × 10^{-2} mmol; voltage scan rate 300 mV s^{-1}

—0.8 V give rise to *i–t* transients indicating that both processes have a catalytic character. The plots of the current function $i_p/v^{\frac{1}{2}}$ *versus* the voltage scan rate *v* show for peak A curves whose slopes decrease and tend to zero with increasing voltage scan rate, while for peak B there is practically no dependence on the scan rate.

The dependence of the peak current ratio i_{pA}/i_{pB} on the scan rate at two different water contents for *NN'*-thiobismorpholine solutions can be observed in Figure 2. The initial slopes decrease with increasing water concentration.

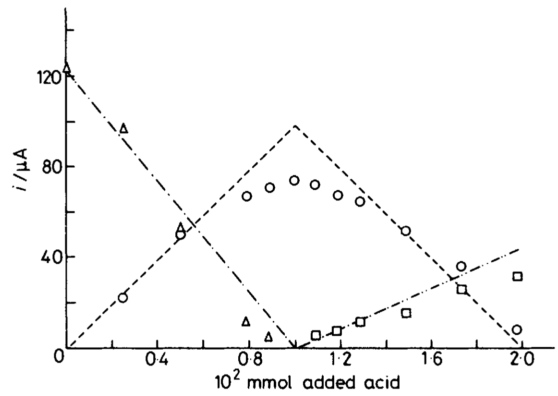


Figure 4. Titration of *NN'*-thiobispiperidine (1 × 10^{-2} mmol) in DMSO (0.1M-TEAP) with toluene-*p*-sulphonic acid. Effect of the addition of acid on the peak currents; voltage scan rate 200 mV s^{-1}: △, peak A; ○, peak D; □, peak B

The effect of a Brönsted acid on the electrochemical behaviour of thiobisamines was investigated by titrating the thiobisamine solutions with toluene-*p*-sulphonic acid. The addition of acid produces the decomposition of the thiobisamine as indicated by the regular decrease of the oxidation peak A and the appearance in solution of other electroactive species: peaks D, B–C, and E (see Figure 3a). Peaks B–C appear in the first cycle voltammogram only when the ratio of acid to thiobisamine is greater than one (Figure 3c). Peak D corresponds to a new species which, as for the corresponding thiobisamine, is electro-oxidized, generating SO_2 at the electrode surface (Figure 3b). Peak E appears at a more positive potential than the thiobisamine.

The effect of acid addition on the currents of the peaks corresponding to *NN'*-thiobispiperidine, SO_2, and to the species that is electro-oxidized at peak D is shown in Figure 4. The current of peak D increases linearly with the acid addition reaching a maximum value at a ratio of thiobisamine to acid of 1 : 1. At this point the peak corresponding to the oxidation of the thiobisamine (peak A) disappears. On the other hand, above this point peak D decreases and disappears at a ratio of 1 : 2 while SO_2 is detected in the solution.

^{1}H N.m.r. measurements of thiobisamine acid mixtures permitted us to detect three sets of signals corresponding to the amine group in the thiobisamine, in the ammonium cation, and in another compound apparently unstable under our measurement conditions.

The number of electrons involved in the oxidation of thiobisamines was determined by controlled-potential coulometry under conditions similar to those described for the voltammogram in Figure 1. Electrolysis at +1.1 V (+0.96 V for thiobispiperidine) yielded two electrons per mole of thiobisamine.

The results of the experiments were qualitatively similar for the two compounds studied. However, the nature of the amine group has some influence on the potential values. In the Table, potential data are compared with the pK_b values of the corresponding amine[22] as well as with the fractional atomic charges on the sulphur and nitrogen atoms obtained from e.s.c.a. studies.[15]

Discussion

The oxidation process observed in the cyclic voltammogram of *NN'*-thiobisamines (Figure 1a) can be ascribed to the form-

Peak potentials (V) *versus* s.c.e., pK_b values, and fractional atomic charges of thiobisamines

	E_{pA}	E_{pD}	pK_b [a]	q_S [b]	q_N [b]
Thiobismorpholine	1.12	0.92	5.51	0.06	−0.087
Thiobispiperidine	0.96	0.78	2.88	0.02	−0.104

[a] pK_b values of the corresponding amine in aqueous medium.[22] [b] Fractional atomic charges calculated from e.s.c.a. studies by Pauling's method.[15]

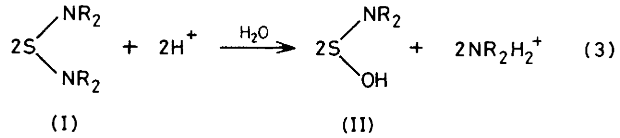
$$2SO_2 + 2\bar{e} \rightleftharpoons 2SO_2^{\cdot -} \rightleftharpoons S_2O_4^{2-} \qquad (1)$$

$$S_2O_4^{2-} \rightleftharpoons SO_2 + SO_2^{2-} \qquad (2)$$

ation of the radical $(R_2N)_2S^{\cdot +}$. The stability of this radical, that can be generated both chemically[3] and electrochemically[4] from thiobisamines, is sufficient to allow investigations by e.s.r.[3,4] However, under our experimental conditions (dimethyl sulphoxide with low water content) the radical $(R_2N)_2S^{\cdot +}$ is unstable, generating SO_2 at the electrode surface. The influence of the water content on the rate of the chemical reactions involved in the formation of SO_2 can be inferred from the data in Figure 2. The ratio i_{pA}/i_{pB} in a medium with low water content shows a relatively strong dependence on the potential-scan rate suggesting a process governed by a relatively slow chemical reaction. By increasing the water content, the rate of the chemical reaction increases and i_{pA}/i_{pB} becomes practically independent of the potential-scan rate.

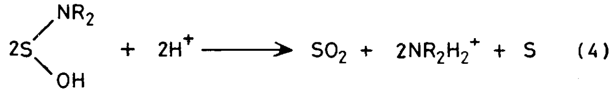
The assignment of the peaks B–C, whose potentials coincide with those of SO_2 in the same medium (Figure 1b), is confirmed by the catalytic character observed for peak B. Such behaviour agrees with the mechanism proposed for the reversible reduction of SO_2,[16-18] namely the formation of the $SO_2^{\cdot -}$ followed by its dimerization to dithionite ion [reaction (1)]. The catalytic character observed for the SO_2 wave can therefore be attributed to the disproportionation of the dithionite ion [reaction (2)]. Other disproportionation reactions of the dithionite ion, which can occur in media containing water, will also generate SO_2 at the electrode.[16]

Analogously to the electro-oxidation, the chemical oxidation of *NN'*-thiobisamines with some copper(II) salts in media with controlled water content also produces SO_2.[2] Moreover, the enhancement of the reactivity of the *NN'*-thiobisamines in the presence of a Lewis acid can also be related to disproportionation of thiobisamines to SO_2 and sulphur observed in acid media in which the presence of hydroxylated derivatives of sulphur(II) as unstable intermediates was also considered.[19-21] The transformation of thiobisamines into SO_2, chemically or electrochemically, can be better understood by analysing the effect of the addition of acid on the cyclic voltammograms of thiobisamines.

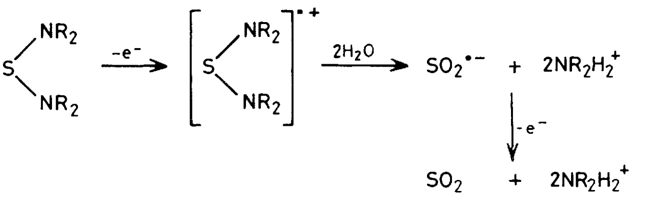


$$2S(NR_2)_2 + 2H^+ \xrightarrow{H_2O} 2S(NR_2)(OH) + 2NR_2H_2^+ \qquad (3)$$

(I) (II)



$$2S(NR_2)(OH) + 2H^+ \longrightarrow SO_2 + 2NR_2H_2^+ + S \qquad (4)$$



$$S(NR_2)_2 \xrightarrow{-e^-} \left[S(NR_2)_2\right]^{\cdot +} \xrightarrow{2H_2O} SO_2^{\cdot -} + 2NR_2H_2^+ \xrightarrow{-e^-} SO_2 + 2NR_2H_2^+$$

Scheme.

The voltammograms in Figure 3 show the formation of an intermediate species (peak D) whose concentration reaches a maximum at a thiobisamine–acid ratio of *ca.* 1 : 1 (see Figure 4). This species, analogously to thiobisamines, generates SO_2 by electrochemical oxidation as well as by acid addition (peak B in Figures 3b and 3c, respectively). The stoicheiometry of the reaction with acid, obtained from titrations such as that illustrated in Figure 4, as well as the electrochemical characteristics of the products of such reactions and the ^1H n.m.r. spectra of the reaction mixtures, which permitted the detection of an intermediate species containing the amine group, suggest reactions (3) and (4). Reactions (3) and (4) proceed rapidly and, although both reactions tend towards the formation of products, the formation of SO_2 only occurs after the total disappearance of the thiobisamine, thus allowing the formation of compound (II) in solution. Peak D should correspond to this intermediate species. Although the hydroxylated species (II) appears to be thermally unstable, its decomposition is, under our experimental conditions, sufficiently slow to obtain reproducible cyclic voltammograms permitting the titrations corresponding to reactions (3) and (4) to be followed.

The total electro-oxidation of thiobisamines, consuming two electrons per mole of thiobisamine and also producing SO_2 can be then described by the mechanism Scheme, which, from the shape of the cyclic voltammograms and the variations with the scan rate, should be an e.c.e. mechanism.[14] In this mechanism the formation of the radical $(R_2N)_2S^{\cdot +}$, unstable in this medium, is followed by hydrolysis yielding the radical species of sulphur(III), $SO_2^{\cdot +}$, which is in turn oxidized to SO_2.

The inertness of *NN'*-thiobisamine appears to be related to the relatively high bond order of the S–N linkage which, as shown by the vibrational characteristics of this bond,[7] is nearly independent of the nature of the amine group. Thus, a decrease of the electron density in the S–N molecular orbitals will increase the reactivity. In such a way both chemical and electrochemical mechanisms for the activation of the hydrolysis of the thiobisamines can be considered as equivalent, both being presumably related to a change in the hybridization of the nitrogen orbitals by increasing their *sp*^{3} character. Such a change should be induced in one case by the co-ordination of a Lewis acid (proton or metal ion) to nitrogen and, in the other, directly by electrolytic ionization.

Acknowledgements

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