Stabilisation of Nitrophenyl Disulphide Ions in Dimethylacetamide

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2-Nitrophenyl and 4-nitrophenyl disulphide ions are stabilised in aprotic dipolar solvents and solutions of these ions are obtained in dimethylacetamide by nucleophilic attack of sulphur by the corresponding thiolates.

Alkyl or aryl disulphide ions are known in solution only as transient species. Stabilisation of inorganic polysulphide ions[1] S_x^{2-} in dipolar aprotic media prompted us to try a similar access to organic disulphide ions. S_x^{2-} are easily obtained by addition of sulphur to a S^{2-} solution[2] following reaction (1). It should be possible to obtain organic disulphides from the corresponding thiolates by the same procedure.

$$S^{2-} + (x-1)/8\ S_8 \rightarrow S_x^{2-} \qquad (1)$$

$$RS^- + 1/8\ S_8 \rightarrow RS_2^- \qquad (2)$$

However the nucleophilicity of anions such as RS^- towards the S–S bond[3] is correlated with their reducing power and the oxidation of thiolate ions [reaction(3)] generally prevails.[4]

$$2RS^- + x/8\ S_8 \rightarrow RS_2R + S_x^{2-} \qquad (3)$$

Limitation of the process to reaction (2) requires a selection of thiolates which present strong opposition to oxidation. We report here the reactions of sulphur with two arylsulphide ions ($2\text{-}NO_2C_6H_4S^-$ = *o*-ArS^- and $4\text{-}NO_2C_6H_4S^-$ = *p*-ArS^-) which are stabilised by the high degree of delocalisation of their electronic charge.

The study was carried out in dimethylacetamide (DMA) which seems to be one of the best solvents for stabilisation of inorganic polysulphide ions.[1a] The RS^- solutions were electrogenerated *in situ*, by controlled potential electrolysis at a gold grid electrode of the corresponding disulphide RS_2R.[5] The bielectronic reductions are not exhaustively achieved and lead to a mixture of RS^- and RS_2R in known concentrations. Reactions were followed by u.v.–visible absorption spectrophotometry coupled with classic voltammetry at a rotating gold disk electrode (at least one reduction wave for sulphur[6] and RS_2R,[5] one oxidation wave[5] for RS^-, and two[6] for stable S_x^{2-}).

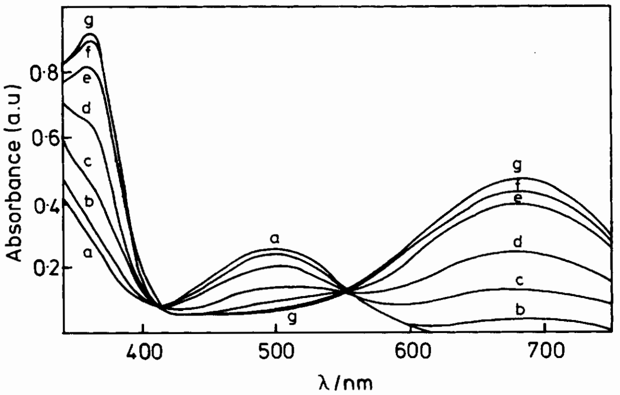

Figure 1. Absorption spectra evolved during the addition of sulphur to a mixed solution of *o*-ArS^- (1.32×10^{-3} M) and *o*-ArS_2Ar (0.40×10^{-3} M) sulphur solution added ($S_8 \times 10^4$ M): (a) 0; (b) 0.10; (c) 0.34; (d) 0.63; (e) 1.05; (f) 1.60; (g) 3.09.

When sulphur is added to an *o*-ArS^- solution, the absorption band of *o*-ArS^- at 502 nm (ε = 2000 $dm^3\ mol^{-1}\ cm^{-1}$) decreases and two unassigned bands (362 and 675 nm) increase, while two isosbestic points (at 407 and 550 nm) are observed (Figure 1). In DMA, the oxidation reaction (3) would lead to formation of $(o\text{-}Ar)_2S_2$ and the $S_3^{-\bullet}$ radical anion (in equilibrium with its dimer S_2^{2-}),[6] the stable polysulphide of the lowest rank.[6] The 362 and 675 nm bands cannot be attributed to these species and reaction (4) does not explain the evolution of these spectra. Nor are the spectra supported by voltammetry: during the addition of sulphur, the characteristic cathodic and anodic waves of $S_3^{-\bullet}$ ($E_{\frac{1}{2}C} = -1.10$ V and $E_{\frac{1}{2}A} = -0.20$ V *vs.* Ag/AgCl, sat. KCl in DMA) do not appear and the reduction wave of $(o\text{-}Ar)_2S_2$ ($E_{\frac{1}{2}} = -0.67$ V) already present in the starting solution (*cf.* above) does not increase. Reaction (4) is also ruled out by the experimental stoicheiometry of the process: whereas 3/8 S_8 per RS^- would be expected after reaction (4), extrapolation of curve (a) of Figure 2 shows that only 1/8 S_8 is consumed, the amount at which absorptions at 675 nm and 362 nm rise to a maximum. From these results we conclude that the formation of the *o*-ArS_2^- ion [λ = 675 (ε = 5000 $dm^3\ mol^{-1}\ cm^{-1}$) and 362 nm (ε = 6000 $dm^3\ mol^{-1}\ cm^{-1}$)] occurs according to reaction (2). The 362 nm band, similar to the u.v. band of $(o\text{-}Ar)_2S_2$ can be attributed to the S–S bond recovered in the *o*-ArS_2^- ion.

$$2RS^- + 3/4\ S_8 \rightarrow RS_2R + 2\ S_3^{-\bullet} \qquad (4)$$

In fact, *o*-ArS^- and *o*-ArS_2^- are in equilibrium when reaction (2) approaches completion: the absorbances at 675

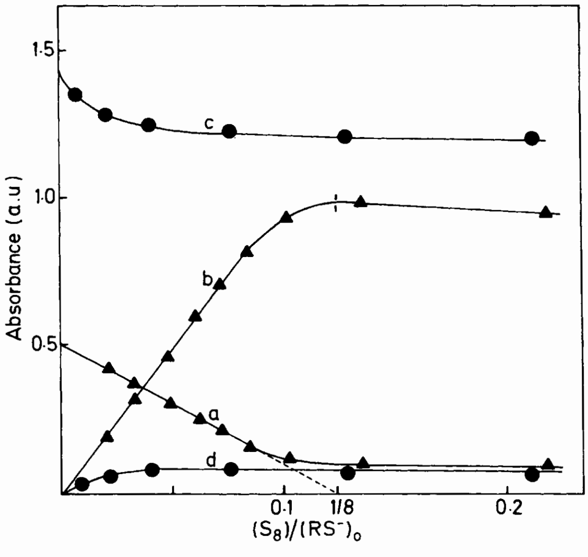

Figure 2. Addition of sulphur to 2- or 4-nitrophenyl sulphide solutions. Variation of maximum visible absorbances *vs.* $(S_8)/(RS^-)_o$ ratio. (a) A_{502} and (b) A_{675} for $(o\text{-}ArS^-)_o$ 2.5×10^{-3} M and $(o\text{-}ArS_2Ar)_o$ 0.65×10^{-3} M; (c) A_{505} and (d) A_{600} for $(p\text{-}ArS^-)_o$ 0.48×10^{-3} M and $(p\text{-}ArS_2Ar)_o = 0.12 \times 10^{-3}$ M.

and 502 nm are no longer linear functions of added sulphur, while the isosbestic points remain. At the same time, the unreacted S_8 begins to be detectable by its first reduction wave[6] ($E_{\frac{1}{2}}$ = −0.34 V). Oxidation of the o-ArS_2^-/o-ArS^- solutions by an excess of sulphur does not seem significant: on addition of S_8 beyond the stoicheiometry of reaction (2), only a weak decrease of the 675 nm band is observed [Figure 2, curve (b)].

In the case of 4-nitrophenyl sulphide ions, addition of sulphur leads to spectral changes similar to those obtained with o-ArS^-: a broad shoulder (λ = 600 nm) and a new band (λ = 325 nm) increase at the expense of the visible band of p-ArS^- (λ = 505 nm, ε = 30 000 $dm^3\ mol^{-1}\ cm^{-1}$) and two isosbestic points are observed at 415 and 555 nm. However, the weak variations of A_{505} [Figure 2, curve (c)] and A_{600} [curve (d)], show that the reaction does not proceed to completion. Oxidation to $(p\text{-}Ar)_2S_2$ and $S_3^{-\bullet}$ *via* reaction (4) is still ruled out by analysis of voltammograms which exhibit no $(p\text{-}Ar)_2S_2$ wave ($E_{\frac{1}{2}}$ = −0.62 V) but do immediately show the reduction wave of unreacted sulphur ($E_{\frac{1}{2}}$ = −0.34 V). Accurate measurements of the limiting current for suitable conditions ($[p\text{-}ArS^-] > 5 \times 10^{-3}$ M) allow determination of the stoicheiometry: the 600 nm absorbance increase indicates a consumption of $8RS^-$ per mole of S_8. These observations support the assignment of the absorptions at 600 nm (ε = 11 000 $dm^3\ mol^{-1}\ cm^{-1}$) and 325 nm (ε = 5 500 $dm^3\ mol^{-1}\ cm^{-1}$) to p-ArS_2^-.

Quantitative analysis of our experimental data, to be presented in a future paper, shows, for example, that 75% of o-ArS_2^- and 15% of p-ArS_2^- are obtained at the 1/8 stoicheiometry for 2×10^{-3} M thiolate solutions. The larger delocalisation of the electronic charge in p-ArS^- compared with o-ArS^- explains the smaller conversion into aryl disulphide ions.

In order to confirm the formation of nitrophenyl disulphide ions in aprotic dipolar medium, alkylation with methyl iodide of o- or p-ArS^- solutions in presence of sulphur were carried out on a preparative scale (using 1.5 g of starting materials). RS_2R were reduced by controlled potential coulometry to give the corresponding thiolates in expected quantities. After addition of sulphur, in slight excess with respect to the 1/8 proportion of reaction (2), addition of MeI resulted in colourless solutions at the expected stoicheiometry for the nucleophilic substitution by sulphide anions. Mixtures were extracted with diethyl ether, then analysed by g.c.–mass spectrometry. In both cases, no higher fragments than molecular ions of the two expected organic mono- and disulphides were found ($NO_2C_6H_4SMe^+$ M^+ 169; $NO_2C_6H_4S_2Me^+$ M^+ 201). ^1H n.m.r. spectra are in agreement with the formation of these two aromatic compounds, with the following chemical shifts (CCl_4) for the methyl protons [δ (3H, s)]: o-ArSMe 2.45; o-ArS_2Me 2.40; p-ArSMe 2.52; p-ArS_2Me 2.46. The proportions ArS_2Me/ArSMe are close to 2/3 for Ar = 2-$NO_2C_6H_4$ and 1/3 for Ar = 4-$NO_2C_6H_4$. Small amounts of MeS_xMe (x = 3—8) are present in the mixtures (less than 8% in total). They probably result from the reaction of methyl iodide with inorganic polysulphides[7] S_x^{2-} produced by a weak oxidation of ArS^- by the excess of sulphur.

These results provide the basis for a possible production of aryl disulphide ions in dipolar aprotic solvents which would allow one to prepare mixed organic disulphides by direct S_N2 pathways. These species could also be used as ligands in the synthesis of metal complexes with polysulphide or thiolate ions, current models for enzymatic catalysis.

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