Formation of the Blue Trisulphur Radical Anion, S_3^-, in Solutions of Alkali Polysulphides in Dimethylformamide, and from Elemental Sulphur and Piperidyl-lithium in Hexamethylphosphoramide

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I.r. and visible spectra identify the blue species in solutions of alkali polysulphides in dimethylformamide (DMF) as S_3^-. Elemental sulphur (S_8) is reduced to S_3^- by secondary amines in hexamethylphosphoramide (HMPA). The reaction of piperidyl-lithium with S_8 in HMPA has been investigated to determine the stoicheiometry and the nature of the final products.

We have shown that alkali polysulphides in HMPA dissociate and disproportionate to give the blue S_3^- radical anion.[1] From the published visible spectra, which show weak but well defined vibrational structure, it is apparent that the same species is present in solutions of alkali polysulphides in DMF.[2] Giggenbach claims, however, that the major species in DMF giving rise to the absorption band $\lambda_{max.}$ 620 nm is the supersulphide ion, S_2^-.[2,3] Since S_3^- and particularly S_2^- have been characterised in the solid state, we have examined the literature to compare the spectroscopic properties of these two radical anions with those of the blue sulphur species in basic solvents. We have also obtained vibrational spectra which give some additional direct information about the species present in DMF solutions of alkali polysulphides.

We reported earlier that elemental sulphur dissolves in HMPA to give S_3^-,[1,4] although the mechanism of the reduction was not clear. We have studied this system further to elucidate the reactants, final products, and stoicheiometry of the reaction.

EXPERIMENTAL

Materials.—HMPA (Aldrich) was initially dried with sodium hydride, then sufficient potassium metal was added to turn the batch completely blue. After distillation under nitrogen or argon (b.p. 90°, 4·7 mmHg, lit.,[5] 115°, 15 mmHg or 69°, 1 mmHg), the solvent was transferred to a Vacuum Atmospheres Corporation glove-box filled with dry oxygen-free nitrogen where it was slowly trickled through freshly regenerated Linde 4A molecular sieves. It showed no impurities by polarography [6] and the conductivity remained constant over several weeks at *ca.* $12 \times 10^6\ \Omega\ cm^{-1}$ (lit.[7] 7—18 × $10^6\ \Omega\ cm^{-1}$). DMF (Baker analysed) was degassed with nitrogen, transferred to the glove-box and trickled through freshly regenerated Linde 4A molecular sieves.

Sulphur (Shawnigan, sublimed grade) was resublimed under vacuum before use. Anhydrous sodium polysulphides were prepared and analysed as described previously.[1] Piperidyl-lithium was prepared by addition of n-butyllithium in hexane (Ventron) to piperidine (Fisher) in pentane at 0° under nitrogen. The solution was warmed to room temperature. The white precipitate was filtered off, washed with pentane, dried, and stored in the glove-box. Sulphur dichloride was prepared from sulphur monochloride (ROC/RIC) by the literature method.[8] Dipiperidyl sulphide, prepared from an excess of piperidine and sulphur dichloride, had m.p. 73° (lit.[9] 74°) after recrystallisation from methanol. Tris(dimethylamino)phosphine sulphide (Alfa) was used as received.

Instrumentation and Procedures.—Conductivities were measured at 25° using a Beckman RC 18 conductivity bridge operating at 1 kHz. The conductometric titration was performed by running a pale green solution of elemental sulphur in HMPA (1·40 × 10^{-2}M in g atom S) into a solution of piperidyl-lithium (1·54 × 10^{-3}M). The solution in the cell went immediately blue. Chromatography was performed using a Tracor 550 with a 180 × 0·6 cm column of SE 30 on Chromosorb W with helium carrier gas and a flame photometric detector operating in the sulphur mode. Samples were prepared for injection by partitioning between hexane and 0·1M-KOH, washing the organic layer three times with brine and drying over

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magnesium sulphate. Spectroscopic measurements were made with the following instruments: i.r. spectra (Perkin-Elmer 337), visible spectra (Beckman DB-G), mass spectra (Varian CH5 operating at 70 eV).

RESULTS AND DISCUSSION

S_2^- Was first discovered by Schulman and Kirk who measured the excitation and emission spectra of the centre in KBr crystals at 77 K.[10] This work has been extended by independent workers,[11,12] and the zero-phonon lines for isotopically substituted S_2^- in both emission [13] and absorption spectra [14] have been observed. The following data are pertinent: $\lambda_{\text{max.}}$ from excitation spectra (KBr, 77 K) 390 nm,[10] (KI, 4·2 K) 426 nm;[11] $\lambda_{\text{max.}}$ from low resolution absorption spectrum (KI, 2 K) 405 nm;[15] $\Delta G_{\frac{1}{2}}''$ (the spacing of the lowest vibrational levels of the ground state) (KI, 2 K) $594{\cdot}8 \pm 0{\cdot}2$ cm^{-1}.[13] The last figure has been confirmed by observation of the Raman spectrum of S_2^- (KI, 298 K) 594 ± 1 cm^{-1}.[16,17] By use of the resonance Raman effect it was shown that the observed Raman band is associated with an optical absorption band at *ca.* 400 nm, in agreement with the excitation spectral data. As expected, no i.r. band was observed for S_2^-, but its presence was confirmed by e.s.r. measurements.[17] The e.s.r. spectrum had been observed previously by Vannotti and Morton [18] and is characterised by extreme anisotropy (KI, 4 K) $g_{zz} = 3{\cdot}0629$, $g_{yy} = 1{\cdot}6369$, $g_{xx} = 1{\cdot}6254$.

S_3^- Has been characterised by e.s.r.[19] and e.n.d.o.r. spectra.[20] It gives a strong resonance Raman effect [17,21] which indicates that the observed Raman band (KI, 300 K), 534 cm^{-1},[17] is associated with an optical absorption band at 610 nm. An i.r. band at 585 cm^{-1} was observed for S_3^-, and is attributed to the antisymmetric stretching mode.[1,17] Raman, i.r., and e.s.r. spectra have shown that the blue colour of ultramarine, $\lambda_{\text{max.}}$ 590 nm, is due to S_3^-,[17,22] and the spatial distribution of S_3^- in the aluminosilicate lattice of ultramarine has been determined by e.s.r. techniques.[23]

Let us compare this data with the spectroscopic properties of solutions of alkali polysulphides in DMF. The species in question is blue, $\lambda_{\text{max.}}$ 618 nm,[2,3] which dictates against it being S_2^- $\lambda_{\text{max.}}$ *ca.* 400 nm (*vide supra*). The e.s.r. spectra are not diagnostic since the anisotropy of the S_2^- absorption and the degeneracy of the π orbitals make it difficult to observe the spectrum in the liquid phase. Giggenbach did, however, observe e.s.r. signals for two radicals, one of which may be S_3^-.[2] He did not report vibrational spectra, but, since DMF has a convenient i.r. window from 640 to 440 cm^{-1}, we have investigated the i.r. spectra of DMF solutions of $Na_2S_{3{\cdot}53}$, $Na_2S_{4{\cdot}65}$, and $Na_2S_{6{\cdot}00}$ (all *ca.* 4×10^{-3}M in g atom S, 1 mm pathlength). At this concentration in 100% DMF, Giggenbach claims that the S_4^{2-} ion is completely dissociated into S_2^- ions.[3] The i.r. spectrum of solutions of $Na_2S_{3{\cdot}53}$ shows a sharp peak at 575 cm^{-1} and a slightly broader, weaker peak at 509 cm^{-1}. The latter peak remains approximately constant in intensity in the spectra of the higher polysulphides but the peak at 573 cm^{-1} decreases in intensity and is very weak in the spectrum of $Na_2S_{6{\cdot}0}$. The behaviour of the 573 cm^{-1} peak is thus qualitatively similar to the behaviour of the optical absorption band at 618 nm.[2,3] S_2^- Is, of course, i.r. inactive but S_3^- has a strong i.r. absorption at 580 cm^{-1} (HMPA),[1] 585 cm^{-1} (KI matrix).[17]

In summary, the suggestion that S_2^- is the blue species in DMF solutions of Na_2S_4 is inconsistent with the published spectra of S_2^-. Furthermore, both i.r. and visible spectra identify the blue species in DMF with that in HMPA, where it has been characterised as S_3^- by a variety of techniques.[1,*]

We reported earlier that elemental sulphur in HMPA is reduced to S_3^-.[1,4] We now find that the rate of reaction and final intensity of colour is dependent on the batch of solvent, suggesting that the reducing agent is a solvent impurity. Indeed sulphur is only sparingly soluble to give a pale greenish yellow solution in HMPA which has been trickled through molecular sieves. Addition of a drop of piperidine, $C_5H_{10}NH$, to this solution caused more sulphur to dissolve giving an intense blue solution with a visible spectrum characteristic of S_3^-.[1] It is apparent that untreated HMPA contains a reducing impurity, probably dimethylamine.

The solutions of sulphur in HMPA in the presence of a secondary amine deviated strongly from Beer's Law. We therefore elected to work with piperidyl-lithium. Solutions of sulphur in HMPA containing a slight excess of piperidyl-lithium, according to equation (1), obeyed Beer's Law over a concentration range $6{\cdot}54 \times 10^{-4}$—$6{\cdot}54 \times 10^{-3}$M in g atom S and gave a value of ε (620 nm) $= 1{\cdot}17 \pm 0{\cdot}02 \times 10^3$ (g atom S)$^{-1}$ cm^{-1}. The true

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[*] *Note added in proof:* In a recent investigation of alkali polysulphides in DMF, it was shown that the absorption band, λ_{max} 618 nm, reaches a maximum when S : Na = 3. At higher S : Na ratios red S_4^-, λ_{max} 513 nm, is formed at the expense of blue S_3^-. These two species and free sulphur are present in a temperature- and concentration-dependent equilibrium. See F. Seel and H. J. Güttler, *Angew. Chem. Internat. Edn.*, 1973, **12**, 420. A reinvestigation of the electrochemical reduction of elemental sulphur in DMSO agrees that the blue species λ_{max} 618 nm is S_3^-. See R. P. Martin, W. H. Doub, jr., J. L. Roberts, jr., and D. T. Sawyer, *Inorg. Chem.*, 1973, **12**, 1921, as suggested in the review by T. Chivers and I. Drummond, *Chem. Soc. Rev.*, 1973, **2**, 233.

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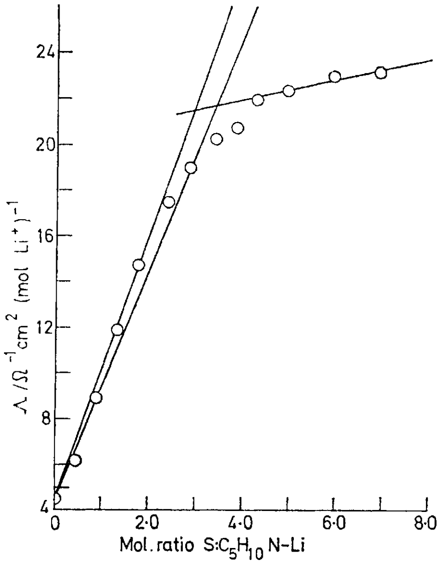
value of the extinction coefficient of S_3^- at 620 nm is 1·41 ± 0·03 × 10^3 (g atom S)$^{-1}$ cm^{-1},[1] so the above value for elemental sulphur indicates that 3·6 ± 0·1 S atoms react to give each S_3^- ion. The results of the conductometric titration of S_8 with piperidyl-lithium are shown in the Figure The value of Λ at the end point (21·4 Ω^{-1} cm^2 mol^{-1}) is reasonable for an electrolyte $Li^+S_3^-$ (*cf.* $Na^+S_3^-$, Λ_0 = 22·4 Ω^{-1} cm^2 mol^{-1}).[1] The titration indicates that 3·2 ± 0·2 S atoms react with each mole of piperidyl-lithium. The stoicheiometry of the reaction is, therefore,



Conductometric titration of S_8 *vs.* $C_5H_{10}NLi$ in HMPA

$$7/8S_8 + 2C_5H_{10}NLi \longrightarrow 2Li^+ + 2S_3^- + [S^{II}] \quad (1)$$

The g.l.c. of the reaction mixture showed the presence of a single organosulphur compound identified as tris(dimethylamino)phosphine sulphide by its mass spectrum and by comparison of its retention time with that of an authentic sample. We showed that dipiperidyl sulphide is converted to tris(dimethylamino)phosphine sulphide on standing in HMPA overnight. The overall reaction of piperidyl-lithium with elemental sulphur may therefore be written,

$$\begin{tikzcd}
7/8S_8 + 2C_5H_{10}NLi \arrow[r] & 2Li^+ + 2S_3^- + (C_5H_{10}N)_2S \arrow[d, "{[(CH_3)_2N]_3PO}"] \\
 & {[(CH_3)_2N]_3PS}
\end{tikzcd}$$

We thank Dr. J. Rolfe for helpful correspondence Tom Martin for performing the g.l.c. experiments, and the National Research Council of Canada and the University of Calgary for financial support.

[3/1556 *Received, 24th July*, 1973]