The nmr spectra show somewhat less shielding for the fluorine atom in the oxygen than in the nitrogen compounds.

The nmr spectra of the compounds $RCF_2N{=}S(R)F$ [Figure 1] show AB structure for the CF_2 group. In $RCXYNSF_2$ derivatives the fluorine atoms in the NSF_2 group are magnetically nonequivalent.[7-9] The observed temperature dependence of the nmr spectra may be accounted for in terms of a hindered rotation around the C–N axis. Conversely bulky substituents at the sulfur atom should also cause steric hindrance, and this should result in magnetic nonequivalence of the CF_2 fluorines. The same could be expected also for the compounds $RCF_2N{=}SCl_2$, $N{=}S(NR_2)Cl$, and $N{=}S(OR)_2$. Presumably coupling between the fluorine atoms attached to the C atom is not observed as a result of a high $J/\nu_0\delta_{AB}$ value.

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Characterization of the Trisulfur Radical Anion S_3^- in Blue Solutions of Alkali Polysulfides in Hexamethylphosphoramide

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Alkali polysulfides dissolve in hexamethylphosphoramide (HMPA) to give deep blue solutions. The blue species has been characterized as S_3^- by electrical transference, conductivity, and magnetic susceptibility measurements and by visible, ultraviolet, infrared, Raman, and electron spin resonance spectra.

Introduction

It has been known for a long time that a blue color develops when sulfur is heated with water and traces of some basic salt.[1,2] Blue solutions are also formed by sulfur in alkali halide melts,[3,4] in sulfur-doped borate glasses,[5] by alkali polysulfides in basic solvents, *e.g.*, dimethylformamide (DMF)[6,7] and dimethyl sulfoxide (DMSO),[8] or by electrochemical reduction of S_8 in DMSO.[9,10] In all cases the blue species is characterized by a visible absorption band at *ca.* 620 nm. The identity of the blue species has been uncertain; Lux and coworkers claim the color is due to neutral molecules S_x ($x = 2$–4)[6,8] while Giggenbach claims that it is due to the radical anion S_2^-.[2,5,7] Giggenbach also suggests that the blue color of ultramarine can be attributed to S_2^-,[7] while other workers[11] propose that S_2^- and/or S_3^- is responsible for the color of the mineral. Merritt and Sawyer suggest that S_8^- is the species formed by electrochemical reduction of elemental sulfur in DMSO,[9] but this has recently been disproved by Bonnaterre and Cauquis[10] who show that the oxidation state of the sulfur in this system is $-^1/_3$; they propose S_6^{2-}. Gruen and coworkers[4] agree that the blue species is sulfur($-^1/_3$) but they attribute it to S_3^-.

The centers S_2^- [12] and S_3^- [13] have both been characterized by esr spectra of sulfur-doped alkali halide crystals and it has been shown by resonance Raman and infrared spectra[14] that S_3^- is associated with a visible absorption band at 610 nm while S_2^- absorbs at 400 nm. Esr and Raman studies of ultramarine show that the blue color is due to S_3^-.[14]

During investigations of HMPA as a solvent for electrochemical reductions we observed that sulfur is sparingly soluble in HMPA to give a blue anionic species[15] which showed the same characteristic structured absorption band at 620 nm as alkali polysulfides in DMF.[7] Since the negatively charged species has been produced from elemental sulfur, the sulfur has either disproportionated or, more probably, been reduced by the solvent. Electrical transference experiments have shown that anionic species with characteristic visible absorption bands at 616 and 400 nm are formed when elemental sulfur dissolves in ethylenediamine.[16] The 616-nm band was attributed to sulfur radical ions ($\cdot S$–S_x–S^-).[16] To elucidate the controversial nature of the blue species we have studied its formation from polysulfides (*i.e.*, sulfur in various mean oxidation states) in HMPA.

Experimental Section

Materials.—The air sensitive, blue solutions were always handled in a dry oxygen-free atmosphere (Vacuum Atmospheres drybox) and allowed to equilibrate for 24 hr before measurements were made. HMPA was obtained from Aldrich and vacuum

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distilled (bp 68° (0.4 mm); lit. 65° (0.4 mm)[17] 68° (1 mm)[18]) from sodium or potassium metal in 500 ml batches rejecting the first 30 ml and last 70 ml. It was stored in a dry, oxygen-free atmosphere and showed no impurities by polarography.[19] The conductivity remained constant over several weeks at *ca.* 12 × 10^6 ohms cm (lit. 7–18 × 10^6 ohms cm[20]). Sulfur (Shawnigan, sublimed grade) was resublimed before use. The following anhydrous sodium polysulfides were prepared by Carius tube reactions of sodium and sulfur in dry liquid ammonia: $Na_2S_{3.08\pm0.06}$, S, 68.2 ± 0.4%; $Na_2S_{3.53\pm0.05}$, S, 71.1 ± 0.3%; $Na_2S_{4.65\pm0.10}$, S, 76.4 ± 0.6%; $Na_2S_{5.8\pm20.18}$, S, 78.8 ± 1.0%; $Na_2S_{7.18\pm0.70}$, S, 83.4 ± 1.2%; $Na_2S_{13.7\pm0.8}$, S, 90.5 ± 0.5%. They were analyzed for sulfur by oxidation to sulfate using basic peroxide or bromine followed by addition of nitric and hydrochloric acids. The sulfate was then determined gravimetrically as barium sulfate.

Physical Measurements.—For the electrical transference experiment a five-compartment cell with sintered glass divisions between the compartments was used. The blue solution was placed in the central compartment and HMPA containing Bu_4NClO_4 in the other four compartments. A dc potential of 50 V was applied across the platinum electrodes in the two end compartments. Conductivity was measured at 25° using a Beckman RC18 conductivity bridge operating at 3 kHz. Magnetic susceptibilities were measured using the nmr method.[21] Infrared spectra were obtained with a Perkin-Elmer 337 spectrometer. Raman spectra were obtained using a He/Ne laser operating at 6328 Å, collinear excitation and viewing with a Cary 81 spectrophotometer. Esr spectra were measured using an X-band spectrometer.

Results and Discussion

Visible and Ultraviolet Spectra.—Solutions of all the polysulfides and very dilute (*ca.* 2 × 10^{-5} *M* S_8) solutions of elemental sulfur gave similar spectra (Figure 1) with no variation in the relative intensities of the peaks at 620 and 277 nm or of the fine structure of the 620 nm peak. Identical spectra were obtained from the blue anodic solutions after electrical transference indicating that the two peaks are due to one negatively charged species. The polysulfide solutions obeyed Beer's law within 2–3% over the concentration range 1 × 10^{-4} to 5 × 10^{-3} g-atom of S/l. We take this as evidence that in this highly basic system the reaction(s) occurring have gone to completion. The experimental results for the intensity of the 620 nm peak for various polysulfides are shown in Figure 2. Since the extinction coefficient is expressed in terms of g-atoms of S/l. in the solution, it is apparent that the mean oxidation state of sulfur makes little difference to the intensity of the 620 nm peak if it is between 0 and $-^2/_7$. This suggests that the sulfur is being reduced rather than disproportionating to give the blue species. The value of ϵ(620 nm) is 1410 ± 30 l. (g-atom of S)$^{-1}$ cm^{-1}. At more negative mean oxidation states ϵ(620 nm) becomes progressively less. We explain this as follows. We considered from all available evidence that the blue species was a radical anion of sulfur, either S_2^- or S_3^-. These species could arise from the lower polysulfides by the disproportionations

$$S_x^{2-} \longrightarrow \left(\frac{2x-2}{3}\right)S_2^- + \left(\frac{4-x}{3}\right)S^{2-} \qquad (1)$$

$$S_x^{2-} \longrightarrow \left(\frac{2x-2}{5}\right)S_3^- + \left(\frac{6-x}{5}\right)S^{2-} \qquad (2)$$

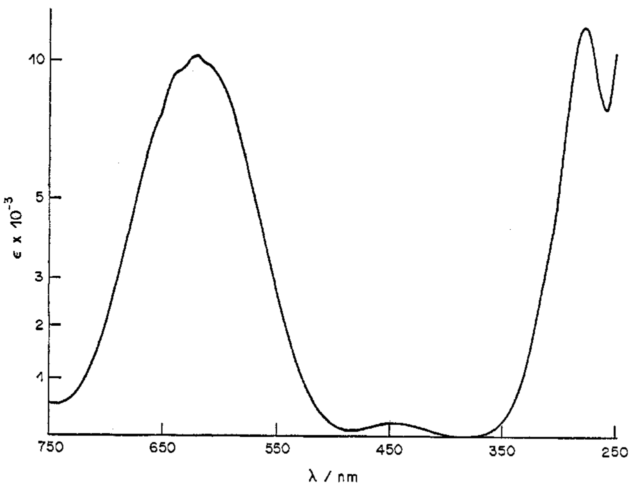

Figure 1.—Absorption spectrum of $Na_2S_{7.18}$ in HMPA (4.76 × 10^{-4} *M*).

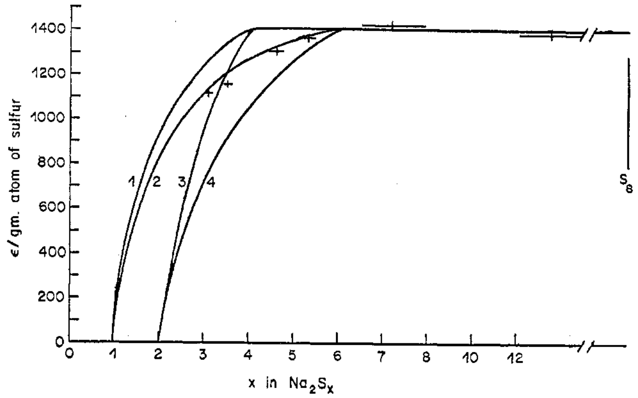

Figure 2.—Experimental values of ϵ(620 nm) in g-atoms of S l.$^{-1}$ cm^{-1} *vs.* *x* in Na_2S_x. The vertical line for S_8 represents deviation from Beer's law.

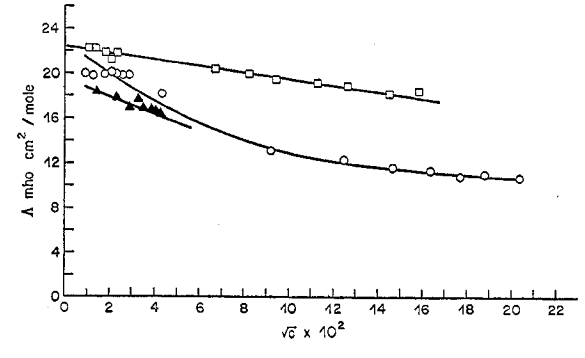

Figure 3.—Conductivity data at 25°: □ = $Na_2S_{7.18}$, ○ = $Na_2S_{13.7}$, and ▼ = S_8.

$$S_x^{2-} \longrightarrow (x-2)S_2^- + \left(\frac{4-x}{2}\right)S_2^{2-} \qquad (3)$$

$$S_x^{2-} \longrightarrow \left(\frac{x-2}{2}\right)S_3^- + \left(\frac{6-x}{4}\right)S_2^{2-} \qquad (4)$$

Given that ϵ(620 nm) = 1410 g-atoms of S l.$^{-1}$ cm^{-1} from the higher polysulfides, the solid lines 1–4 in Figure 2 show the values of ϵ(620 nm) for various polysulfides calculated on the basis of eq 1–4. There is good agreement between eq 2 and the experimental results, supporting assignments of S_3^- to the blue species.

Conductivity.—In HMPA 1:1 electrolytes generally

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have molar conductances in the range 20–25 mhos cm^2/mol (*e.g.*, LiCl, $\Lambda_0 = 24.2$;[22] $KClO_4$, $\Lambda_0 = 21.5$ mhos cm^2/mol[23]) and cation mobilities are small (*e.g.*, Na^+, $\lambda_0^+ = 5.9$ mhos cm^2/mol[23]). Figure 3 shows the conductivity data for $Na_2S_{7.18}$, $Na_2S_{13.7}$, and S_8 calculated on the assumption that all sulfur is present as S_3^-. Although there is a small variation in Λ_0 with cation the solutions behave as moderately strong 1:1 electrolytes and Λ_0 is in the range expected for $Na^+S_3^-$. Calculation of the results on the basis of higher sulfur radicals, *e.g.*, S_4^-, gives Λ_0 values which are definitely high.

Magnetic Susceptibility.—Magnetic susceptibilities of solutions of $Na_2S_{7.18}$ and $Na_2S_{13.7}$ (*ca.* 2×10^{-1} g-atom of S/l.) were found to be $(+10.2 \pm 0.8) \times 10^{-6}$ cgsu/g of sulfur at 35° indicating the presence of a large concentration of free radicals. Although these solutions are *ca.* 50 times more concentrated than the solutions for which Beer's law has been verified, if all the sulfur present is converted to the blue species, this corresponds to $\mu_{eff} = 1.27 \pm 0.05$ BM for S_2^-; 1.56 ± 0.06 BM for S_3^-; and 2.26 ± 0.06 BM for S_4^-.

Since S_3^- has a bent configuration[24] most of the spin–orbit coupling (λ) will be quenched and μ_{eff} is expected to be near 1.73 BM, the spin-only value. A similar value is expected for S_4^-. S_2^- on the other hand has a $^2\Pi_{3/2}$ ground state and provided the spin–orbit coupling is greater than kT (a reasonable assumption for the second row-element since $\lambda \simeq kT$ for NO[25]) the orbital angular momentum will add to the electron spin to give an expected value of 2 BM. Thus the magnetic data are in best agreement with the presence of S_3^- radical anions.

Electron Spin Resonance Spectra.—The blue solutions of alkali polysulfides in HMPA showed no esr signal at 25°. On cooling to $-196°$ the solutions turned green (*i.e.*, blue plus yellow, where yellow is presumably the dimer S_6^{2-}) and exhibited a sharp three-line absorption with $g_1 = 2.003 \pm 0.001$, $g_2 = 2.033 \pm 0.001$, and $g_3 = 2.047 \pm 0.001$. In addition there was a shoulder at $g = 2.052$. These values agree well with the published values for S_3^- in alkali halide crystals.[13] While this is not conclusive evidence that the blue species is S_3^- (or even of the presence of S_3^- [26]) we note the following two observations by Giggenbach. Borate glasses doped with sulfur showed a similar esr triplet only when the absorption spectrum showed a peak at 590 nm.[5] When blue solutions of Na_2S_4 in DMF were cooled, an esr absorption with $g_{av} = 2.027$ became weaker and finally disappeared as the color changed from blue through green to yellow.[7] Thus the esr data, while not conclusive, are consistent with the suggestion that the blue species is S_3^-.

Vibrational Spectra.—Fairly concentrated solutions (2×10^{-1} g-atom of S/l.) of the higher polysulfides in HMPA show a strong infrared absorption at 580 cm^{-1} attributable to the antisymmetric stretching mode of S_3^-.[11,14] An intense solvent absorption obscures any peaks which may occur below 550 cm^{-1}. However, very dilute solutions (3×10^{-3} g-atom of S/l.) when excited with the 6328 Å light of a He/Ne laser show a resonance Raman effect with a strong band at 533 cm^{-1} and overtones at 1067, 1597, and 2126 cm^{-1}. These values are in good agreement, both in frequency and in number of overtones, with the results obtained for the totally symmetric stretching vibration of S_3^- in alkali halide crystals.[14] In addition we note a weak band in the Raman spectrum at 232 cm^{-1} approximately one-tenth of the intensity of the 533-cm^{-1} band which we tentatively assign to the symmetric bending mode of S_3^-. This mode is also expected to show enhanced intensity due to the resonance Raman effect. The three frequencies 580, 533, and 232 cm^{-1} which we assign to S_3^- are accountably higher than the corresponding frequencies of H_2S_3 (488, 477, and 211 cm^{-1})[27] since H_2S_3 has an extra π antibonding electron over S_3^-.

The Nature of the Cation Derived from the Solvent.—Although it is known that HMPA is susceptible to attack by molecular oxygen,[19] the products were not identified. We can add the following observations on the products of oxidation of HMPA by elemental sulfur. The solution in the cathodic compartment of the electrical transference cell was diamagnetic and colorless, showing only a gradual rise in the base line of the uv spectrum between 400 nm and the solvent cutoff at 250 nm. Its equivalent conductivity is quite small ($\lambda_0^+ \simeq 3$ mhos cm^2/mol) suggesting either a large or heavily solvated species.

Conclusion

Direct observations (*i.e.*, resonance Raman, infrared, and esr spectra) and indirect measurements (*i.e.*, visible–uv spectra, conductivity and magnetic susceptibility) strongly suggest that the intense blue species formed by alkali polysulfides or elemental sulfur in HMPA can be attributed to the S_3^- radical anion.

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