As shown in Figure 4 there are six infrared-active absorptions, two of which dominate in the spectrum after several diffusion cycles (trace d). In a matrix of pure CO, however, the lower of these two absorptions at 1958 cm^{-1} becomes much stronger indicating that the two absorptions do not arise from the same molecular species and that the 1958-cm^{-1} band originates from the most highly coordinated species. The frequencies are tabulated in Table IV. Yb is electronically and chemically similar to the group IIa elements for which there are no known carbonyls. As a result there is no analogy from which to extrapolate even a tentative stoichiometry for the compounds. The annealing pattern is definitely different from that observed in the case of Nd and in previous studies of tetra- and hexacoordinated carbonyls in that the monotonic relation between rate of disappearance of an absorption upon diffusion and the frequency of absorption is no longer found. Without further data on other lanthanide carbonyls from which to draw some analogy, it is futile to conjecture about the stoichiometry of the ytterbium carbonyls. It is possible to conclude that Yb does form several carbonyls, however. The frequencies of the natural and ^{13}C-enriched spectra are shown in Table IV.

In summary, carbonyl compounds of Nd and Yb have been synthesized in argon matrices. The most highly coordinated Nd compound has been tentatively identified as $Nd(CO)_6$.

Table IV. Observed Vibrational Frequencies in the CO Stretching Region of Yb in Argon Matrices Doped with CO

Designation	^{12}CO	^{13}CO	Designation	^{12}CO	^{13}CO
1	2008	1964	4	1976	1936
2	1995	1953	5	1966	1923
3	1986	1943	6	1958	1917

Since Nd is a typical lanthanide, the other typical rare earth metals might be expected to form similar carbonyls. The compound(s) formed by Yb, on the other hand, are not analogous and could not be identified by the infrared spectrum.

It would be of interest to try to collect some of the carbonyl compounds at higher temperatures for further characterization; however, this was not feasible with the present apparatus. At temperatures above about 40°K the vapor pressure of the matrix resulted in loss of the insulating vacuum, with concomitant rapid evaporation of the He refrigerant and peeling of the residual matrix from the window.

Registry No. $Nd(CO)_6$, 40299-73-8.

Acknowledgments. We wish to thank Mr. Paul Palmer of Dr. F. H. Spedding's group for donating samples of Nd and Yb.

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Further Studies of the Electrochemical Reduction of Sulfur in Aprotic Solvents

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The reduction of sulfur and the solution chemistry of the various polysulfide products have been investigated in dimethyl sulfoxide by cyclic voltammetry, controlled-potential electrolysis, and absorption spectroscopy. At a gold electrode sulfur is reduced by two electrons at a potential of −0.6 V *vs.* sce to produce $S_8{}^{2-}$ and other polysulfides. These products yield, by a variety of reactions, a blue radical species, $S_3{}^-$, with an absorption maximum at 618 nm. Electrolytic reduction of sulfur yields a second process at a potential of −1.29 V with an overall stoichiometry of four electrons per S_8 molecule; the major stable product is the $S_4{}^{2-}$ species. The dissociation of $S_6{}^{2-}$ into $S_3{}^-$ has a pK_d value of 2.11 on the basis of spectrophotometric measurements. Equilibrium constants of other disproportionation and dissociation reactions for the various polysulfides also have been evaluated.

Although the sulfur-polysulfide system in aprotic solvents has been studied extensively, numerous questions remain unresolved. In particular, the nature of the blue species (618 nm) that results from sulfur reduction in aprotic or basic solvents has not been rationalized. In a previous study[1] our group reported that the blue color was due to $S_8{}^-$, the one-electron reduction product of elemental sulfur. Subsequent studies have now established that this stoichiometry is in error, probably by an inexplicable consistent misreading of the coulometer; the primary reduction step is a two-electron process. This corrected interpretation of our previous results is consistent with the recent report of Bonnaterre and Cauquis,[2] who proposed that the initial reduction of sulfur in dimethylformamide or dimethyl sulfoxide proceeds by two electrons to produce $S_8{}^{2-}$ with an absorption maximum at 505 nm. They proposed that $S_8{}^{2-}$ undergoes a dismutation reaction to give $S_6{}^{2-}$ as the blue species

$$4S_8{}^{2-} \rightleftharpoons 4S_6{}^{2-} + S_8 \qquad (1)$$

Chivers and Drummond[3] agreed with Bonnaterre and Cauquis that the blue species corresponds formally to $S_6{}^{2-}$ but assigned $S_3{}^-$ as the species responsible for the 618 nm absorbance.

Giggenbach[4] proposed yet another species, $S_2{}^-$ (formed by the dissociation of $S_4{}^{2-}$), to be responsible for the blue color of reduced sulfur in aprotic solvents. In view of these conflicting reports and the need for a rational explanation of the diverse observations, a further study of the electrochemical reduction of sulfur in aprotic solvents has been undertaken.

Experimental Section

The equipment and procedures for the electrochemical and spectrophotometric measurements were the same as those summarized in the previous paper.[1] Controlled-potential coulometry was carried out in a Dry-Lab glove box with a large gold-foil electrode. Cyclic voltammetry of reduced sulfur was performed in the glove box.

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[1] M. V. Merritt and D. T. Sawyer, *Inorg. Chem.*, 9, 211 (1970).

[2] R. Bonnaterre and G. Cauquis, *J. Chem. Soc., Chem. Commun.*, 293 (1972).

[3] T. Chivers and I. Drummond, *Inorg. Chem.*, 11, 2525 (1972).

[4] W. Giggenbach, *J. Inorg. Nucl. Chem.*, 30, 3189 (1968).

Solutions were transferred to spectrophotometric cells and stoppered under a dry nitrogen atmosphere.

Baker analyzed reagent grade dimethyl sulfoxide, DMSO, was dried over calcium hydride and distilled under vacuum. Elemental sulfur (Mallinckrodt) was recrystallized from toluene. The sodium polysulfides were synthesized by allowing stoichiometric amounts of elemental sulfur and sodium metal to react in liquid ammonia under a dry nitrogen atmosphere; the material was isolated by evaporating away all of the ammonia. Analysis for sulfide was performed by adding an aliquot of a known concentration of sulfuric acid to an aqueous solution of the polysulfide salt. The solution was boiled to drive off hydrogen sulfide and back-titrated with standardized base. Qualitative chemical and spectrophotometric tests confirmed the absence of sulfur compounds other than sulfides in the synthesized polysulfides.

Results

Electrochemistry. Figure 1 illustrates a cyclic voltammogram of elemental sulfur in dimethyl sulfoxide (DMSO) at a gold electrode. Controlled-potential electrolysis at −0.70 V indicates that the reduction of S_8 at −0.60 V is a two-electron reduction. Current, however, continues to flow even after the S_8 has been reduced by two electrons. To determine the nature of the reduction process and the number of electrons involved, cyclic voltammetry has been used to measure the concentration of unreduced sulfur remaining in solution at various time intervals during a coulometric electrolysis at −0.70 V. Figure 2 is a plot of electrons per S_8 *vs.* the per cent S_8 electrolyzed.

Controlled-potential coulometry at a potential past the second reduction wave results in a four-electron reduction of S_8 (after correction for background currents). Again a small residual current remains at the end of the electrolysis, possibly due to a disproportionation reaction to give $S_8{}^{2-}$ and other sulfides as products.

The anodic voltammetric wave at −1.17 V (Figure 1) is associated with the cathodic peak at −1.29 V. Because the ratio of the anodic peak current to the cathodic peak current is less than 1 and decreases with decreasing scan rate, a chemical reaction appears to occur after the reduction step.

The anodic peak at −0.30 V (see Figure 1) is observed for the anodic voltammetric scan of all polysulfides from $S_8{}^{2-}$ to S^{2-}. The potential of this wave becomes more positive with increasing scan rate and is sensitive to the polysulfide chain length and to concentration. By scanning in an anodic direction through this peak and then scanning in a cathodic direction the peak at −0.6 V is regenerated, indicating that S_8 or cyclic S_x is the product of this oxidation.

Addition of 35% aqueous perchloric acid (millimolar level) to an elemental sulfur solution causes the prewave at −1.14 V (Figure 1) to increase in size and the peak at −1.29 V to decrease in size. The anodic peak at −1.17 V decreases upon addition of acid and a broad ill-defined wave at approximately −0.8 V is formed. Another smaller anodic wave at −0.1 V also appears.

The small anodic wave at −0.78 V for cyclic voltammograms of S_8 solutions (Figure 1) only is observed after the cathodic peak at −1.29 V is scanned first. For the polysulfides, this peak only is observed for the initial anodic scan of a Na_2S_4 solution. A cathodic scan of a tetrasulfide solution (with a rest potential of −0.93 V) does not give a peak at −1.29 V. However, if the peak at −0.78 V is first scanned anodically and the scan reversed at −0.7 V, the peak at −1.29 V is produced.

Spectrophotometry. Figure 3 illustrates the absorption spectra for DMSO solutions of Na_2S_8, Na_2S_4, and Na_2S_6. Spectra for the electrolysis products from the first and the second reduction steps of S_8 are analogous to those for Na_2S_8 and Na_2S_4, respectively. Likewise, the spectrum for a sulfur solution which has been electrolytically reduced by 2.7 electrons per S_8 is similar to that for Na_2S_6 in Figure 3. These results are consistent with the electrochemical data and their interpretation. The visible spectra for DMSO solutions of polysulfides, Na_2S_x, all contain a peak at 618 nm. The intensity of this absorbance is dependent on the concentration of the polysulfide and on the polysulfide chain length. Figure 4 illustrates the dependence of the

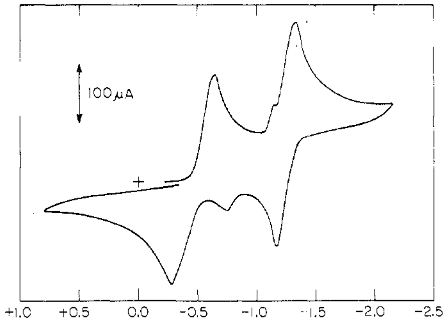

Figure 1. Cyclic voltammogram of 2.9×10^{-3} F S_8 in DMSO (0.1 F TEAP) at a scan rate of 0.1 V/sec (Au electrode).

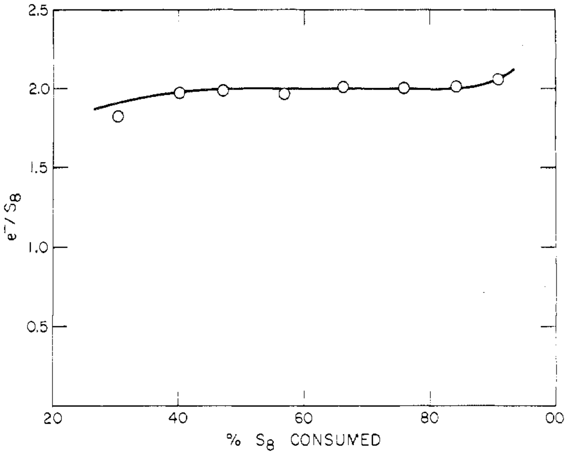

Figure 2. Electron stoichiometry (e^-/S_8) for the controlled-potential electrolysis of S_8 as a function of the percentage of S_8 consumed. Conditions: control potential, −0.70 V *vs.* sce at a gold electrode; initial S_8 concentration in DMSO (0.1 F TEAP), 6.67×10^{-3} M. S_8 concentration monitored by cyclic voltammetry.

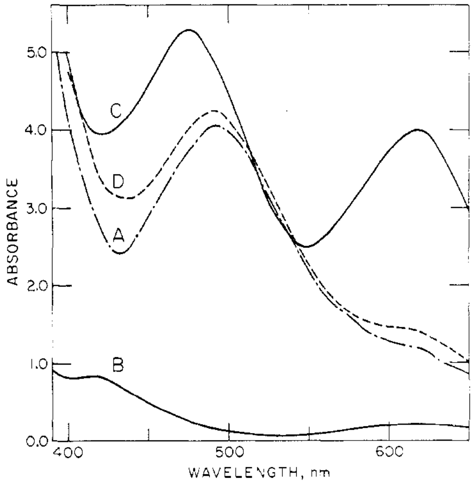

Figure 3. Absorption spectra of polysulfides in DMSO solutions in 0.1-cm cells: A, 10 mF Na_2S_8; B, 10 mF Na_2S_4; C, 20 mF Na_2S_6 (or 10 mF Na_2S_8 plus 10 mF Na_2S_4); D, sum of curve A plus curve B.

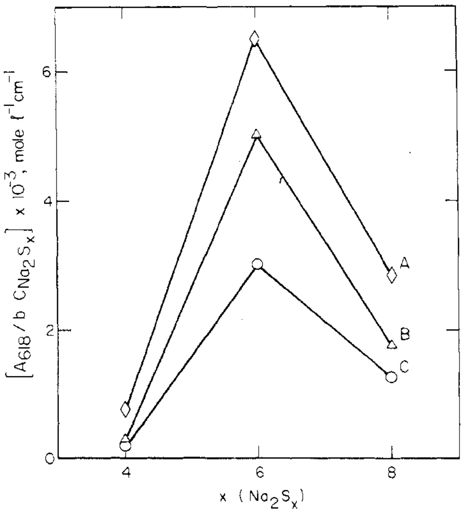

Figure 4. Apparent molar absorptivity at 618 nm for a series of polysulfide solutions in DMSO as a function of x in Na_2S_x. Formal Na_2S_x concentrations: A, 10^{-4} F; B, 10^{-3} F; C, 10^{-2} F.

apparent molar absorptivity at 618 nm on the concentration and chain length, x, of the polysulfide. The apparent molar absorptivity reaches a maximum at $S_6{}^{2-}$ for a constant sulfide concentration, indicating $S_6{}^{2-}$ or a species obtained from $S_6{}^{2-}$ is responsible for the blue color. Solid Na_2S_6 is orange, which implies that $S_6{}^{2-}$ is not the blue species.

The effect of the concentration of Na_2S_6 on the apparent molar absorptivity at 618 nm is illustrated in Figure 5. This behavior is indicative of a dissociation reaction involving $S_6{}^{2-}$ in which the product is the blue chromophore. Because the apparent molar absorptivity reaches a plateau at low concentration, due to the almost complete dissociation of $S_6{}^{2-}$, the true molar absorptivity can be estimated. Assuming that the blue species is $S_3{}^-$, in agreement with Chivers and Drummond,[3] the molar absorptivity is approximately 4×10^3 l. mol^{-1} cm^{-1}. Solutions of Na_2S_6 also contain a broad peak at 475 nm for high sulfide concentrations which probably is due to the $S_6{}^{2-}$ species (Figure 3).

The visible absorption spectrum of Na_2S_8 in DMSO (Figure 3) contains a peak at 492 nm in addition to the peak at 618 nm. As the formal concentration of $S_8{}^{2-}$ is increased, the peak at 492 nm increases relative to the peak at 618 nm, indicating that the 492-nm peak is due to $S_8{}^{2-}$.

The solution spectrum of Na_2S_4 includes a major peak at 420 nm which increases in size relative to the peak at 618 nm as the concentration of $S_4{}^{2-}$ is increased. On the basis of this, the 420-nm absorption band is assigned to $S_4{}^{2-}$. Solutions of Na_2S_4 reach equilibrium slowly; for most cases more than 24 hr is required.

Discussion and Conclusions

The electrochemical evidence confirms that elemental sulfur is reduced by two electrons at −0.6 V

$$S_8 + 2e^- \rightleftharpoons S_8{}^{2-} \qquad E_p = -0.6\ \text{V} \tag{2}$$

The irreversibility of the process probably is due to the change of structures; elemental sulfur has a cyclic structure and the polysulfide product is a linear chain.[5] Opening the S_8 ring stabilizes the double negative charge of the $S_8{}^{2-}$ product and thus shifts the oxidation potential in a positive direction.

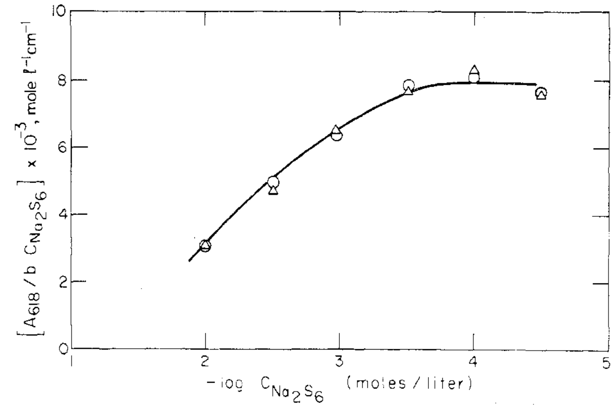

Figure 5. Apparent molar absorptivity of Na_2S_6 at 618 nm in DMSO as a function of its formal concentration, $C_{Na_2S_6}$.

The presence of the anodic wave at −0.3 V for all polysulfides indicates that this wave is due to the general oxidation of sulfides

$$S_x{}^{2-} \rightleftharpoons (x/8)S_8 + 2e^- \tag{3}$$

From electrostatic considerations the oxidation potential would be expected to become more negative as the polysulfide chain length is decreased. However, due to the poorly defined shape of the anodic waves accurate measurements of the oxidation potentials are not possible for the individual polysulfides. The potentials of the higher members of the series are sufficiently close to preclude differentiation.

The second reduction wave of S_8 can be assigned to the two-electron reduction of $S_8{}^{2-}$

$$S_8{}^{2-} + 2e^- \rightleftharpoons S_8{}^{4-} \qquad E_p = -1.29\ \text{V} \tag{4}$$

The anion $S_8{}^{4-}$ is unstable and dissociates to the $S_4{}^{2-}$ species

$$S_8{}^{4-} \rightarrow 2S_4{}^{2-} \tag{5}$$

Reaction 5 is slow in comparison to the time scale of a cyclic voltammogram as demonstrated by the oxidation wave for $S_8{}^{4-}$ which has approximately the same peak current as the reduction wave (Figure 1). However, during the course of a controlled-potential electrolysis there is sufficient time for reaction 5 to go to completion such that only $S_4{}^{2-}$ remains at the end.

The prewave at 1.14 V for the voltammetric reduction of S_8 probably is due to the reduction of a protonated form of the $S_8{}^{2-}$ anion

$$HS_8{}^- + 2e^- \rightleftharpoons HS_8{}^{3-} \qquad E_{pc} = -1.14\ \text{V} \tag{6}$$

that results from proton abstraction from the solvent. The small oxidation wave at −0.75 V (Figure 1) appears to be due to the reverse of reaction 6. Because this wave is observed for solutions of the $S_4{}^{2-}$ species, a protonation equilibrium is implied

$$HS_4{}^- + S_4{}^{2-} \rightleftharpoons HS_8{}^{3-} \tag{7}$$

Consideration of the spectroscopic evidence (Figures 3-5) indicates that the blue species (618 nm) in aprotic solvents results from the dissociation of $S_6{}^{2-}$

$$S_6{}^{2-} \rightleftharpoons 2S_3{}^- \qquad K_d \tag{8}$$

The formal oxidation state of sulfur is the same as that proposed by Bonnaterre and Cauquis,[2] but the increase in apparent molar absorptivity with decreasing concentration indicates that the radical anion, $S_3{}^-$, and not the hexasulfide, $S_6{}^{2-}$, is responsible for the absorbance at 618 nm. The apparent dissociation constant of reaction 8 is given by the expression

$$K_d' = [S_3{}^-]^2/[S_6{}^{2-}]_T \tag{9}$$

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(5) G. Nickless, Ed., "Inorganic Sulphur Chemistry," Elsevier, New York, N. Y., 1968, pp 690, 691.

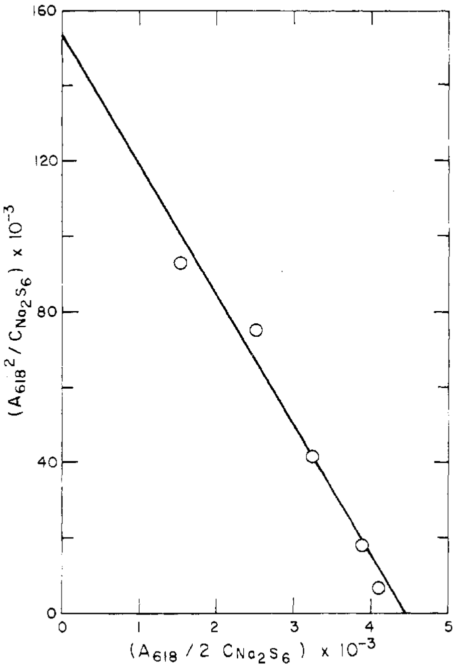


Figure 6. Analysis of spectrophotometric data for the 618-nm peak of Na_2S_6 solutions as a function of their formal concentration, $C_{Na_2S_6}$. Slope −34.6; ordinate intercept 1.54×10^5.

Substitution of $A_{618}/\epsilon_{S_3^-}$ for the concentration of S_3^- and $[C_{S_6^{2-}} - (A_{618}/2\epsilon_{S_3^-})]$ for the concentration of S_6^{2-} (including any S_4^{2-} and S_8^{2-} formed by disproportionation of S_6^{2-}), where A_{618} is the absorbance at 618 nm, $\epsilon_{S_3^-}$ the molar absorptivity of S_3^-, and $C_{S_6^{2-}}$ the formal concentration of S_6^{2-}, gives an expression that can be rearranged to

$$\frac{A_{618}{}^2}{C_{S_6^{2-}}} = \left(K_d \epsilon_{S_3^-}{}^2\right) - \left(K_d \epsilon_{S_3^-}\right)\left(\frac{A_{618}}{2C_{S_6^{2-}}}\right) \qquad (10)$$

By plotting $A_{618}{}^2/C_{S_6^{2-}}$ *vs.* $A_{618}/2C_{S_6^{2-}}$, as illustrated in Figure 6, a straight line is obtained with an intercept of $K_d'\epsilon_{S_3^-}{}^2$ and slope of $-K_d'\epsilon_{S_3^-}$. Dividing the intercept by the slope gives the molar absorptivity of S_3^-, 4.45×10^3 l. mol^{-1} cm^{-1}, which is in reasonable agreement with the value obtained from Figure 5. The value of K_d' calculated from either the slope or the intercept is 7.7×10^{-3}.

The spectrophotometric data for Na_2S_8, Na_2S_6, and Na_2S_4 solutions (Figure 3) confirm that the uv-visible spectrum for a 20 m*F* solution of Na_2S_6 is identical with that for a solution which contains 10 m*F* Na_2S_8 and 10 m*F* Na_2S_4. Furthermore, addition of the spectrum for a 10 m*F* Na_2S_8 solution to that for a 10 m*F* Na_2S_4 solution is completely different from the spectrum for their mixed solution at the same concentrations. These two observations are strongly supportive of the conclusion that these three polysulfide ions are in equilibrium *via* a disproportionation reaction

$$2S_6{}^{2-} \rightleftharpoons S_4{}^{2-} + S_8{}^{2-} \quad K_1 \qquad (11)$$

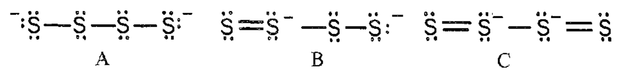
Again, the data of Figure 3 plus the values of K_d' and $\epsilon_{S_3^-}$ permit evaluation of K_1; the average value is 4×10^{-2}. Such a value confirms that the degree of disproportionation of $S_6{}^{2-}$ solutions is limited to about 28% and that combinations of $S_4{}^{2-}$ and $S_8{}^{2-}$ ions react to a major degree to form $S_6{}^{2-}$ ions.

The latter conclusion may account for some of the complications encountered in the electrochemical reduction of the $S_8{}^{2-}$ species. Although the $S_6{}^{2-}$ species is reduced at essentially the same potential as $S_8{}^{2-}$, its formation from the $S_4{}^{2-}$ product and $S_8{}^{2-}$ reactant *via* reaction 11 probably affects the diffusional process and the chronopotentiometric data.

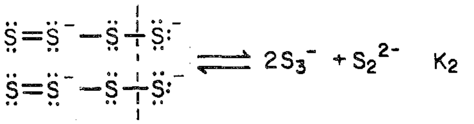
The degree of disproportionation of $S_6{}^{2-}$, as indicated by K_1, allows evaluation of the true dissociation constant for reaction 8, K_d, because the equilibrium concentration of $S_6{}^{2-}$ can be estimated; the value of K_d is 9×10^{-3}. The molar absorptivity of the $S_6{}^{2-}$ species at 475 nm is 3.8×10^3 l. mol^{-1} cm^{-1} based on the data of Figure 3 and the values of K_d and K_1.

Although the blue color is most intense in a solution of Na_2S_6, it also is observed in solutions of the other polysulfides as well (Figures 3 and 4).

The presence of S_3^- in tetrasulfide solutions can be explained by a reaction in which $S_2{}^{2-}$ is formed. Giggenbach[4] has proposed three resonance forms for $S_4{}^{2-}$



and has concluded that in dimethylformamide (DMF) dissociation of resonance form C yields S_2^- as the blue species. However, consideration of resonance form B allows the proposal of a binuclear reaction process



(12)

which would still be consistent with Giggenbach's data.[4] The observed slowness of formation of the blue species from $S_4{}^{2-}$ may be due to the necessity of bringing two dianions together. Consideration of the data in Figure 4 in combination with the molar absorptivity for S_3^- as well as other spectrophotometric measurements for Na_2S_4 (Figure 3) allows the equilibrium constant for reaction 12, K_2, to be evaluated; the average value is 4×10^{-7}. On the basis of this result and the data of Figure 3 the molar absorptivity of the $S_4{}^{2-}$ species at 420 nm is 0.9×10^3 l. mol^{-1} cm^{-1}.

The low value of K_2 confirms that reaction 12 proceeds to only a limited extent in DMSO. The more fully reduced sulfur species ($S_2{}^{2-}$ and S^{2-}) have virtually no absorbance at 618 nm. The intense blue color observed by Giggenbach[4] in DMF solutions can be attributed to a stabilizing effect of the DMF solvent on the S_3^- species.

With respect to $S_8{}^{2-}$ solutions and the presence of a 618-nm absorption peak, the reaction

$$4S_8{}^{2-} \rightleftharpoons 4S_6{}^{2-} + S_8 \quad K_3 \qquad (13)$$

has been proposed[2] as a route to $S_6{}^{2-}$. This is consistent with the present electrochemical and spectrophotometric evidence. The data of Figure 4 for Na_2S_8, when combined with the value for K_d (reaction 7) permit evaluation of K_3 for reaction 13 in terms of the 618-nm absorbance for S_3^-; the average value is 8×10^{-8}. On the basis of this result and the data of Figure 3 the molar absorptivity of the $S_8{}^{2-}$ species at 492 nm is 4.0×10^3 l. mol^{-1} cm^{-1}.

The results of the present investigation provide the basis for the selective production and identification of polysulfide ions in aprotic solvents. Studies of the reactivity of such ions and of S_3^- with transition metal ions are in progress. The goal is to gain a better understanding of the metal-sulfur chemistry of metalloenzymes.

Registry No. S_8, 10544-50-0; Na_2S_8, 12439-15-5; Na_2S_4, 12034-39-8; Na_2S_6, 37188-08-2; S_3^-, 12597-04-5; S_6^-, 12597-13-6; S_4^{2-}, 12597-07-8; S_8^{2-}, 12764-43-1.

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Notes

Contribution from the Department of Chemistry, East Texas State University, Commerce, Texas 75428

Tetraperoxychromate(V)-Diperoxychromate(VI) Equilibrium in Basic Aqueous Hydrogen Peroxide Solutions[1]

Bryan L. Bartlett and D. Quane*

Received June 8, 1972

In basic aqueous hydrogen peroxide solutions chromate is present as the red-brown tetraperoxychromate(V) ion, CrO_8^{3-}, and in neutral solutions as the violet diperoxychromate(VI) ion, $HCrO_6^-$.[2] It has been shown that interconversion reactions between these species take place readily on adjustment of the basicity of the solution.[2a,3] The structure of the tetraperoxychromate ion in the solid state has been firmly established on the basis of X-ray diffraction studies of the potassium salt.[4] Various formulas have been given for the violet species.[2] The uncertainty in identification of this species has been due to the instability of its solid salts. $HCrO_6^-$, now generally accepted as the correct formula, was proposed by Griffith[5] on the basis of analytical and spectroscopic data. The present spectrophotometric study of the equilibrium existing in aqueous hydrogen peroxide solutions between the tetraperoxy and diperoxy species provides supporting evidence for Griffith's formula.

Assuming that the structure of the violet peroxychromate is that proposed by Griffith, $HCrO_6^-$, two reaction schemes involving the interconversion of the two peroxides might be written. The first possibility involves oxygen evolution on conversion of the tetraperoxychromate to the diperoxy species.

$$CrO_8^{3-} + 2H^+ \rightleftarrows HCrO_6^- + {}^3/_4 O_2 + {}^1/_2 H_2O \qquad (1)$$

Rapid oxygen evolution has been observed on addition of K_3CrO_8 to neutral peroxide solutions.[3] However, once equilibrium is obtained, oxygen evolution at 0° is only slight, and the equilibrium relationship may also be represented by

$$HCrO_6^- + {}^3/_2 H_2O_2 \rightleftarrows CrO_8^{3-} + 2H^+ + H_2O \qquad (2)$$

For both of these reaction schemes, at a given ionic strength and peroxide concentration (and for reaction 1, under constant partial pressure of oxygen), an apparent equilibrium constant would be given by the relationship

$$K_a = [CrO_8^{3-}][H^+]^2/[HCrO_6^-] \qquad (3)$$

from which the following relationship is derived.

$$pK_a = 2\text{ pH} - \log([CrO_8^{3-}]/[HCrO_6^-]) \qquad (4)$$

It can be shown that in a given solution of absorptivity λ_ϵ at some arbitrary wavelength λ, the concentration ratio is given by

$$\frac{[CrO_8^{3-}]}{[HCrO_6^-]} = \frac{{}^\lambda\epsilon_A - {}^\lambda\epsilon}{{}^\lambda\epsilon - {}^\lambda\epsilon_B} \qquad (5)$$

where ${}^\lambda\epsilon_A$ is the absorptivity at λ of a solution containing only the diperoxychromate ion and where ${}^\lambda\epsilon_B$ is the absorptivity at λ of a solution containing only tetraperoxychromate. Thus, for a series of spectra run under identical conditions of solvent composition and ionic strength, a plot of log ${}^\lambda\epsilon_A - {}^\lambda\epsilon/{}^\lambda\epsilon - {}^\lambda\epsilon_B$ *vs.* the pH of the solution should give a straight line with a slope of 2. Furthermore, where log ${}^\lambda\epsilon_A - {}^\lambda\epsilon/{}^\lambda\epsilon - {}^\lambda\epsilon_B = 0$, the apparent p$K$ is equal to twice the pH at the intercept. Such plots were prepared at two wavelengths, one on either side of the isosbestic, at 500 and 425 nm, corresponding to the maximum and minimum, respectively, of the diperoxychromate absorption spectrum.

Experimental Section

Reagents and Glassware. Hydrogen peroxide (90%), obtained from the FMC Corp., was diluted to the desired concentration using deionized distilled water. All other chemicals were standard, reagent grade. Sodium perchlorate solutions were standardized by pipeting a known volume into a flask, evaporating to dryness, and weighing the residue. Carbonate-free sodium hydroxide was prepared according to the method of Kolczynski, Roth, and Shanley.[6] All glassware used was cleaned several times using the method recommended by Easton, Mitchell, and Wynne-Jones[7] in order to minimize peroxide decomposition during the course of the measurements.

Spectrophotometric Measurements. The following procedure was used for preparing solutions for spectrophotometric measurements of the tetraperoxy–diperoxy equilibria. Neutral and 0.10 *M* sodium hydroxide stock solutions were prepared having the desired peroxide concentration and total ionic strength (sodium perchlorate was used as the ionic medium). A series of solutions of varying basicity was prepared using differing ratios of the two stock solutions. The neutral solution containing no added base was generally the least basic solution in the series. In some series (those at 1.0 *M* total ionic strength) it was necessary to add perchloric acid in order to obtain a solution in which the equilibrium was shifted to complete diperoxychromate formation. Preparation of solutions was carried out in volumetric flasks immersed in an ice–salt bath to minimize peroxide decomposition. A weighed amount of J. T. Baker reagent grade K_2CrO_4 was added to each of eight 50-ml volumetric flasks. The flasks were then filled to 50 ml with each of a set of eight peroxide solutions, prepared as described above, the chromate was dissolved, and the resulting solution was placed in an ice bath at 0°. The solutions were allowed to sit for about 1.5–2 hr to achieve equilibrium. The spectrum of each solution was then recorded from 600 to 350 nm using a Cary Model 15 recording spectrophotometer whose sample compartment was continuously purged with nitrogen to prevent fogging of the cell. As quickly as possible after recording the spectrum, the pH of each solution was determined using a Beckman Research Model pH meter using a glass electrode and a calomel reference electrode containing 4 *M* NaCl. The observed readings were corrected using the empirical correction factors determined by Kolczynski, Roth, and Shanley for aqueous hydrogen peroxide solutions.[6]

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(1) Taken from the B.S. Honors Thesis of B. L. B., East Texas State University, 1972; presented, in part, at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(2) Reviews of, and extensive references to, earlier work on chromium peroxide systems can be found in (a) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, 6, 279 (1964); (b) S. B. Brown, P. Jones, and A. Suggett, *Progr. Inorg. Chem.*, 13, 159 (1970).

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(5) W. P. Griffith, *J. Chem. Soc.*, 3948 (1962).

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(7) M. F. Easton, A. G. Mitchell, and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **48**, 796 (1952).