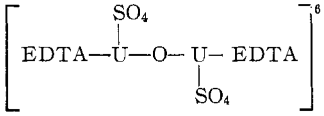
proton nmr peaks at low temperatures can be explained by a decrease in the exchange rate for water molecules with coordinated SO_4^{2-} ions to give a stable solution structure of the form



$$\left[\mathrm{EDTA}-\overset{\mathrm{SO_4}}{\overset{|}{\mathrm{U}}}-\mathrm{O}-\underset{\mathrm{SO_4}}{\underset{|}{\mathrm{U}}}-\mathrm{EDTA}\right]^{6-}$$

Acknowledgment.—We thank Professor R. C. Neuman, Jr., and Miss V. Jonas of this department for supplying the IBM Fortran computer programs and for helpful discussions. This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-34, Project No. 45. We are grateful to the National Science Foundation for a predoctoral traineeship to D. L. E.

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Electrochemical Reduction of Elemental Sulfur in Aprotic Solvents. Formation of a Stable S_8^- Species

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The electrochemical reduction of elemental sulfur has been investigated in several aprotic solvents using a gold electrode. Reduction occurs by two one-electron steps with S_8 the electroactive species. The stoichiometry and kinetics of the reduction have been studied by chronopotentiometry, cyclic voltammetry, and controlled-potential electrolysis. The first step has a voltammetric E_p value of −0.62 V *vs.* sce in DMSO; the second reduction step has an E_p value of −1.29 V *vs.* sce. Controlled-potential electrolysis at the first potential yields a new stable oxidizable sulfur species with an anodic E_p value of −0.23 V *vs.* sce. The electronic spectrum for the product of the first reduction step, "S_8^-," exhibits absorption maxima at 490 and 618 mμ. Concentration studies establish that the S_8^- species undergoes dimerization with a formation constant of 5000 M^{-1}.

The polarographic reduction of elemental sulfur in protic solvents has been studied extensively;[1-3] the final product is mercuric sulfide.[1,2] The electrochemical reduction of sulfur also has been examined in fused salts; sulfide is assumed to be the product in a LiCl–KCl eutectic.[4] The present paper summarizes the results of a detailed investigation of the electrochemistry of elemental sulfur in aprotic solvents.

Experimental Section

A solid-state potentiostat–amperostat[5] with a Sargent Model SR recorder, a Moseley Model 7035A X-Y recorder, and a Tektronix Model 564 oscilloscope was used for all electrochemical operations and measurements. A conventional two-compartment electrochemical cell with a three-electrode system was used for coulometric experiments; a large gold foil (reagent grade) functioned as the working electrode. For chronopotentiometric and cyclic voltammetric studies a gold billet sealed in a polyethylene tube (gold-inlay electrode) was used as the working electrode. The area of the gold-inlay electrode was determined by reduction of ferricyanide ion in water. An aqueous Ag–AgCl reference electrode was used which has been described previously;[6] its potential was 0.000 V *vs.* sce. The isolated counterelectrode was a large platinum gauze. All solutions were deaerated with prepurified nitrogen prior to electrochemical measurements.

Baker Analyzed reagent grade dimethyl sulfoxide (DMSO) was used without further purification. The supporting electrolyte, tetraethylammonium perchlorate (TEAP) (Distillation Products Industries), was recrystallized three times from water. Elemental sulfur (Mallinckrodt) was recrystallized from benzene. A sample of sodium polysulfide was supplied by FMC Corp. The visible spectra were recorded with a Cary Model 14 spectrophotometer.

Results

Cyclic Voltammetry and Coulometry.—Figure 1 illustrates cyclic voltammograms of elemental sulfur in DMSO at a gold electrode. The curves indicate that the reduction proceeds by two steps, each of which involves the same number of electrons. Furthermore, the product of each reduction step can be reoxidized to the starting material on the time scale of Figure 1, even though these processes are irreversible by electrochemical criteria. That is, the peak potential for each reduction is separated from the corresponding anodic peak potential by more than 56 mV and the peak potentials are dependent on the scan rate. Qualitatively, the same electrochemical behavior is observed with sulfur in tetrahydrofuran and dimethylformamide at a gold electrode, or in DMSO at a platinum or graphite electrode; the peak potentials are slightly different. The sulfur system behaves most reversibly in DMSO with gold as the electrode material; consequently, this system has been used for the remainder of the studies.

A series of controlled-potential electrolyses at −0.60 V *vs.* sce have established that one electron per eight

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[1] G. Hauck and M. v. Stackelberg, *Leybold Polarograph. Ber.*, **4**, 81 (1956); *Chem. Abstr.*, **54**, 15023*i* (1960).

[2] S. I. Zhdanov and B. A. Kiselev, *Collection Czech. Chem. Commun.*, **31**, 788 (1966).

[3] R. E. Humphrey, *Anal. Chem.*, **34**, 167 (1962).

[4] F. G. Bodewig and J. A. Plambeck, *J. Electrochem. Soc.*, **116**, 607 (1969).

[5] A. D. Goolsby and D. T. Sawyer, *Anal. Chem.*, **39**, 411 (1967).

[6] D. T. Sawyer and J. L. Roberts, Jr., *J. Electroanal. Chem.*, **12**, 90 (1966).

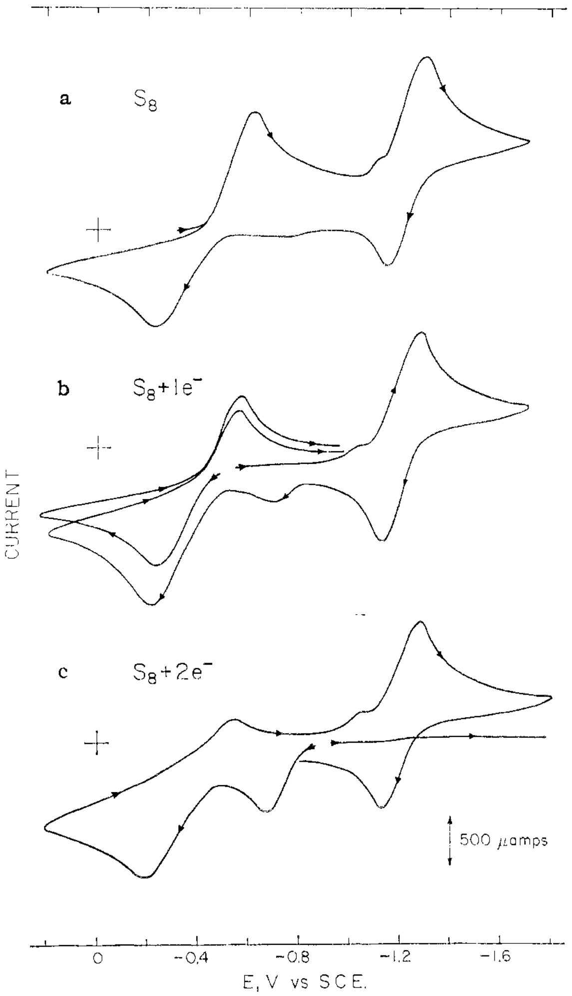

Figure 1.—Cyclic voltammetry of S_8 and its reduction products in DMSO (0.1 *F* TEAP) at an Au electrode; scan rate, 0.1 V sec^{-1}: (a) 4.26 m*M* S_8; (b) 4.26 m*M* "S_8^-"; (c) 4.26 m*M* "S_8^{2-}."

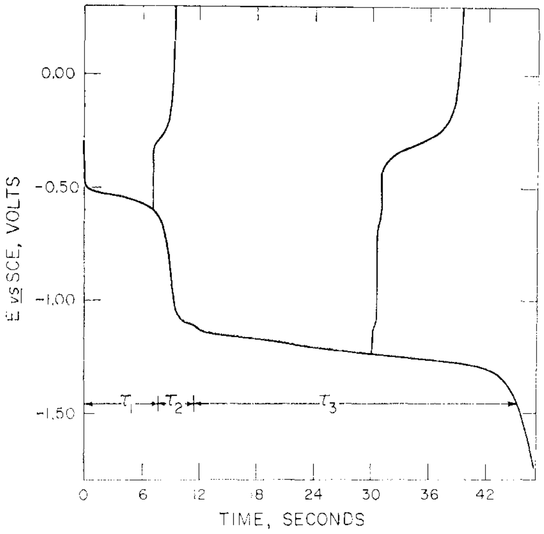

Figure 2.—Chronopotentiometry of 4.26 m*M* S_8 in DMSO (0.1 *F* TEAP) at an Au electrode: i, 100 μA; τ_1, transition time for the first reduction; $\tau_2 + \tau_3$, transition time for the second reduction.

sulfur atoms is consumed in the first reduction (1 e^-/(7.8 ± 0.4 sulfur atoms)). Cyclic voltammetry of these solutions (see Figure 1) indicates that the reduction product, "S_8^-," is the same as from the cyclic voltammograms of elemental sulfur; *i.e.*, the product formed within a few tenths of 1 sec after the addition of one electron is stable. Additional electrochemical and spectrophotometric studies have established that the "S_8^-" species is stable for at least several weeks in an inert atmosphere. Reoxidation of "S_8^-" solutions at 0.00 V *vs.* sce consumes the same number of coulombs as the reduction, within experimental error.

The same product is obtained either by reduction of "S_8^-" solutions at −1.20 V *vs.* sce or by reduction of elemental sulfur solutions at the same potential. The stoichiometry of these reductions also has been established by coulometry—1.0 ± 0.1 e^-/"S_8^-" or 2.0 ± 0.2 e^-/S_8. The cyclic voltammograms of these solutions (Figure 1) indicate that the initial product is unstable and yields a final product which is not a simple two-electron adduct of S_8. Cyclic voltammograms of sodium polysulfide ($Na_2S_{9.5}$) solutions (with the same approximate concentrations as those of the "S_8^{2-}" solutions) are nearly identical with those obtained from "S_8^{2-}" solutions. This similarity indicates that the decomposition of the initial product of the two-electron reduction of elemental sulfur probably is polysulfide. The "S_8^{2-}" product can be reoxidized to elemental sulfur as determined by chronopotentiometry of the reoxidized solution.

The small prewave at −1.1 V *vs.* sce in Figure 1 appears to be due to a protonated form of the "S_8^-" species. Addition of perchloric acid causes this peak to grow at the expense of the one at −1.3 V *vs.* sce. In contrast, addition of a small amount of base results in the disappearance of this peak. Addition of acid followed by addition of an equivalent amount of base leads to the regeneration of the original cyclic voltammogram. Cyclic voltammetry also indicates that the reduction of the protonated species is an irreversible process. The same reversibility of protonation is observed in the visible spectra of "S_8^-" solutions. Addition of acid causes the visible absorbance to disappear (the solution goes from its purple-green color to colorless); subsequent addition of an equivalent amount of base yields the original spectrum.

Chronopotentiometry.—Chronopotentiometry has been used to study the kinetics and mechanisms for the reduction of S_8; a typical chronopotentiogram is shown in Figure 2. The dependence of the ratio of the transition time τ_1 to ($\tau_2 + \tau_3$) is dependent upon the current i and is greater than $^1/_3$ (the theoretical value for a simple two-step reduction in which the same number of electrons is involved in each step). This type of behavior is indicative of a kinetic complication preceding the second reduction step. A further indication of some sort of equilibrium for the "S_8^-" system is the dependence of the ratio τ_1/t_{rev} upon current density.

If mass transport to the electrode is a diffusion-controlled process, then the Sand equation relates the

TABLE I

CHRONOPOTENTIOMETRIC DATA FOR THE REDUCTION OF S_8 AND OXIDATION OF "S_8^-" IN DMSO (0.1 *F* TEAP) AT A GOLD ELECTRODE

C, m*M*	$i\tau^{1/2}/C$, μA sec$^{1/2}$ mM^{-1}
	A. Reduction of S_8
1.13	72.46 ± 4.55
1.50	69.44 ± 3.46
1.88	66.44 ± 3.41
3.76	65.87 ± 1.93
4.98	63.47 ± 0.41
	Av 67.53
	B. Oxidation of "S_8^-"
1.50	38.12 ± 3.29
1.88	38.69 ± 1.00
3.76	42.81 ± 3.86
	Av 39.87

transition time to the concentration[7]

$$\frac{i\tau^{1/2}}{C} = \frac{\pi^{1/2} n F D^{1/2} A}{2} \qquad (1)$$

where i is the current, τ the transition time, C the concentration, n the number of electrons transferred, D the diffusion coefficient of the electroactive species, and A the electrode area. Reduction of S_8 in DMSO is a diffusion-controlled process; *i.e.*, $i\tau^{1/2}/C$ is constant within experimental error as shown in Table IA. The data have been obtained with a minimum variation of i of at least a factor of 20 for each concentration; in most cases a range of 50 has been used. The slight concentration dependence of $i\tau^{1/2}/C$ may be associated with the formation of the complex $S_8ClO_4^-$; this species has been shown to exist in alcoholic solution.[2] The average value of $i\tau^{1/2}/C$ has been used to calculate a diffusion coefficient for S_8 in DMSO containing 0.1 *F* tetraethylammonium perchlorate (TEAP): $D_{S_8} = 1.44 \times 10^{-5}$ cm^2 sec^{-1}.

The dependence of the $E_{1/4}$ value for the first chronopotentiometric reduction step on concentration and current density is indicative of an electrochemically irreversible process. The potential–time relationship for an irreversible reduction is given by the expression[7]

$$E = \frac{0.059}{\alpha n_a} \log \frac{nFACk^\circ_{f,h}}{i} + \frac{0.059}{\alpha n_a} \log\,[1 - (t/\tau)^{1/2}] \qquad (2)$$

where E is the potential *vs.* nhe, α the transfer coefficient, n_a the number of electrons in the rate-controlling step, F the faraday constant, A the electrode area, C the concentration, $k^\circ_{f,h}$ the heterogeneous rate constant, t the time of electrolysis, and τ the transition time.

The value of αn_a for the reduction of S_8 has been determined from the slope of plots of E *vs.* log $[1 - (t/\tau)^{1/2}]$. The intercept, $E_{t=0}$, is equal to the first term in eq 2; from the intercept a value of the heterogeneous rate constant, $k^\circ_{f,h}$, for the transfer of an electron to the S_8 species can be calculated. The kinetic parameters for a series of S_8 concentrations are summarized in Table IIA.

TABLE II

KINETICS PARAMETERS FOR THE REDUCTION OF S_8 AND OXIDATION OF $(S_8)_2^{2-}$ IN DMSO (0.1 *F* TEAP) AT A GOLD ELECTRODE

C, m*M*	*i*, μA	αn_a	$-\text{Log } k^\circ_{f,h}$
		A. Reduction of S_8	
1.13	40	0.66	8.11
	30	0.68	8.15
	25	0.74	8.67
	20	0.69	8.24
1.50	40	0.69	8.76
	30	0.71	8.93
	25	0.71	8.76
1.88	60	0.79	9.80
	40	0.65	8.39
	30	0.69	8.76
3.76	100	0.80	10.35
	80	0.74	9.59
	60	0.72	9.37
	50	0.58	9.41
	Av	0.70 ± 0.06	8.49 ± 0.82
		B. Oxidation of $(S_8)_2^{2-}$	
		$(1 - \alpha)n_a$	$-\text{Log } k^\circ_{b,h}$
1.13	10	0.27	7.40
	15	0.27	7.31
	20	0.26	7.24
	30	0.28	7.14
1.88	15	0.22	7.44
	30	0.24	7.27
	40	0.23	7.24
3.76	30	0.33	7.57
	40	0.31	7.63
	60	0.31	7.44
	Av	0.30 ± 0.03	7.37 ± 0.30

Oxidation of "S_8^-."—Solutions of "S_8^-" have been produced by controlled-potential electrolysis of S_8 solutions at −0.60 V *vs.* sce. Chronopotentiograms for the oxidation of "S_8^-" back to S_8 have been recorded for each solution over a minimum current range of 10; $i\tau^{1/2}/C$ is constant within experimental error as indicated in Table IB. The average value of $i\tau^{1/2}/C$ has been used to obtain the diffusion coefficient of "S_8^-": $D_{\text{"}S_8^-\text{"}} = 1.13 \times 10^{-5}$ cm^2 sec^{-1}. As shown in a later section, the species oxidized is a dimer for which this is its diffusion coefficient.

The $E_{1/4}$ values for the chronopotentiometric oxidation of "S_8^-" are dependent upon the current density and concentration; consequently, the relation for an electrochemically irreversible oxidation is applicable,[7] *i.e.*

$$E = -\frac{0.059}{(1 - \alpha)n_a} \log \frac{nFACk^\circ_{b,h}}{i} - \frac{0.059}{(1 - \alpha)n_a} \log\,[1 - (t/\tau)^{1/2}] \qquad (3)$$

Plots of E *vs.* log $[1 - (t/\tau)^{1/2}]$ yield straight lines from which values for $(1 - \alpha)n_a$ and log $k^\circ_{b,h}$ can be obtained. The kinetic parameters for the oxidation of $(S_8)_2^{2-}$ are summarized in Table IIB for a series of concentrations and current densities.

Reduction of "S_8^-."—In contrast to the chrono-

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(7) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954, pp 179–216.

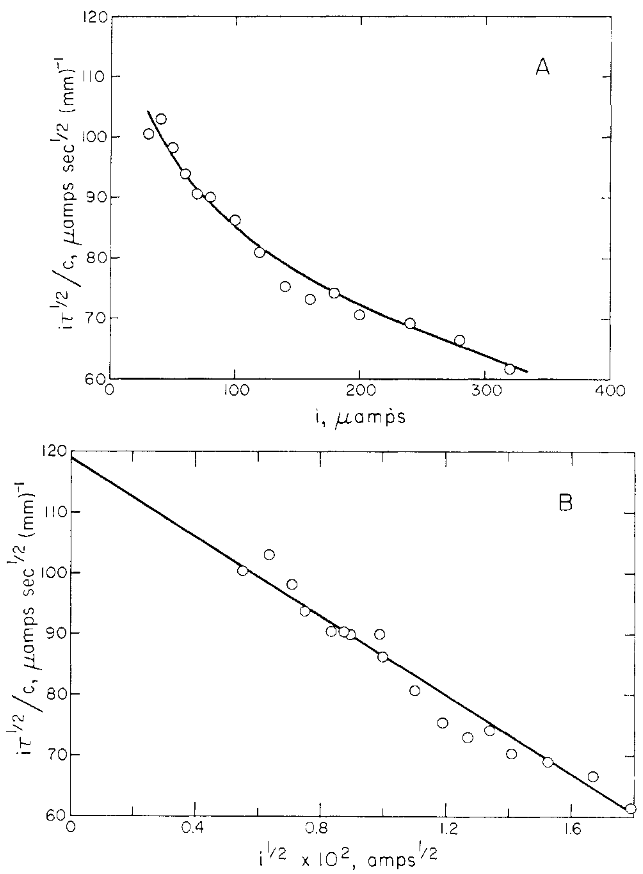

Figure 3.—Analysis of chronopotentiometric data for the reduction of 1.88 mM "S_8^-" in DMSO (0.1 F TEAP) at an Au electrode.

potentiometric oxidation of the "S_8^-" solutions, the chronopotentiometric reduction of "S_8^-" is not diffusion controlled on the basis of the inconstancy of $i\tau^{1/2}/C$ (the quantity decreases with increasing current density). The difference in behavior in the oxidation and reduction of "S_8^-" indicates that a minimum of two species must be present in equilibrium with one another.

Reinmuth has treated the variation of $i\tau^{1/2}$ with i and concentration and has analyzed the dependence of $i\tau^{1/2}$ on these parameters in terms of various kinetic schemes for reactions preceding the electron-transfer step.[8] For the reduction of "S_8^-," a plot of $i\tau^{1/2}$ *vs.* i yields values for $\partial(i\tau^{1/2})/\partial i$ and $\partial^2(i\tau^{1/2})/\partial i^2$ which are both negative (see Figure 3A). This is an indication that the process preceding the reduction is of the type $Y \rightleftharpoons pO \rightarrow R$. For such a system, $i\tau^{1/2}$ should be a linear function of $i^{1/p}$ at low current densities. Linear curves are obtained for plots of $i\tau^{1/2}$ *vs.* $i^{1/2}$ as illustrated in Figure 3B. These results indicate that the "S_8^-" system includes a dimerization equilibrium

$$(S_8)_2^{2-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2S_8^- \qquad (4)$$

with the monomer being the electroactive species for reduction. Because the oxidation is diffusion controlled, a different species must be the oxidizable material; *i.e.*, the dimeric form of "S_8^-." Furthermore, if the oxidation is diffusion controlled and the reduction is not, $k_r \gg k_f$.

Extrapolation of the plots of $i\tau^{1/2}/C$ *vs.* $i^{1/2}$ to zero current yields the same intercept (within experimental error), which is equal to $(nF\pi^{1/2}D^{1/2}A)/2$ from eq 1. The diffusion coefficient for the monomer, S_8^-, has been evaluated from this intercept: $D_{S_8^-} = 4.0 \times 10^{-5}$ cm^2 sec^{-1}. The slope of these plots is given by the expression $\pi^{1/2}(nFD^{1/2})^{1/2}(k_r^{1/2}K)^{-1/2}$, where K is the dissociation constant for the dimer.[8] A value for $k_r^{1/2}K$ has been obtained from the slope: 3.56×10^2 sec$^{-1/2}$ $M^{1/2}$ (see Figure 3B). From spectral studies discussed in a subsequent section, a value of 2×10^{-4} M has been determined for K. Therefore, k_r has a value of 3×10^{12} sec^{-1} M^{-1}; *i.e.*, the dimerization is diffusion controlled. Combination of this value with K yields a value for k_f of 5×10^8 sec^{-1}.

Spectroscopic Studies.—Magnetic resonance studies indicate that the dissociation constant of the dimer is much less than unity if the monomeric form is paramagnetic. Attempts to detect an esr signal for concentrated solutions of "S_8^-" were unsuccessful. Concentrated DMSO solutions of "S_8^-" (>0.01 F) also have been examined by proton nmr. If the solutions were paramagnetic, a shift in the solvent line should be observed.[9] The position of the DMSO line in the "S_8^-" solutions was invariant with respect to an external standard of DMSO. Approximate calculations indicate that a paramagnetic shift should have been observed if at least 10% of the "S_8^-" were present in a monomeric paramagnetic form. Because a shift is not observed, the dissociation constant for the dimer must be less than 10^{-3} M, which is in agreement with the electrochemical data.

The visible absorption spectra for "S_8^-" solutions exhibit two maxima at 490 and 618 mμ. The latter peak is predominant at low concentrations, whereas the former becomes the major peak at high concentrations (see Figure 4); this behavior is characteristic of a monomer–dimer equilibrium. Consequently, the 618-mμ maximum can be assigned to absorbance from the monomer; the dimer exhibits the 490-mμ absorbance. At total "S_8^-" concentrations of less than 1×10^{-4} F, the absorbances at both wavelengths are linear functions of concentration; *i.e.*, only the monomer is present in solution in concentrations large enough to have a

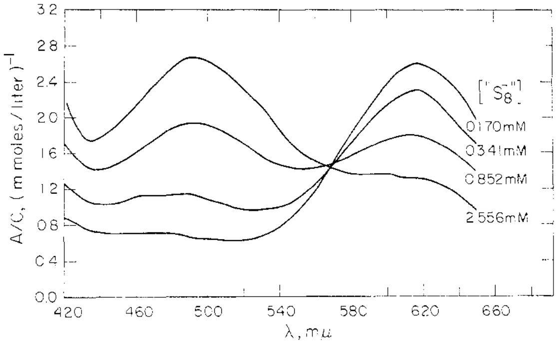

Figure 4.—Visible spectra of "S_8^-" in DMSO solutions at several concentrations.

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(8) W. H. Reinmuth, *Anal. Chem.*, **33**, 322 (1961).

(9) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

TABLE III

REDOX REACTIONS AND EQUILIBRIA FOR S_8 IN DMSO AT A GOLD ELECTRODE

	E_p *vs.* sce, V	
	Cathodic	Anodic
$S_8 + e^- \rightarrow S_8^-$	-0.62	
$2S_8^- \rightleftarrows (S_8)_2^{2-}$, $K_f = 5 \times 10^3$ M^{-1}		
$(S_8)_2^{2-} \rightarrow 2S_8 + 2e^-$		-0.23
$S_8^- + e^- \rightleftarrows S_8^{2-}$	-1.29	-1.15
$S_8^{2-} \rightarrow mS_n^{2-/m}$		

measurable effect. Therefore, the molar absorbtivities of the monomer can be evaluated: $a_{\text{monomer}}(618\ \text{m}\mu) = 2.58 \times 10^3\ M^{-1}\ \text{cm}^{-1}$; $a_{\text{monomer}}(490\ \text{m}\mu) = 0.52 \times 10^3\ M^{-1}\ \text{cm}^{-1}$. These molar absorbtivities have been used to determine the dissociation constant and the molar absorptivities for the dimer. The spectra of 12 solutions with total concentrations of "S_8^-" varying from 0.0852 to 4.26 mM have been used to obtain the best fit for the constants. The resulting values are $K = (2 \pm 1) \times 10^{-4}\ M$, $a_{\text{dimor}}(490\ \text{m}\mu) = 5.32 \times 10^3\ M^{-1}\ \text{cm}^{-1}$, $a_{\text{dimer}}(618\ \text{m}\mu) = 2.12 \times 10^3\ M^{-1}\ \text{cm}^{-1}$. The existence of one isosbestic point in Figure 4 indicates that only two species are responsible for the absorbance in this portion of the spectrum.

Summary and Conclusions

The oxidation–reduction reactions of S_8 and its reduction products, as well as their equilibria, are summarized in Table III. These proposals are consistent with the electrochemical and spectroscopic data.

Although the S_8^- and $(S_8)_2^{2-}$ species have not been isolated, the simplicity of the electrochemistry implies that the monomer exists as an eight-membered ring. Recent studies of the anion of heptasulfurimide are pertinent and indicate possibilities for further work in this area.[10] The anion of heptasulfurimide, which is isoelectronic with S_8, has been shown to exist as an eight-membered ring. Preliminary cyclic voltammetric studies of the anion of heptasulfurimide have shown that its electrochemical reduction in DMSO is almost identical with that of S_8. The presence of nitrogen, with its large magnetic moment in the eight-membered ring, should facilitate the structure determination *via* magnetic resonance techniques.

Additional studies are in progress to determine the chemical reactivity of the "S_8^-" species with a variety of inorganic and organic reagents. Preliminary results indicate that there is a significant interaction between transition metal ions and "S_8^-."

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[10] B. A. Olsen and F. P. Olsen, *Inorg. Chem.*, **8**, 1736 (1969), and references therein.

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A Study of the Thermal Decomposition of Europium(III) Oxalate Using the Mössbauer Effect

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The thermal decomposition of $Eu_2(C_2O_4)_3 \cdot 10H_2O$ was investigated using conventional thermal analytical techniques and also optical and Mössbauer spectrographic methods. Contrary to previous investigations, the intermediate in the decomposition of europium(III) oxalate, which has a 1:1:3 composition europium–carbon–oxygen (*i.e.*, Eu–C–3O), is not europium(II) carbonate but is most probably a carbonylcarbonate of trivalent europium, $Eu_2O_2OCOCO_2$. The final intermediate in the decomposition is EuO_2CO_3.

Introduction

Although the thermal decomposition of rare earth oxalates has been extensively studied, there is substantial disagreement among investigators regarding the complex nature of these decompositions. Perhaps of greatest interest are those in which the rare earth ion is known to have a variable valence. Since changes in oxidation state of the metal ion have frequently been observed during the thermal decomposition of transition metal oxalates, it is of interest to investigate such possibilities in the decomposition of rare earth oxalates. Europium(III) is the rare earth ion most readily reduced and Glasner, *et al.*,[1] have suggested that divalent europium is formed as an intermediate in the thermal decomposition of europium(III) oxalate. However, thermodynamic considerations similar to those of Dollimore, *et al.*,[2] indicate that divalent europium should not form.

The unequivocal determination of the formation of europium(II) in such a complicated decomposition from thermal analysis data alone is difficult. Fortunately,

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[1] A. Glasner, E. Levey, M. Steinberg, and W. Bodenheimer, *Talanta*, **11**, 405 (1964).

[2] D. Dollimore, D. Griffiths, and D. Nicholson, *J. Chem. Soc.*, 2617 (1963).