SO_2F at −75° to form $Xe(OSO_2F)_2$;[32,33] and (3) F_5XeOSO_2F reacts very slowly with $HOSO_2F$ at 22°. In conclusion it seems likely that a variety of pentafluoroxenon compounds are possible where the very stable XeF_5^+ could exist in combination with anions resistant to oxidation and fluorination.

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[32] R. J. Gillespie, D. A. Humphreys, A. Nelzer, and B. Landon, "Symposium on the Chemistry of Noble Gas Compounds," 160th National Meeting of the American Chemical Society, Chicago, Ill., September 14–16, 1970.

[33] The synthesis of $FXeOSO_2F$ from XeF_2 and $HOSO_2F$ at the same temperature as the synthesis of $Xe(OSO_2F)_2$ by varying the stoichiometry of the reactants implies that the reaction of XeF_2 with $HOSO_2F$ proceeds n a stepwise manner.

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Electrochemical Reduction of Sulfur Dioxide in Dimethylformamide

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The reduction of sulfur dioxide in dimethylformamide has been investigated by means of cyclic voltammetry, chronopotentiometry, and controlled-potential electrolysis. At a gold electrode SO_2 is reduced by a one-electron process to a product which is complexed by SO_2 to give a blue species (580 nm). The reduction product also dimerizes to dithionite, $S_2O_4^{2-}$, which is complexed at low SO_2 concentrations to give a red species (485 nm). On the basis of the electrochemical and spectroscopic data, mechanisms are proposed for the reduction of SO_2 and the subsequent equilibration reactions. The equilibrium constants for the dimerization reaction and the complexation reaction of SO_2 with dithionite have been determined.

An electrolyzed solution of SO_2 in dimethylformamide (DMF) exhibits esr lines which have been assigned to two postulated reduction products of SO_2, an anion radical and its complex (eq 1, 2).[1] On the basis

$$SO_2 + e^- \rightleftarrows SO_2^- \qquad (1)$$

$$xSO_2 + SO_2^- \rightleftarrows (SO_2)_xSO_2^- \qquad K \qquad (2)$$

of a temperature study of the esr data the value of K was found to be 1.86×10^6 at 0° with x assumed to be 2.

Rinker and Lynn[2,3] reduced sulfur dioxide with sodium amalgam to produce a blue radical in dimethylformamide. On the basis of spectroscopic studies the blue species was concluded to be $(SO_2)SO_2^-$. Upon standing $Na_2S_2O_4$ was found to precipitate out of solution.

More recently[4] the electrochemical reduction of SO_2 in dimethyl sulfoxide was reported with dithionite ($S_2O_4^{2-}$) and SO_2^- as the primary products. The present paper summarizes the results of an electrochemical and spectroscopic study of sulfur dioxide reduction in dimethylformamide and the chemistry of the several product species that are formed in solution.

Experimental Section

Electrochemical measurements were made with an instrument based on Philbrick operational amplifiers[5] or one constructed from solid-state components.[6] A Moseley Model 7030A X-Y recorder and a Sargent Model SR recorder were used with the above instruments.

A three-electrode system was employed for all measurements with the platinum counterelectrode isolated by a fine-porosity glass frit from the working electrode compartment. The reference electrode was an aqueous silver–silver chloride electrode corrected to 0.000 V *vs.* sce by adjustment of the tetramethylammonium chloride concentration. Connection to the sample solution was by means of a cracked glass-bead tip immersed into a Luggin capillary filled with the supporting electrolyte solution. Three types of working electrode were used: a gold-foil electrode for coulometry, a gold-inlay electrode (made by sealing a gold rod in a polyethylene tube), and a platinum-inlay electrode (Beckman No. 39273).

Controlled-potential coulometry was performed in a Dry-Lab glove box with a large gold-foil electrode. For cyclic voltammetry and chronopotentiometry air was excluded by first bubbling the solution with nitrogen and then maintaining a steady stream of nitrogen over the surface.

Spectroscopic measurements were made with a Cary Model 14 spectrophotometer. Solutions were transferred to the cells and stoppered with ground-glass stoppers under a dry nitrogen atmosphere. The supporting electrolyte concentration was adjusted to 0.25 *F* for all of the spectroscopic studies.

Mallenckrodt reagent grade dimethylformamide was dried over calcium hydride and distilled at 50 Torr. The supporting electrolyte, tetraethylammonium perchlorate (TEAP), was prepared from Matheson Coleman and Bell tetraethylammonium bromide (99%) and Mallenckrodt perchloric acid (70%), reagent grade, and was recrystallized from water three times.

Matheson anhydrous sulfur dioxide was used without purification. Stock solutions were prepared by dissolving sulfur dioxide in previously degassed dimethylformamide. Analysis of SO_2 in the stock solution was performed by adding an aliquot to a known concentration of iodine solution and back-titrating with thiosulfate. Sulfur dioxide concentrations also were determined by titration with standardized base.

Results

Reduction of sulfur dioxide in dimethylformamide yields a well-defined cyclic voltammogram, as illustrated in Figure 1, with a cathodic peak at −0.84 V *vs.* sce and an anodic peak at −0.74 V *vs.* sce. This is in close agreement with the observations of Bonnaterre and Cauquis[4] for dimethyl sulfoxide solutions. In ad-

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[1] K. P. Dinse and K. Mobius, *Z. Naturforsch. A*, **23**, 695 (1968).

[2] R. G. Rinker and S. Lynn, *J. Phys. Chem.*, **72**, 4706 (1968).

[3] R. G. Rinker and S. Lynn, *Ind. Eng. Chem.*, **8**, 339 (1969).

[4] R. Bonnaterre and G. Cauquis, *Electroanal. Chem.*, **32**, 215 (1971).

[5] D. D. DeFord, private communication, presented at the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., 1958.

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

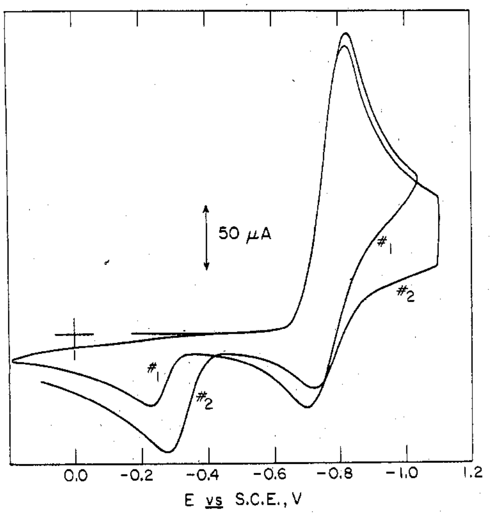

Figure 1.—Cyclic voltammograms of 5×10^{-3} *F* SO_2 in DMF (0.1 *F* TEAP) at a scan rate of 0.1 V/sec (platinum electrode). Scan no. 2 held at −1.1 V for 30 sec.

dition there is an anodic peak at −0.25 V. The difference in peak potentials of the cathodic and anodic peaks indicates that the reduction is not reversible within the time scale and concentration range used in the electrochemical studies.

Figure 1 also indicates that if the potential is held more cathodic than −0.84 V for about 30 sec and then scanned anodically, the peak at −0.25 V increases while the peak at −0.74 V decreases (scan no. 2). This effect can be seen clearly in Table I, where the ratio of the peak current at −0.25 V to the peak current at −0.74 V is given for several concentrations and scan rates. Each cathodic scan has been initiated at the rest potential of the electrode (∼−0.4 V), with the scan direction reversed at −1.0 V. The relative heights of the anodic peaks are sensitive to the initial condition of the electrode and the switching potential.

Table I

Anodic Peak Current Ratios ($i_{-0.25}/i_{-0.74}$) for Cyclic Voltammetry of SO_2 at Various Scan Rates and Concentrations with a Platinum Electrode in DMF (0.1 *F* TEAP)

$10^3[SO_2]$, *M*	Scan rate, V/sec 0.01	0.02	0.05	0.1	0.2	0.5
0.96		Trace	Trace	0	0	0
2.68	0.43	0.22	0.14	Trace	0	0
4.16	0.71	0.70	0.54	0.25	Trace	0
5.46	1.19	0.89	0.35	0.24	0.05	0
6.52	1.27	1.07	0.76	0.36	0.14	0.05

Platinum and gold electrodes give similar electrochemical results, but with the former a larger ratio for i_{pa}/i_{pc} is observed. The gold electrode is less susceptible to hysteresis effects than platinum.

To determine the nature of the two anodic peaks, cyclic voltammograms have been recorded during the course of an electrolysis. The peak at −0.25 V initially increases in size relative to the peak at −0.74 V. However, as the electrolysis nears completion, the peak at −0.74 V becomes the larger peak and at low concentrations is the only peak present at the end of the electrolysis. In addition to these two peaks, a new minor anodic peak is observed at −0.95 V for the cyclic voltammogram of a completely reduced SO_2 solution.

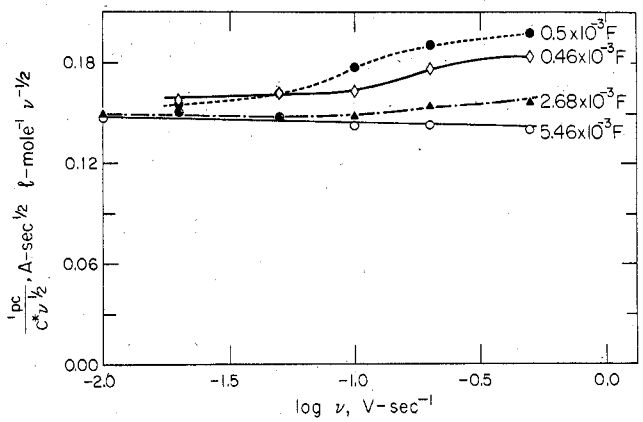

Figure 2.—Plots of $i_{pc}/C\nu^{1/2}$ *vs.* log ν for the voltammetric reduction of SO_2 at several concentrations in DMF (0.1 *F* TEAP) (platinum electrode).

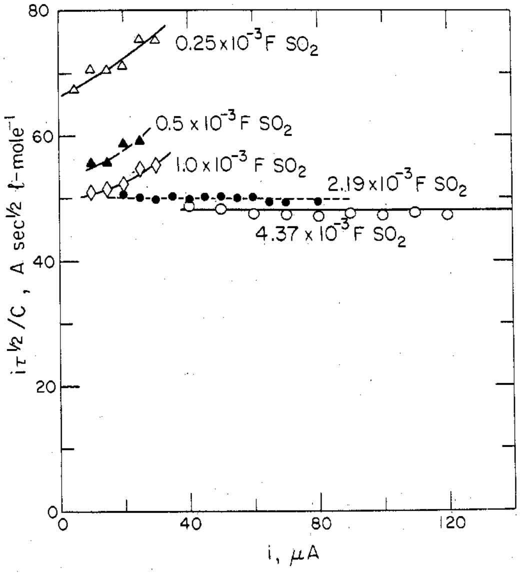

Figure 3.—Plots of $i\tau^{1/2}/C$ *vs.* i for the chronopotentiometric reduction of several concentrations of SO_2 in DMF (0.1 *F* TEAP) at a platinum electrode.

At low scan rates the ratio i_{pa}/i_{pc}, where i_{pa} is the peak current for the anodic peak at −0.74 V and i_{pc} is the peak current for the cathodic peak at −0.84 V, is approximately 0.5 and increases to about 0.8 at high scan rates. This infers that a chemical reaction occurs after the electron-transfer reaction.

Plots of $i_{pc}/C\nu^{1/2}$ *vs.* log ν, where C is the bulk concentration of SO_2 and ν is the scan rate, are presented in Figure 2. As the concentration of SO_2 is increased, the effect of the chemical reaction on the peak current becomes more pronounced and indicates that SO_2 is consumed in the chemical reaction.

The chronopotentiogram for SO_2 has two reduction waves with $E_{\tau/4}$ values of −0.82 and −1.64 V. The second wave increases in length relative to the first as the current is decreased. A plot of $i\tau^{1/2}/C$ remains constant for the first wave for concentrations greater than 2×10^{-3} *M*, but at smaller concentrations the value of $i\tau^{1/2}/C$ increases with increasing current density (see Figure 3). This behavior is in agreement with the cyclic voltammetry data and clearly shows the effect of a chemical reaction.

Sulfur dioxide is reduced completely at a potential

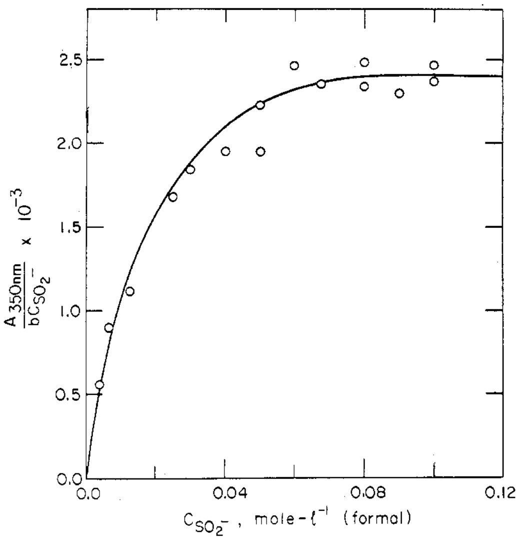

Figure 4.—The molar absorptivity at 350 nm of SO_2^- solutions as a function of $C_{SO_2^-}$ (0.01-cm cells), where $C_{SO_2^-}$ is assumed to be equal to the concentration of SO_2 before electrolysis.

of −0.95 V (one electron per SO_2) at concentrations below 10^{-3} *M*, but the electrolysis is slow, probably due to complex formation. This effect becomes more pronounced as the concentration of SO_2 is increased.

When controlled-potential electrolysis is carried out at −1.80 V, current continues to flow until the SO_2 is reduced by one electron. At this potential the rate of reduction is unaffected by concentration in contrast to reduction at −0.95 V.

When $NaClO_4$ is added to an electrolyzed solution of SO_2, a white precipitate is formed. The infrared spectrum of this substance is similar to the spectrum of sodium dithionite ($Na_2S_2O_4$), but impurities in both substances are a major difficulty. The uv spectrum of $Na_2S_2O_4$ in water at pH 12 has a peak at 318 nm, as does the precipitate. Methylene Blue is readily reduced by an aqueous solution of the precipitate. This reagent is specific for dithionite in the presence of other sulfur species.[7]

The absorption spectrum of an electrolyzed solution of SO_2 contains one peak at 350 nm. Figure 4 is a plot of the molar absorbance at 350 nm *vs.* the formal concentration of SO_2^-. As the formal concentration decreases, the molar absorptivity decreases, which indicates that this peak is due to the dimer $S_2O_4^{2-}$.

Addition of SO_2 to a solution of electrolyzed SO_2 produces a highly colored solution with absorption peaks at 485 and 580 nm. When the ratio of C_{SO_2} to $C_{SO_2^-}$ is below 0.5, the peak at 485 nm is the major peak present, but as $C_{SO_2}/C_{SO_2^-}$ is increased above 0.5, this peak decreases and the peak at 580 nm increases. Figure 5 illustrates plots of absorbance at 485 nm *vs.* $C_{SO_2}/C_{SO_2^-}$ for two SO_2^- concentrations. Because the curves have a maximum at $C_{SO_2}/C_{SO_2^-}$ equal to 0.5, a complex of stoichiometry $(SO_2)S_2O_4^{2-}$ is implied. When the concentration of reduced SO_2 is below 0.01 *F*, the peak at 485 nm is not observed for any value of $C_{SO_2}/C_{SO_2^-}$ and only the peak at 580 nm is observed.

A plot of absorbance at 580 nm *vs.* $C_{SO_2}/C_{SO_2^-}$ (for a constant SO_2 concentration) contains no sharp breaks and therefore conclusions cannot be drawn as to the stoichiometry of this complex. However, the curve does plateau at $C_{SO_2}/C_{SO_2^-}$ ratios above 300.

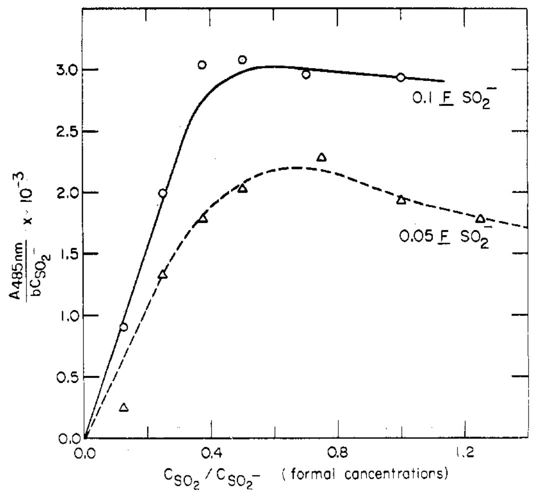

Figure 5.—The molar absorptivity at 485 nm of two SO_2^- solutions as a function of the $SO_2:SO_2^-$ mole ratio (0.01-cm cells).

Two smaller absorption peaks are observed at 405 and 395 nm for SO_2^- and SO_2^--containing solutions. These peaks are only observed when the ratio $C_{SO_2}/C_{SO_2^-}$ is greater than 0 and they appear to be associated with the peak at 580 nm and not the peak at 485 nm.

Discussion and Conclusions

The electrochemical evidence indicates that SO_2 is reduced by one electron to give several colored species as well as dithionite. The cathodic peak at −0.85 V, which corresponds to the one-electron reduction of SO_2

$$SO_2 + e^- \rightleftharpoons SO_2^- \qquad (3)$$

yields a species that appears to react with free SO_2 to form a blue complex species with an adsorption maximum at 580 nm; see eq 4 where x can equal 1 or more.

$$xSO_2 + SO_2^- \rightleftharpoons (SO_2)_xSO_2^- \qquad (4)$$

This conclusion is in agreement with previous spectroscopic studies.[1-3] Reduced SO_2 also undergoes a dimerization reaction (eq 5) to form dithionite on the

$$2SO_2^- \rightleftharpoons S_2O_4^{2-} \qquad K_{\text{dimer}} \qquad (5)$$

basis of the precipitates formed by addition of $NaClO_4$ and the uv absorption spectra. Spectroscopic data indicate that dithionite reacts with free SO_2 to form a species with an absorption maximum near 485 nm; see eq 6. Reactions 4 and 6 have the effect of lowering

$$SO_2 + S_2O_4^{2-} \rightleftharpoons (SO_2)S_2O_4^{2-} \qquad K_f \qquad (6)$$

the effective SO_2 concentration and thereby decreasing the value of $i_{pc}/Cv^{1/2}$ in cyclic voltammetry and of $i\tau^{1/2}/C$ in chronopotentiometry. If the complexation reactions are kinetically limited, a decrease in the concentration of SO_2 will lower the reaction rates to give increased values for $i\tau^{1/2}/C$ and $i_{pc}/Cv^{1/2}$.

The chemical reversibility of the reactions 4–6 is demonstrated by the fact that SO_2 can be reduced completely at ~0.95 V to give a colorless solution. The blue complex can then be generated by addition of SO_2. Also, a cyclic scan of reduced SO_2 will give a cathodic peak for SO_2 after an initial anodic scan.

The equilibrium constant for reaction 5 has been

[7] R. G. Rinker, T. P. Gordon, D. M. Mason, R. R. Sakaida, and W. H. Corcoran, *J. Phys. Chem.*, **64**, 573 (1960).

calculated from the data of Figure 4 by using the asymptote of the right portion of the curve to determine the molar absorptivity of dithionite; this gives a value of 4.8×10^3 cm^{-1} l. mol^{-1}. The remaining data points of the curve have been used to evaluate the dimerization constant, K_{dimer}; the value is $2.4 \pm 0.5 \times 10^1$ l. mol^{-1}.

The absorbance at 485 nm, which is proportional to the concentration of $(SO_2)S_2O_4^{2-}$, has been used to evaluate the equilibrium constant for reaction 6, K_f. The dithionite concentration in this equilibrium has been calculated from the dissociation constant for dithionite and the absorbance at 485 nm. For the conditions of measurement the blue complex $(SO_2)_xSO_2^-$ has been assumed to have an insignificant concentration relative to the SO_2 concentration. This assumption only is valid for low values of $C_{SO_2}/C_{SO_2^-}$. The formation constant, K_f, is approximately 10 on the basis of such calculations.

The cyclic voltammetry peak at -1.65 V probably is due to the reduction of the dithionite complex $(SO_2)S_2O_4^{2-}$, because this is the major species in the solution near the end of an electrolysis and, at this potential, the electrolysis proceeds rapidly to a stoichiometry of one electron per SO_2. Also, addition of SO_2 to such a reduced solution gives a blue complex and a cyclic scan with a reduction peak for SO_2 after an initial anodic scan.

Because the ratio of the anodic peak at -0.74 V to the cathodic peak at -0.84 V increases with increasing scan rate, this peak can be assigned to the oxidation of SO_2^-, which is in agreement with the work of Bonnaterre and Cauquis.[4] The small oxidation peak at -0.95 V probably is due to decomposition products or impurities.

The anodic peak at -0.25 V appears to be due to the oxidation of the blue complex $(SO_2)_xSO_2^-$. This peak is observed when the formal concentration of SO_2^- is below 0.01 F, a condition where the red complex $(SO_2)S_2O_4^{2-}$ is not present. Also, cyclic scans during an electrolysis experiment indicate that the peak current for this peak increases as the electrolysis proceeds to the halfway point and then decreases to zero at the end of the electrolysis.

The highly colored complex species observed in the DMF solvent system are in marked contrast to the results of Bonnaterre and Cauquis[4] for dimethyl sulfoxide (DMSO) solutions. Although the complexes are weak, they appear to be stabilized by the DMF solvent system, especially the blue $(SO_2)_xSO_2^-$ complex.[2] Also, a comparison of the dimerization constants for dithionite formation in DMF and DMSO indicates that the dimerization reaction is favored in DMSO.

Some information about the relative rates of formation of dithionite and the $(SO_2)_xSO_2^-$ complex can be gained by comparing Table I and the ratio of the anodic peak current to the cathodic peak current. From the ratio of the anodic peak current to the cathodic peak current, which is always less than 1.0, there is evidence that SO_2^- is involved in a chemical reaction even at low concentrations. Because the anodic peak at -0.25 V (due to the blue complex) is only important at SO_2 concentrations above 2×10^{-3} M, dithionite formation must be used to explain the disappearance of SO_2^- at lower concentrations. The data in Figure 2 indicate that at the fastest scan rates and the lowest SO_2 concentrations the complications due to complexation are largely overcome.

An alternate mechanism is that dimerized SO_2 is reduced by two electrons to dithionite which reacts with free SO_2. This mechanism seems unlikely because if a dimerization reaction preceded the electron transfer, then $i_{po}/Cv^{1/2}$ would increase with decreasing scan rate. Figure 2 indicates the opposite behavior.

Another possible mechanism is the initial formation of the blue complex from dimeric SO_2 and disproportionation of the product to form dithionite. However, the ratio $i_{pa(-0.25\ V)}/i_{pa(-0.74\ V)}$ increases with decreasing scan rate, which indicates that complex formation occurs after electron transfer. Figure 2 also indicates a postchemical step.

Thus, the evidence supports the conclusion that the rate of formation of dithionite is faster than the rate of complex formation. The inert electrochemical behavior of dithionite implies that its dissociation product, SO_2^-, is the active species for reducing reactions. This may be true in aqueous media also and may account for the selective reactivity of dithionite.

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