ELECTROCHEMICAL REDUCTION OF SULFUR DIOXIDE AT A MERCURY ELECTRODE

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The polarographic behavior of sulfur dioxide at a dropping mercury electrode has been investigated by several workers. In neutral or alkaline media, no reduction wave is observed, but a well-defined wave is obtained in acidic solutions. GOSMAN¹ assumed that sulfur dioxide is reduced to dithionous acid (H₂S₂O₄). According to KOLTHOFF AND MILLER², however, two electrons are required for the reduction of sulfur dioxide and they conclude that the reduction product is sulfoxylic acid (H_2SO_2) . The height of the wave decreases markedly with increasing pH and a small second wave is observed above pH 4. KOLTHOFF AND MILLER postulate that the first of these waves is due to reduction of bisulfite ion to dithionite ion and that the second wave is a further reduction to thiosulfate ion. CĚRMÁK³ has investigated the reduction of sulfur dioxide by polarography and by cyclic voltage sweep chronoamperometry at a hanging mercury drop. He concludes that the first wave is a reversible oneelectron reduction to HSO₂ and that the second wave observed at higher pH-values is due to a further reduction to sulfoxylate ion. In strongly acidic media, HSO₂ is rapidly decomposed, and he suggests that the overall reaction at low pH-values is a two-electron reduction to sulfoxylic acid. The reversible behavior of sulfur dioxide in strongly acidic media also has been demonstrated by oscillopolarography⁴.

The reduction of sulfur dioxide at solid electrodes was first investigated by JELLINEK AND JELLINEK⁵. They conclude that dithionite ion is formed upon reduction of bisulfite ion at platinum, nickel, copper and lead electrodes. According to FEHÉR and co-workers^{6,7}, a mixture of various polysulfites is formed upon reduction of sulfur dioxide at platinum and gold electrodes in strongly acidic media. They also conclude that the reduction product is dithionite ion between pH 3.2 and pH 6.2 and that only hydrogen is formed upon reduction of bisulfite ion at higher pH-values. KLYANINA AND SHLYGIN⁸ conclude that the reduction product at a platinized-platinum electrode in strongly acidic solutions is colloidal sulfur.

The previous work presents conflicting results and views. Because a number of new techniques are now available for studying electrode reactions, a further investigation of the reduction of sulfur dioxide has been undertaken. The present work discusses the results of an investigation of the reduction of sulfur dioxide at a mercury electrode using chronopotentiometry, controlled-potential coulometry, and cyclic voltammetry.

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EXPERIMENTAL

Apparatus

The electrochemical measurements were made with a versatile electronic instrument previously described by DEFORD⁹. It is based on the use of Philbrick operational amplifiers and is capable of performing chronopotentiometry, controlled-voltage coulometry and cyclic voltammetry by appropriate interconnection of the operational modules. A Sargent Model SR strip-chart recorder was used in conjunction with the DeFord instrument. Cyclic voltammograms were obtained with a F. L. Moseley X-Y recorder.

The electrochemical cell (Leeds and Northrup No. 7961 coulometric cell) consisted of a tall-form beaker fitted to a polyethylene top by means of a polyethylene snap ring. The top was provided with holes for the gas-inlet tubes, the working electrode, the platinum counter electrode (which was isolated in a glass tube with a fine-porosity fritted-glass disc), and a cracked glass-bead salt bridge containing a Beckman saturated calomel electrode (S.C.E.). The shield tubes were filled with the supporting electrolyte used in the sample solution. The solution was stirred with a magnetic stirrer and a Teflon-covered stirring bar.

The mercury electrode was made by abrading a platinum inlay electrode (Beckman No. 39273) with 2/0 Buchler Ltd. carborundum paper while the electrode surface was immersed in a pool of mercury¹⁰. When the electrode was not in use it was stored in pure mercury to ensure that it remained completely amalgamated. Before the stored electrode was used, the excess mercury was removed by gentle tapping. The area of the amalgamated electrode was determined by measuring its mean diameter with a cathetometer and was found to be 0.195 cm².

Reagents

All chemicals were reagent-grade and were used without further purification. The aqueous sulfur dioxide solutions were prepared by dissolving appropriate amounts of anhydrous sodium sulfite in the supporting electrolyte. Pure nitrogen was used to de-aerate the solution just prior to the introduction of sulfite ion. The solutions were kept below $10^{-2} F$ in total sulfite concentration, and used within r h after preparation. The cell was flushed with nitrogen just prior to the introduction of the sample solution, filled and sealed. This procedure was adequate to minimize loss of dissolved sulfur dioxide by air oxidation and volatilization. The space above the solution phase was kept as small as possible in order to minimize the amount of sulfur dioxide in the gas phase after equilibration. Perchloric acid, sulfuric acid, and acetate buffers were used as supporting electrolytes. The pH of the solutions was determined with a Leeds and Northrup Model 7403 pH meter.

RESULTS

Chronopotentiometry

At platinum and gold electrodes, only poorly-defined reduction waves of sulfur dioxide are obtained. When amalgamated platinum is used, the waves are well-defined, but the transition time is not reproducible and a prewave is sometimes observed on the chronopotentiograms due to the adsorption of the reduction products on the electrode. Because of this, and the fact that the transition time increases in proportion to the time the electrode has been in contact with the solution, reproducible results require that the electrode be removed from the solution between each run, the mercury wiped off, and the electrode washed with pure mercury. If the solution is stirred for one minute before the electrode is replaced and allowed to become quiescent for at least one minute before recording of the chronopotentiogram, reproducible results have been obtained at all pH-values.

At low pH-values, only one well-defined reduction wave is obtained for sulfur dioxide, but when the pH of the supporting electrolyte is increased above pH 3.5, a small second wave is observed. Two typical chronopotentiograms at pH I (curve Ia) and at pH 5.0 (curve 2a) are shown in Fig. I. Curves Ib and 2b represent current reversal after approximately 6 sec. The small transition time of the reverse wave indicates that the reduction product is rapidly decomposed. The $E_{0.22}$ potential of the reverse wave indicates that the electrode process is almost reversible at low



Fig. 1. Chronopotentiograms of dissolved SO₂ at a mercury electrode. $10^{-3} F$ Na₂SO₃ in 0.1 F HClO₄ (Curve 1a) and in 0.2 F acetate buffer, pH = 5.0 (Curve 2a). Curves 1b and 2b obtained by current reversal after approx. 6 sec. Electrode surface area, 0.195 cm²; current, 40 μ A (Curve 1) and 20 μ A (Curve 2).

Fig. 2. Variation of $i\tau \frac{1}{2}$ with electrolysis time. 10⁻³ F Na₂SO₃ in HClO₄ and acetate buffers. pH of solns. indicated on curves.

pH-values, but becomes less reversible with increasing pH of the supporting electrolyte.

If the mass transport to the electrode is controlled by linear diffusion in an unstirred solution then¹¹

$$i\tau^{\frac{1}{2}}/C^{0} = \frac{1}{2}nF\pi^{\frac{1}{2}}D^{\frac{1}{2}}A\tag{I}$$

where i is the current, τ the transition time, A the electrode area, C^o the bulk con-

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centration, n the number of electrons involved in the overall reaction, F the faraday, and D the diffusion coefficient.

Chronopotentiometric data for 1.0 F and 0.1 F perchloric acid solutions are summarized in Table 1. The data establish that the value of $i\tau^{\dagger}/C^{0}$ increases with decreasing current density and that the overall electrode process is not diffusioncontrolled. The increase in $i\tau^{\dagger}$ is less pronounced at higher pH-values, but is still too great to be due to convection in the electrolysis cell (see Fig. 2). The value of $i\tau^{\dagger}$ increases linearly with increasing transition time, which indicates that a chemical reaction is occurring during the electrolysis. Below pH 1.5, the rate of this reaction increases with increasing concentration of H⁺, as indicated by the slopes of the lines in Fig. 2.

TABLE 1

CHRONOPOTENTIOMETRIC DATA FOR THE REDUCTION OF DISSOLVED SULFUR DIOXIDE IN PERCHLORIC ACID AT A MERCURY ELECTRODE

i(μA)	t(sec)	₽Н	it ±/C ^o (A sec ± cm ³ mole ⁻¹)
90	3.0	0	I 57
δo	4.2	0	164
70	6.3	ο	173
60	11.3	0	201
55	17.4	0	230
70	4.6	1.0	150
65	5.5	1.0	152
60	6.5	I.O	153
55	7. <u>9</u>	1.0	154
50	10.0	1.0	158
45	12.6	I.O	160
40	18.0	I.O	170

Total sulfite concn., 10-8 mole cm-3; electrode area, 0.195 cm²

The contribution to $i\tau^{\frac{1}{2}}$ from the chemical reaction can be corrected by extrapolating the values of $i\tau^{\frac{1}{2}}/C^{0}$ to zero transition time. Following this procedure, a diffusion-controlled value of 143 A sec^{$\frac{1}{2}$} cm^{$\frac{3}{2}$} mole⁻¹ is obtained for $i\tau^{\frac{1}{2}}/C^{0}$ from pH o to pH 1.5. Using this value and a value of 2.0×10^{-5} for the diffusion coefficient of dissolved sulfur dioxide in acidic solutions², the number of electrons in the reduction reaction, *n*, is calculated from eqn. (1) to be 1.92.

When the pH of the supporting electrolyte is increased above pH 1.5, the value of $i\tau^{\dagger}$ (extrapolated to zero transition time) decreases with increasing pH, and above pH 7 no wave is observed (see Fig. 3). The decrease in $i\tau^{\dagger}$ is due probably to a decrease in the concentration of undissociated sulfur dioxide with increasing pH. Hence, the value of C^{0} in eqn. (1) is no longer equal to the total amount of sulfite in the solution and the value of n cannot be calculated from this equation for solutions above pH 1.5.

Chronopotentiograms for solutions above pH 2 indicate a highly irreversible process. The potential-time relationship for such processes in unstirred solutions is given by¹¹

$$E = \frac{0.059}{\alpha n_{\rm a}} \log \frac{nFC^0 k_{t,\rm b}^0}{i_0} + \frac{0.059}{\alpha n_{\rm a}} \log \frac{\tau^{\pm} - \tau^{\pm}}{\tau^{\pm}}$$
(2)

where E is the potential of the working electrode vs. the normal hydrogen electrode, α the transfer coefficient, n_a the number of electrons in the rate-controlling step of the reduction process, F the faraday, $k_{I,b}$ the forward heterogeneous rate constant, i_0 the current density, C⁰ the concentration of the active species in the bulk of the



Fig. 3. Variation of $i\tau^{\frac{1}{2}}/C^{\circ}$ (extrapolated to zero transition time) with pH of supporting electrolyte. Open circles represent values for the total wave, $i(\tau_1 + \tau_2)^{\frac{1}{2}}/C^{\circ}$.

Fig. 4. Galvanostatic studies of reduction of SO₂ at several pH-values. 10⁻³ F Na₂SO₃ in HClO₄ and acetate buffers. pH of solns. indicated on curves. Electrode area, 0.195 cm²; current in μ A.

solution in mM, τ the transition time for reduction in an unstirred solution, and t the time after the electrolysis is started. At t = 0 eqn. (2) reduces to:

$$E_{t=0} = \frac{0.059}{\alpha n_{\rm A}} \log \frac{n F C^0 k_{t,\rm h}^0}{i_0}$$
(3)

By applying a constant current and recording the potential of the working electrode as a function of time, $E_{t=0}$ can be obtained by extrapolation of the potential-time curve to zero.

Plots of log *i vs.* $E_{t=0}$ that have been obtained for solutions at different pHvalues are given in Fig. 4. The mean value for αn_{θ} , which is obtained from the slopes, is 1.10±0.05, and indicates that the charge-transfer step involves two electrons in the pH range 1-5.

The quarter-wave potential of the chronopotentiometric wave obtained in 0.1 F perchloric acid is -0.37 V vs. S.C.E., which is in excellent agreement with the polarographic half-wave potential previously reported for the reduction of sulfur dioxide in 0.1 F nitric acid². By increasing the pH of the supporting electrolyte, the reduction wave is shifted to more negative potentials. The quarter-wave potentials of the chronopotentiometric wave are plotted against pH in Fig. 10 (open circles.) The potentials are shifted linearly to more negative values with increasing pH (the slope is -0.072 V/pH unit), indicating that hydrogen ions are consumed in the reduction of sulfur dioxide.

The value of $i\tau^{\dagger}$ for the single wave observed at low pH-values and for the

first wave above pH 4, increases linearly (at a given pH) with the concentration of the total sulfite concentration (Table 2). The value of $i\tau_2^{\dagger}$ for the second wave, however, appears to reach a limiting value when the total sulfite concentration is increased above 1 mM.

TABLE 2

CHRONOPOTENTIOMETRIC DATA FOR THE REDUCTION OF DISSOLVED SULFUR DIOXIDE IN 0.1 F perchloric acid and in acetate Buffer

pН	C ⁰⁻ IO ⁰ , (moles cm ⁻³)	it1 ±/C ⁰ (A sec± cm ³ mole ⁻¹)	it3 [±] ·10 ⁶ , (A sec [±])	$i[(\tau_{\frac{1}{2}}+\tau_2)^{\frac{1}{2}}-\tau_1^{\frac{1}{2}}]\cdot I0^{\circ}$ (A sec [±])
T.0	0.5	141		
I.O	1.0	142		
1.0	1.5	143		
I.O	2.0	141		
I.O	2.5	142		
5.0	0.5	48	23	8
5.0	1.0	49	45	15
5.0	1.5	48	62	18
5.0	2.0	50	65	18
5.0	2.5	48	67	19

Total sufite concn., C^0 ; values of $i\tau \frac{1}{2}$ obtained by extrapolation to zero transition time

Coulometry

Coulometric reductions at controlled potential have been performed to determine the number of electrons involved in the overall reduction reaction. These experiments have been carried out using a small electrolysis cell with a Teflon stirring bar and a mercury pool as the cathode. The potential of the cathode has been controlled at the chronopotentiometric quarter-wave potential for the same supporting electrolyte.

Below pH 1, the number of coulombs consumed in the reduction of dissolved sulfur dioxide indicates that 4-6 electrons are involved in the overall reduction. Colloidal sulfur appears in the solution a few minutes after the electrolysis is started. The sulfur reacts with the mercury pool, which first turns yellow and then black because of the formation of mercuric sulfide.

For solutions above pH 2, the current is approximately constant and independent of the time of electrolysis. The current increases with increasing concentration of sulfur dioxide, but does not level off even after electrolyzing for several hours. Colloidal sulfur and a film of mercuric sulfide on the mercury pool are observed also between pH 2 and pH 5. A few hours after the electrolysis is started, the number of coulombs consumed is much greater than the calculated value for quantitative reduction of sulfur dioxide to sulfide ion. Apparently, the over-potential for reduction of hydrogen ions is greatly decreased when a film of mercury sulfide is formed on the cathode. Hence, the current measured is due partly to reduction of hydrogen ions, and the number of electrons involved in the reduction of sulfur dioxide cannot be determined by this method. The formation of mercuric sulfide indicates, however, that the final reduction product is sulfur or sulfide in solutions between pH o and pH 5.

Cyclic voltammetry

Voltammetric experiments have been performed using the same electrode and the same electrolysis cell as in chronopotentiometry. Reproducible waves are obtained when the voltammograms are recorded for a fresh solution, and when the electrode has been cleaned and washed carefully with pure mercury between each potential sweep.

In strongly acidic media well-defined waves are obtained. When the voltammograms are recorded at a fast scan rate, the heights of the cathodic and anodic peaks are identical and the separation of the peaks is 60 mV, indicating a reversible two-electron reduction. At a given pH-value, the peak potential of the cathodic wave coincides with the chronopotentiometric quarter-wave potential.

As indicated in Fig. 5, a second small anodic peak is observed on the voltammogram. When the voltage sweep is repeated without cleaning the electrode, the height of this peak increases and a new cathodic adsorption peak appears on the



Fig. 5. Cyclic voltammograms of 10^{-3} F Na₂SO₃ in 0.1 F HClO₄. Dashed line represents second potential sweep. Scan rate, 0.05 V sec⁻¹.

Fig. 6. Cyclic voltammogram of Na₂S in 0.1 F HClO₄. Scan rate, 0.10 V sec⁻¹.

voltammogram. The cathodic adsorption peak is never observed on the first cathodic sweep at a clean mercury electrode, but it always is present at the second sweep and its height increases with the number of following cathodic sweeps. The adsorption peak shifts to more negative potentials with increasing pH of the supporting electrolyte and its height decreases with increasing pH; above pH 3, no adsorption peak is observed. Identical peaks appear on the voltammograms resulting from the addition of a minute amount of sodium sulfide to a supporting electrolyte of the same pH-value (Fig. 6). This indicates that the adsorption peaks are from a reaction of the mercury electrode with the sulfur or sulfide ion formed by decomposition of the reduction product of sulfur dioxide.

The height of the anodic peak resulting from the reduction of sulfur dioxide decreases with decreasing scan rates. As indicated in Fig. 7, the ratio of the anodic to the cathodic peak currents is constant in strongly acidic media at scan rates above o.r V sec⁻¹. However, at lower scan rates the ratio decreases, which indicates that the electron-transfer reaction is followed by an irreversible chemical reaction¹². The latter is probably responsible for the formation of sulfur and the adsorption peaks.

A number of voltammograms have been recorded at different scan rates for a series of solutions with different pH-values. Figure 8 indicates that the cathodic peak current decreases with increasing pH of the supporting electrolyte; above pH 7 no cathodic wave is observed. The same decrease in i/v^{\dagger} is also observed at slower scan rates and indicates, in agreement with the chronopotentiometric data given in Fig. 3, that the concentration of the electroactive species decreases with increasing pH of the supporting electrolyte.



Fig. 7. Ratio of anodic to cathodic peak currents as a function of scan rate. 10^{-3} F Na₂SO₃ in HClO₄. pH indicated on curves.

Fig. 8. Variation of the cathodic peak current function $(i/r \frac{1}{2}C^0)$ with pH in HClO₄ and in acetate buffers. Scan rate, 0.1 V sec⁻¹.

The anodic current also decreases rapidly with increasing pH, and above pH 3.5 a new anodic peak appears at a less negative potential. The peak potential of this wave has a constant value of -0.39 vs. S.C.E., independent of pH. A typical voltammogram for an acetate buffer at pH 5.5 is shown in Fig. 9; the cathodic peak is less well-developed than at low pH-values. The current decreases slowly when the potential is increased above the peak potential, indicating that the current is controlled in part by a slow chemical reaction³.

A small cathodic wave at -1.0 V vs. S.C.E. (corresponding to the second chronopotentiometric wave) is observed for voltammograms recorded with solutions above pH 4.5. This wave only is observed at slow scan rates (less than 0.1 V sec⁻¹), the peak potential is independent of pH, and its height appears to be independent of the total sulfite concentration. When the voltage scan is repeated after stirring the solution and without cleaning the electrode, the height of this wave increases at the expense of the first cathodic wave, the total current at -1.0 V remaining constant. This implies that the second peak is the result of an adsorbed species on the electrode.

The peak potential of the first cathodic wave is shifted linearly to more negative values with increasing pH (see Fig. 10, curve A). At pH-values above 2,

the anodic peak is poorly-developed; its peak potential is indicated by curve B in Fig. 10. The peak potential of a well-defined second anodic wave, which appears on voltammograms recorded for solutions above pH 3.5, is given by curve C in Fig. 10.



Fig. 9. Cyclic voltammogram of 10^{-3} F Na₂SO₃ in 0.2 F acetate buffer (pH 5.5). Scan rate, 0.05 V sec⁻¹.

Fig. 10. Variation of cathodic (Curve A) and of anodic (Curve B) peak potentials with pH for SO_2 . Curve C, peak potential of second anodic wave. Scan rate, 0.1 V sec⁻¹. Open circles represent chronopotentiometric quarter-wave potentials.



Fig. 11. Variation of the cathodic peak current function $(i/v^{\frac{1}{2}}C^{0})$ with rate of voltage scan. pH of solns. indicated on curves.

Voltammograms recorded at different scan rates indicate that the cathodic peak current only is independent of the voltage scan rate at certain pH-values (see Fig. 11). Above pH 3, the current function increases with decreasing scan rate, indicating that the electron transfer is followed by a chemical reaction¹². The decrease in the current function with decreasing scan rate at very low pH-values is due probably to increased irreversibility of the overall electrode reaction.

Several investigators^{1-3.5-7} have suggested that dithionite ion is formed upon

reduction of sulfur dioxide at pH-values between pH 3 and pH 6. Therefore, the cyclic peak potentials and the chronopotentiometric behavior of sodium dithionite have been determined. Because dithionous acid is decomposed rapidly in acidic medium to give sulfur dioxide and thiosulfate ion⁵, the curves have been obtained by adding sodium dithionite to the supporting electrolyte in the cell and immediately recording the data.

Between pH 4 and pH 6 a well-defined anodic chronopotentiometric wave with a quarter-wave potential of -0.39 V vs. S.C.E. is obtained. A few minutes after the solution is mixed, a reduction wave for sulfur dioxide and a second oxidation wave for mercury going to mercuric thiosulfate appear on the chronopotentiogram. The value of $i\tau^{\frac{1}{2}}$ for the cathodic wave increases with the time elapsed after mixing the solution, whereas the value for the first anodic wave decreases. This indicates that dithionite ion is decomposed to sulfur dioxide and thiosulfate ion. Colloidal sulfur (probably formed by decomposition of the thiosulfate ion) is observed in the solution after it has been standing for 10-20 min. The rate of decomposition of dithionite ion increases rapidly with decreasing pH.

Cyclic voltammograms of sodium dithionite in acetate buffers show a welldefined anodic wave. The peak potential is -0.39 V vs. S.C.E. and is independent of pH between pH 4 and pH 6. This peak potential coincides with that of the anodic wave obtained for the product of the reduction of sulfur dioxide (curve C, Fig. 10) and with the chronopotentiometric quarter-wave potential for the oxidation of dithionite ion.

According to FURNESS¹³ and CĚRMÁR¹⁴, dithionite ion gives rise to a welldefined anodic wave at the dropping mercury electrode. The half-wave potential of this wave is constant, independent of pH between pH 4 and pH 10, and is due to an irreversible oxidation of dithionite ion to sulfur dioxide. The half-wave potential given by FURNESS¹³ ($E_4 = -0.43$ V vs. S.C.E.), is only 40 mV more negative than the peak potential determined in the present work and strongly indicates that dithionite ion is formed upon reduction of sulfur dioxide in solutions above pH 3.5.

DISCUSSION AND CONCLUSIONS

All experimental results indicate that sulfur dioxide in a strongly acidic medium is reduced reversibly to sulfoxylic acid

 $SO_2 + 2 H^+ + 2 e^- \rightleftharpoons H_2SO_3$

This reaction has been suggested previously by KOLTHOFF AND MILLER² and by CĚRMÁK³. Sulfoxylic acid is unstable in the presence of strong acids and disproportionates into sulfur and sulfur dioxide

$$2 \operatorname{H}_2 \operatorname{SO}_2 \to \operatorname{S} + \operatorname{SO}_2 + 2 \operatorname{H}_2 \operatorname{O}$$
(5)

Hence, the final reduction product is sulfur and the overall electrode reaction becomes irreversible. The sulfur dioxide formed by reaction (5) is reduced at the electrode and causes $i\tau^+$ to increase with increasing time of electrolysis. The slopes of the lines in Fig. 2 indicate that the rate of reaction (5) increases with increasing concentration of H⁺. The formation of sulfur by decomposition of sulfoxylic acid has been confirmed by cyclic voltammetry and by coulometry. Colloidal sulfur may react slowly with the mercury electrode to form a film of mercuric sulfide. According

(4)

to HALL¹⁵, elemental sulfur is reduced to hydrogen sulfide at a mercury electrode. Hence, the second anodic peak observed for voltammograms recorded at low pH-values (Fig. 5) is due probably to the reaction

$$Hg + H_2S \rightarrow HgS + 2 H^+ + 2 e^-$$

When the cathodic scan is repeated without cleaning the electrode, the mercuric sulfide formed by reaction (6) is reduced, giving rise to the cathodic adsorption peak.

Cyclic voltammetry indicates that dithionous acid or dithionite ion is formed upon reduction of sulfur dioxide in solutions above pH 3. The chronopotentiometric data (Fig. 2) and the shift of the cathodic peak potential, as well as the chronopotentiometric quarter-wave potential, with increasing pH indicate, however, that reaction (4) takes place between pH 0 and pH 7. The dithionite ion probably is formed therefore by a secondary chemical reaction.

When the pH is increased above pH I, the rate of reaction (5) is slow and the concentration of bisulfite ion increases to favor the reaction

$$H_2SO_2 + HSO_3^- \rightleftharpoons HS_2O_4^- + H_2O \tag{7}$$

This reaction probably is rapid, based on the observation of VAN DER HEIJDE¹⁶ that the exchange of ³⁵S between labeled bisulfite ion and dithionite ion is complete within IO-20 sec for solutions below pH 7. The dithionite ion is unstable⁵ in acidic media and is decomposed slowly to give sulfur and sulfur dioxide.

$$HS_{2}O_{4}^{-} + H^{+} \rightarrow H_{2}S_{2}O_{4}$$

$$2 H_{2}S_{2}O_{4} \rightarrow 2 SO_{2} + H_{2}S_{2}O_{3} + H_{2}O$$
(8)
(9)
(9)

$$H_2S_2O_3 \rightarrow S + SO_2 + H_2O \tag{10}$$

The rates of reactions (8-10) increase with decreasing pH; however, between pH 3 and pH 7 the reactions probably do not go to completion.

The concentration of undissociated sulfur dioxide decreases with increasing pH and causes the chronopotentiometric constant, $i\tau^{\dagger}$, and the cathodic peak current, to decrease. The values, however, are greater than the values calculated from the dissociation constants of sulfur dioxide. The difference between the theoretical and experimental values is probably due to the formation of sulfur dioxide by reactions (9) and (10). These reactions also are responsible for the increase in the value of $i\tau^{\dagger}$ with increasing time of electrolysis (Fig. 2) and the increase in the value of i/ν^{\dagger} at slow scan rates (Fig. 11). Reaction (9) also explains the kinetic behavior of the polarographic wave that has been observed by CĚRMÁK³ for solutions above pH 4.

KOLTHOFF AND MILLER² have suggested that the second small polarographic wave observed above pH 4 is due to reduction of dithionite ion to thiosulfate ion. CERMÁK³ has observed that the half-wave potential of this wave is independent of pH; the wave may be due to the reduction of dithionite ion to sulfoxylate ion (a reaction which does not involve H⁺ ions). The half-wave potential of this wave, however, is shifted to more positive values in the presence of di- and tri-valent cations³. Cyclic voltammetry of sulfur dioxide in slightly acidic media indicates that the second peak only is observed at slow scan rates and its height increases at the expense of the first wave when the voltage scan is repeated without cleaning the electrode. Chronopotentiometric experiments establish that $i\tau^{\dagger}$ reaches a limiting value upon increasing the concentration of the electroactive species. The second

(6)

wave disappears completely in the presence of 0.001% dodecylamine perchlorate (a surface-active substance which prevents adsorption of other substances)¹⁷.

These experiments indicate that the second wave is due to an inhibited electrode reaction, the inhibition being caused by adsorption of the reduction product of sulfur dioxide. The electrode reaction is similar to the reduction of certain metal chelates^{18,19} where adsorption complicates the reduction process. One reaction is taking place at the clean mercury surface and the second reaction at the surface covered with the adsorbed reduction products. When the applied potential is increased above a certain value, the adsorbed layer is either desorbed or the electroactive species penetrates through the adsorbed layer to give rise to the second wave. In the presence of strong surface-active agents, the adsorption of the reduction products is prevented and only a single wave is obtained.

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SUMMARY

The electroreduction of sulfur dioxide has been studied by chronopotentiometry, controlled-potential coulometry, and cyclic voltammetry. The results of these investigations lead to the conclusion that dissolved sulfur dioxide undergoes a reversible two-electron reduction to sulfoxylic acid. At pH values less than pH 3 the sulfoxylic acid is rapidly decomposed into elemental sulfur and sulfur dioxide. Between pH 3 and pH 7 the sulfoxylic acid reacts with bisulfite ion to form dithionous acid, which is slowly decomposed to sulfur dioxide, thiosulfate ion and sulfur. Hence, the final reduction product of sulfur dioxide is sulfur and the overall reaction is irreversible. Above pH 7 no reduction of sulfur dioxide is observed.

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