

Stoichiometry and Kinetics of the Reaction between Chlorine Dioxide and Sulfur(IV) in Basic Solutions

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The reaction between chlorine dioxide and sulfur(IV) has been studied in phosphate and borate buffer solutions in the pH 8–13 range where, in the presence of a slight excess of sulfur(IV), the major products are chlorite ion and sulfate ion with only minor amounts of chlorate ion and chloride ion. In the presence of phosphate buffer, the relative amount of chlorate ion produced is less than 3% whereas in the presence of borate buffer as much as 21% chlorate ion is produced. These results should be compared directly with the disproportionation of chlorine dioxide in basic solution which is considerably slower and results in a 50% yield of chlorite ion and 50% chlorate ion. The rate of reaction has also been measured in phosphate buffer solutions at 10 °C. The rate of reduction of chlorine dioxide is first order in total sulfur(IV) concentration. The second-order rate constants at pH 8.7, 10.0, and 11.5 are calculated to be 7.5×10^5 , 8.6×10^5 , and $1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively.

Introduction

Recent studies on the reactions of sulfur(IV) with various metal ions such as $\text{Fe}(\text{CN})_6^{3-}$,¹⁻⁴ $\text{Fe}(\text{phen})_3^{3+}$,⁵ $\text{Cr}(\text{VI})$,⁶ and IrCl_6^{2-} ^{7,8} have suggested that the sulfur(V) radical is formed from sulfur(IV) via a one-electron process and the resulting sulfur(V) is either oxidized further by these oxidants or dimerized to form dithionate ion. These metal ion oxidants, except $\text{Cr}(\text{VI})$, act as one-electron oxidants and cannot be reduced to the lower oxidation states.

On the other hand, in the reaction between sulfur(IV) and an oxidant which has more than one stable low oxidation state, it is expected that the oxidation of sulfur(IV) to sulfur(VI) may proceed via a single two-electron transfer process or a combination of one- and two-electron processes.⁹ The reaction between sulfur(IV) and chlorine dioxide seems to be consistent with this expectation, since chlorine dioxide is reduced to chlorite ion via a one-electron reduction and/or to hypochlorite ion or hypochlorous acid presumably via two-electron or more complicated reduction pathways.¹⁰

The reaction between sulfur(IV) and chlorine dioxide has been studied in acidic solutions¹¹ but the mechanistic details have not been elucidated owing to the rapid successive reductions by sulfur(IV) of the chlorous acid and hypochlorous acid intermediates. In contrast with the acidic solutions where these reactions are rapid, we have discovered that chlorite ion reacts only very slowly with either sulfur(IV) or hypochlorite ion in basic solutions.¹⁰⁻¹²

Experimental Section

Materials. Reagent grade chemicals were used throughout. Borate buffer solutions were prepared by neutralizing boric acid solutions with sodium hydroxide solution. Chlorine dioxide was generated from the oxidation of chlorite ion by peroxodisulfate ion in aqueous solution and was collected¹⁰ in distilled water at 0 °C by passing a constant stream of air through the reacting solution. The stock solution was stored at 0 °C.

The chlorine dioxide and sulfur(IV) concentrations were determined iodometrically. The amount of chlorite ion found in the stock solution was negligibly small. The chlorine dioxide concentrations in the kinetic measurements were determined spectrophotometrically¹³ at 360 nm ($\epsilon 1.24 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

Stoichiometry. The stoichiometric measurements for the chlorine dioxide–sulfur(IV) reaction were carried out in 0.17 M borate or phosphate solutions involving a slight excess of sulfur(IV) which had been previously deoxygenated. The reaction was initiated by injecting the chlorine dioxide solution into these solutions with a calibrated glass syringe.¹⁴ The reactions were stirred with a magnetic stirrer and were relatively rapid such that they were finished within 5 s.

The remaining sulfur(IV) was determined iodometrically at pH 10–11 under 1 atm of nitrogen. The main chlorine-containing product of the reaction was chlorite ion, and the side products were chloride

Table I. Reduction of ClO_2 by Excess Sulfite^a

pH	$\frac{[\text{ClO}_2^-]_{\text{prod}}}{[\text{ClO}_2]_{\text{i}}}$	$\frac{[\text{S}(\text{IV})]_{\text{cons}}}{[\text{ClO}_2]_{\text{i}}}$	$\frac{[\text{ClO}_3^-]_{\text{prod}}}{[\text{ClO}_2]_{\text{i}}}$
7.03	0.29	1.31	0.21
8.14	0.49	0.96	0.18
9.28	0.58	0.89	0.15
10.13	0.63	0.82	0.13
11.37	0.78	0.69	0.08
11.62	0.83	0.64	0.06
12.00	0.91	0.58	0.03
12.73	0.98	0.49	<0.01

^a Measured at 25 °C in borate buffer solutions; $(2.1\text{--}2.5) \times 10^{-3} \text{ M ClO}_2$ and $(3.8\text{--}4.5) \times 10^{-3} \text{ M S}(\text{IV})$; $[\text{S}(\text{IV})]/[\text{ClO}_2]$ ratio of 1.5–2.0 for all experiments. ^b Key: prod = produced; i = initial; cons = consumed.

Table II. Reduction of ClO_2 by Excess Sulfite^a

pH	$\frac{[\text{ClO}_2^-]_{\text{prod}}}{[\text{ClO}_2]_{\text{i}}}$	$\frac{[\text{S}(\text{IV})]_{\text{cons}}}{[\text{ClO}_2]_{\text{i}}}$	$\frac{[\text{ClO}_3^-]_{\text{prod}}}{[\text{ClO}_2]_{\text{i}}}$
8.64	0.66	1.13	0.03
9.84	0.67	1.07	
10.37	0.70	1.05	
11.30	0.79	0.90	
11.52	0.79	0.90	0.02
12.49	0.92	0.64	
12.97	0.97	0.52	0.02

^a Measured at 25 °C in phosphate buffer solutions; $(1.2\text{--}1.4) \times 10^{-3} \text{ M ClO}_2$ and $(2.3\text{--}2.7) \times 10^{-3} \text{ M S}(\text{IV})$; $[\text{S}(\text{IV})]/[\text{ClO}_2]$ ratio of 1.7–2.0 for all experiments.

ion and chlorate ion. Hypochlorite ion was not detected because the reduction of this ion by sulfur(IV) was very rapid under the present conditions. The chlorite ion and chlorate ion concentrations were determined by the iodometrical method at pH 2 and by iron(II)-catalyzed iodometry in 3 M sulfuric acid solution, respectively. The chloride ion concentration was obtained from the chlorine balance.

Kinetic Measurements. The rate of the chlorine dioxide–sulfur(IV) reaction was measured by following the disappearance of chlorine dioxide at 380 nm with a Durrum-Gibson stopped-flow spectrophotometer in 0.03 M phosphate buffer solutions at 10 °C. Only chlorine dioxide has an appreciable absorbance at this wavelength. The reactant solutions were prepared by adding an appropriate amount of chlorine dioxide or sulfur(IV) solutions, just before each measurement, to the deoxygenated phosphate solutions.

Results

Stoichiometry. Tables I and II summarize the stoichiometric results. The relative amount of chlorite ion produced increases with pH and approaches unity above pH 12.5 in both borate and phosphate solutions. The relative amounts of chlorate ion produced are significantly different between these two buffer

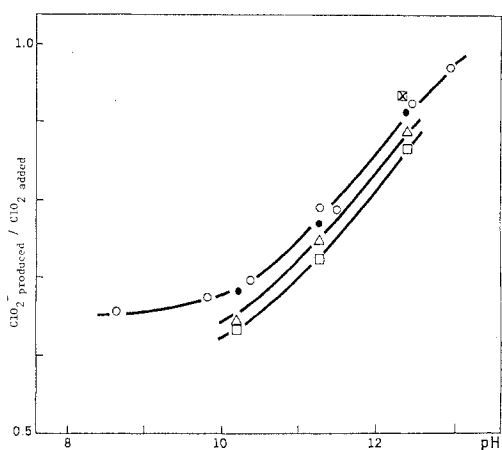


Figure 1. Dependence of relative amount of chlorite ion on sulfur(IV) concentration in the phosphate solution with 0.17 M K_2HPO_4 at room temperature: (○) $[ClO_2] = (1.2-1.4) \times 10^{-3}$, $[S(IV)] = (2.3-2.7) \times 10^{-3}$ M; (◻) $[ClO_2] = 4.7 \times 10^{-4}$, $[S(IV)] = 1.42 \times 10^{-3}$ M; (●) $[ClO_2] = (4.6-5.1) \times 10^{-4}$, $[S(IV)] = (3.3-3.8) \times 10^{-3}$ M; (Δ) $[ClO_2] = (4.6-5.2) \times 10^{-4}$, $[S(IV)] = (7.9-8.3) \times 10^{-3}$ M; (◻) $[ClO_2] = (4.7-5.2) \times 10^{-4}$, $[S(IV)] = 1.88 \times 10^{-2}$ M.

solutions. In borate solutions, the amount of chlorate ion increases as pH decreases, whereas in phosphate solution the production of chlorate ion is small, constant, and independent of pH. The ratio $[S(IV)]_{consumed}/[ClO_2]_{init}$ is reduced from above 1 to 0.5 as the pH increases, and the ratio also depends on the specific buffer used.

Figure 1 shows the dependence of the relative amounts of chlorite ion produced on the sulfur(IV) concentration in the presence of a large excess of sulfur(IV) (from 3×10^{-3} to 1.88×10^{-2} M). The relative amounts of chlorite ion produced were reduced by 4–5% as the sulfur(IV) concentrations were increased, but the relative amounts were independent of the chlorine dioxide concentration.

Kinetic Measurements. The rates of reaction were measured by following the disappearance of chlorine dioxide in 0.03 M phosphate solutions at 10 °C. The reaction was very rapid and could not be followed under pseudo-first-order conditions with respect to sulfur(IV). Thus, the kinetic data were collected using a slight excess of sulfur(IV). The concentrations ranged from 2×10^{-4} to 1.4×10^{-3} M sulfur(IV) and from 1×10^{-4} to 7×10^{-4} M chlorine dioxide.

Under these conditions, the data were treated according to the second-order rate equation

$$-d[ClO_2]/dt = k_{obsd}[ClO_2]/[S(IV)]$$

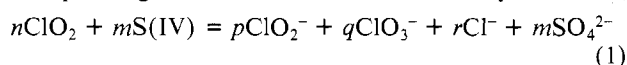
where $[S(IV)]$ denotes the analytical sulfur(IV) concentration. This equation was integrated in terms of the $[S(IV)]/[ClO_2]$ ratio which resulted in

$$\ln [ClO_2] - \ln ([S(IV)]_0 - C[ClO_2]_0 + C[ClO_2]) = -k_{obsd}t$$

where $[S(IV)]_0$ and $[ClO_2]_0$ denote the initial concentrations and the coefficient C is known from the stoichiometric results. The latter equation fitted the data obtained from the first observable points to at least 75% reaction. The observed second-order rate constants are shown in Table III. A slight pH dependence is noted.

Discussion

The overall stoichiometry of the reaction between chlorine dioxide and sulfur(IV) in the presence of excess sulfur(IV) in the pH range of 8–13 can be best described by reaction 1,



where S(IV) denotes all species of sulfur(IV). The coefficients n , m , p , q , and r depend on both the pH and the specific buffer

Table III. Typical Observed Second-Order Rate Constants for the Reaction between Chlorine Dioxide and Sulfur(IV)^a

pH	$10^4 \times [S(IV)]$, M	$10^4 \times [ClO_2]$, M	$[S(IV)]/[ClO_2]$	$10^{-5}k_{obsd}$, $M^{-1} s^{-1}$
8.7	5.1	3.8	1.3	7.4 ± 0.3
	10.1	6.2	1.6	7.4 ± 0.3
	8.6	4.8	1.8	9.2 ± 0.2
	2.6	1.3	2.0	7.0 ± 0.5
	5.0	1.1	4.7	7.6 ± 0.3
			av ^b	7.8 ± 1.3
10.0	2.8	1.9	1.5	7.1 ± 0.1
	6.4	3.8	1.7	9.6 ± 0.2
	13.2	6.9	1.9	7.4 ± 0.3
	7.6	3.7	2.0	8.6
	7.5	2.7	2.8	13.6
			av ^c	8.6 ± 2.0
11.5	2.9	2.6	1.1	14.3 ± 0.3
	6.3	4.2	1.5	11.2 ± 0.4
	8.7	4.9	1.8	11.5 ± 0.5
	9.2	4.5	2.1	11.2 ± 0.4
			av ^d	12.1 ± 0.4

^a Measured at 10 °C in 0.03 M K_2HPO_4 buffer. ^b Fourteen experiments total. ^c Fifteen experiments total. ^d Eight experiments total.

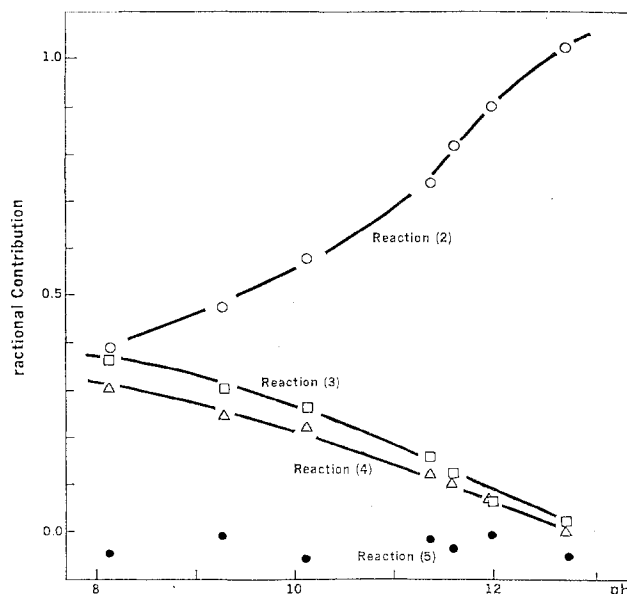
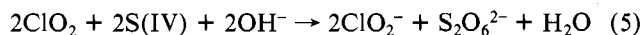
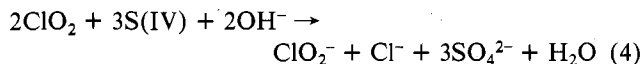
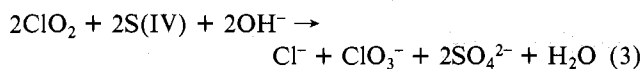


Figure 2. Results of calculated fractional contributions in the borate solution.

solution used. During the course of the reaction, a part of the chlorine dioxide is reduced to chlorite ion or chloride ion, whereas the other part is oxidized to chlorate ion. Since the reaction between chlorite ion and sulfur(IV) is relatively slow under the present conditions,¹² the presence of chloride ion as a product suggests that chlorine dioxide must be reduced to chloride ion via a direct two-electron-transfer process or a more complicated multielectron-transfer process in which chlorite ion is not produced as an intermediate. On the time scale of the sulfur(IV)–chlorine dioxide reactions reported here, it should be noted that in this pH region direct reactions between chlorine dioxide or chlorite ion and the probable halogen-containing intermediates may be too slow to make important contributions.^{10,13,15} Moreover, from a comparison of $[S(IV)]_{consumed}/[ClO_2]_{init}$ with $[ClO_2^-]_{produced}/[ClO_2]_{init}$ it is apparent that sulfur(IV) simultaneously plays the role of a one- and two-electron reductant.

On the basis of these observations, reaction processes 2–5

$$2ClO_2 + S(IV) + 2OH^- \rightarrow 2ClO_2^- + SO_4^{2-} + H_2O \quad (2)$$



may be used to account for the overall reaction given by eq 1. Reaction 2 predominates at a high pH, where sulfur(IV) acts as a one-electron reductant. Reaction 3, which produces both chlorate ion and chloride ion, can be considered as an apparent disproportionation of chlorine dioxide accelerated by the presence of sulfur(IV), although the uncatalyzed disproportionation reaction in base produces¹⁶ only chlorite ion and chlorate ion. Reaction 4 results in the production of both chloride ion and chlorite ion. In reaction 4, sulfur(IV) simultaneously acts as a one- or a two-electron reductant. Reaction 5 corresponds to the dimerization of sulfur(V) and would account for the production^{1,7,8} of dithionate ion ($\text{S}_2\text{O}_6^{2-}$). If the fractional contributions of reactions 2–5 are denoted by the letters *a*, *b*, *c*, and *d*, respectively, the following relationships are obtained under the conditions of a slight excess of sulfur(IV):

$$a + b + c + d = 1$$

$$a + \frac{1}{2}c + d = [\text{ClO}_2^-]_{\text{produced}} / [\text{ClO}_2]_{\text{init}}$$

$$\frac{1}{2}a + b + \frac{3}{2}c + d = [\text{S(IV)}]_{\text{consumed}} / [\text{ClO}_2]_{\text{init}}$$

$$\frac{1}{2}b = [\text{ClO}_3^-]_{\text{produced}} / [\text{ClO}_2]_{\text{init}}$$

$$\frac{1}{2}b + \frac{1}{2}c = [\text{Cl}^-]_{\text{produced}} / [\text{ClO}_2]_{\text{init}}$$

In the experiments using borate buffer, these successive equations can be solved completely by use of the data given in Table I. The results are shown in Figure 2. Similarly, in the case of the phosphate buffer *a*, *b*, and *c* can be obtained directly from the data in Table II with the assumption that *d* = 0. In order to examine this assumption, the calculated values of *b* can be compared with the observed values. Figure 3 shows the results, which indicate that this assumption is satisfactory within the experimental uncertainty. It can be concluded from these results that the overall reaction in both of the buffer solutions does not include reaction 5. In other words, dithionate is not produced and the fractional contributions of reactions 2–4 depend on both the pH and the nature of the specific buffer solution.

The value of the parameter *a* increases with pH, which supports the role of sulfur(IV) as a one-electron reductant.^{2-5,8} Moreover, it is always observed that the contribution of this term is much larger in the borate solutions than in the phosphate solutions. Under all conditions observed, the contribution to the overall reaction of the direct sulfur(IV)-catalyzed disproportionation^{10,16} reaction changes markedly—from virtually no contribution in the presence of phosphate buffer to a marked increase with decreases in pH in the borate solutions. It is for this reason that the effect of several buffers was examined in detail and that the kinetics of the overall reaction were studied in phosphate buffer to allow a detailed understanding of the microscopic details of the reaction mechanism.

Hypochlorous acid reacts with chlorine dioxide in low-pH solutions producing chlorate and chloride ions,¹⁵ but the reaction rate is much slower than that between sulfur(IV) and hypochlorous acid.¹⁰ On the other hand, it is not unreasonable to expect formation of the chlorine(II) radical by means of a two-electron reduction of chlorine dioxide by sulfur(IV) followed by a consecutive reaction with chlorine dioxide to produce chlorate ion. Similarly, the production of chloride ion in reaction 4 may be attributed to the reaction between sulfur(IV) and the chlorine(II) radical in which chlorine(I)

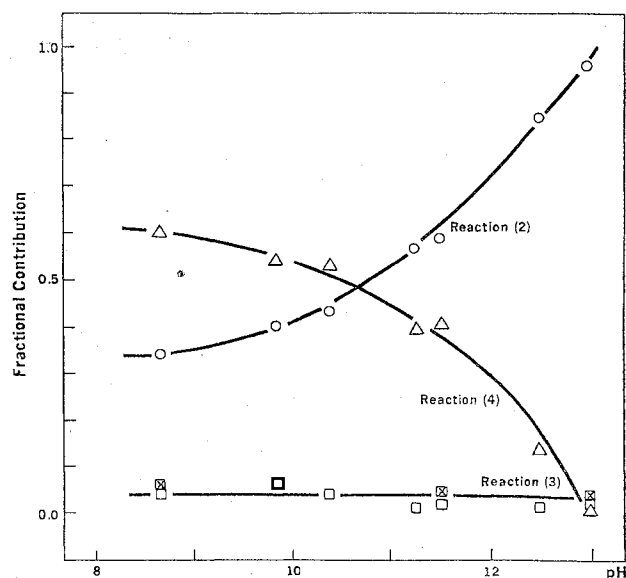
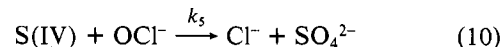
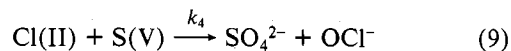
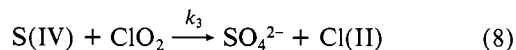
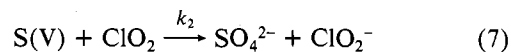
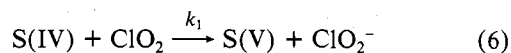


Figure 3. Results of calculated fractional contributions in the phosphate solution. \blacksquare corresponds to the observed value for *b*.

is produced but rapidly reduced to chloride ion by sulfur(IV).^{11,12} The chlorine(I) intermediate can be produced from the reaction between chlorite ion and sulfur(IV),¹¹ but this reaction does not occur under the present conditions. However, the recent study of electrochemical oxidation of hypochlorite ion has suggested the presence of the chlorine(II) radical.¹⁷ Therefore, the chlorine(II) radical appears to be a reasonable intermediate for the production of chlorate ion and chloride ion via reactions 3 and 4.

The kinetic study demonstrated that the overall reaction is first order with respect to chlorine dioxide and first order with respect to sulfur(IV). The kinetic study also demonstrated that any contribution from a second-order term in sulfur(IV) must be negligible in the pH 7–11 region. The stoichiometric results which are shown in Figures 2 and 3 are also consistent with the absence of dithionate ion as a reaction product.

The kinetics and stoichiometry of the overall reaction can be discussed in terms of eq 6–10.



Sulfur(V) is formed in reaction 6 and terminated by reactions 7 and 9. The chlorine(II) radical is formed via a two-electron-transfer process and terminated by reaction 9. The small amount of chlorate ion observed is produced by an alternative termination of the chlorine(II) radical by reaction with chlorine dioxide or the chlorite ion intermediate.

If the concentrations of the chlorine(II) radical and the sulfur(V) intermediates are assumed as steady-state species, rate eq 11 is derived. This overall form of the rate law is

$$-d[\text{ClO}_2]/dt = 2k_1[\text{ClO}_2][\text{S(IV)}] \quad (11)$$

consistent with the experimentally observed rate law and with the observation that chlorine dioxide is thermodynamically a more powerful oxidizing agent than is chlorite ion.

Figure 4 shows the relationship between the pH dependence of the second-order rate constants and that of the fractional

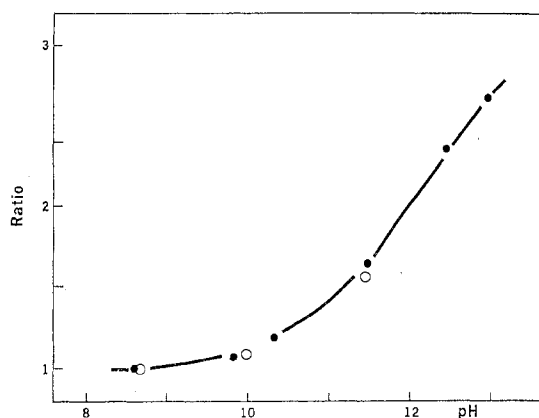
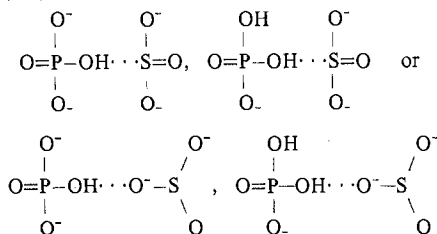


Figure 4. Correlation between the second-order rate constant and the fractional composition of reaction 2 in the phosphate solution: (○) $k_{\text{pH}}/k_{\text{pH } 8.7}$, (●) $a_{\text{pH}}/a_{\text{pH } 8.64}$.

contribution of reaction 2 (the fractional parameter a). It can be seen from eq 11 that the rate constant is described as $2k_1$ and that the parameter a involves the direct contribution from eq 7 which is consistent with the overall mechanism suggested above.

Figure 1 indicates that the amounts of chlorite ion produced depend to a minor extent on the sulfur(IV) concentration. The parallel curves are obtained by connecting data at the same initial concentrations of sulfur(IV), which suggests that the dimeric form of sulfur(IV) may make a minor contribution to the overall process (reaction 1) at high concentrations of sulfur(IV). The recent study¹⁸ of the oxygen-exchange reaction between sulfur(IV) and water has demonstrated the possible importance of the dimeric species $\text{S}_2\text{O}_3^{2-}$ in the pH range 8–10 and at high concentrations of sulfur(IV) (>0.05 M). However, at low concentrations of sulfur(IV) reported in this paper ($<5 \times 10^{-3}$ M), the contribution from the dimeric sulfur(IV) species appears to be minimal.

The results shown in Figures 2 and 3 would seem to suggest that the two-electron process does vary with pH. Since the proton dissociation constant¹⁹ for HSO_3^- is 4.6×10^{-7} , the resulting concentration of HSO_3^- is probably kinetically insignificant; however, the interaction between the buffer species (H_2PO_4^- and HPO_4^{2-}) and sulfite ion could be of importance in the pH 8–12 range. Thus, the pH dependence for the two-electron-transfer process could involve various tautomers²⁰ of sulfur(IV) such as



in which the sulfur(IV) could act as a two-electron reductant.

The stoichiometric results clearly indicate that the dimerization of sulfur(V) does not occur to any appreciable extent under the conditions reported. This dimerization has been reported in the copper(II)-catalyzed reduction of iron(III) and the reduction^{7,8} of IrCl_6^{2-} by sulfur(IV) but not in the reaction⁸ between $\text{Fe}(\text{phen})_3^{3+}$ and sulfur(IV), in spite of the reported presence of sulfur(V) as an intermediate. Although estimation of the rate constant for dimerization of sulfur(V) is difficult, some limits can be determined from these observations and the rate constants of $2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for reaction between IrCl_6^{2-} and SO_3^{2-} , $9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for reaction between $\text{Fe}(\text{phen})_3^{3+}$ and SO_3^{2-} , and $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for reaction of ClO_2 and SO_3^{2-} ; the dimerization seems to be rather slow and may not occur in the reactions of sulfur(IV) with rate constants $>10^4 \text{ M}^{-1} \text{ s}^{-1}$.

Although the kinetic studies were not also carried out in borate solutions, it is highly probable that a strong interaction between the borate species as a strong electron donor and either sulfur(IV) or chlorine dioxide appears to be one of the significant factors governing the overall reactivity. The details of these interactions will be reported elsewhere.²¹

In conclusion, the primary reaction corresponds to the direct one-electron reduction of chlorine dioxide to form chlorite ion. Clearly, the reaction is very rapid and above pH 11 results in 100% yield of sulfate ion and chlorite ion.

Registry No. ClO_2 , 10049-04-4; SO_3^{2-} , 14265-45-3.

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