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Kinetics and Mechanism of the Oxidation of Sulfite by Chlorine Dioxide in a Slightly Acidic Medium

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The sulfite−chlorine dioxide reaction was studied by stopped-flow method at $I = 0.5$ M and at 25.0 ± 0.1 °C in a slightly acidic medium. The stoichiometry was found to be $2\ SO_3^{2-} + 2{\cdot}ClO_2 + H_2O \rightarrow 2SO_4^{2-} + Cl^- + ClO_3^- + 2H^+$ in $\cdot ClO_2$ excess and $6SO_3^{2-} + 2{\cdot}ClO_2 \rightarrow S_2O_6^{2-} + 4SO_4^{2-} + 2Cl^-$ in total sulfite excess ($[S(IV)] = [H_2SO_3] + [HSO_3^-] + [SO_3^{2-}]$). A nine-step model with four fitted kinetic parameters is suggested in which the proposed adduct $\cdot SO_3ClO_2^{2-}$ plays a significant role. The pH-dependence of the kinetic traces indicates that SO_3^{2-} reacts much faster with $\cdot ClO_2$ than HSO_3^- does.

Introduction

The chlorite−thiosulfate reaction displays a remarkable range of “exotic” kinetic phenomena including complex periodic and aperiodic oscillation[1,2] and chaos[3] in CSTR, and shows extreme sensitivity to stirring rate effects and fluctuations[4] in batch condition. So far no attempt has been made to unravel the kinetics and mechanism of this reaction because of its complexity. Three long-lived intermediates and/or end products—tetrathionate, hypochlorous acid, chlorine dioxide—have been established in this reaction that can react further with not only the reactants but also with each other, making the mechanism particularly complicated. Systematic investigations in the last 15 years have provided the kinetics and mechanism of several subsystems of the parent reaction such as that of the hypochlorous acid-chlorite,[5] thiosulfate-chlorine dioxide,[6] tetrathionate−hypochlorous acid,[7] and tetrathionate−chlorine dioxide[8] and that of the decomposition of chlorous acid.[9] Very recently a five-step model has been published[10] for interpreting the unusual kinetic behavior of the chlorite−tetrathionate reaction in which HSO_3^- plays a crucial role to regulate the concentration of the autocatalyst HOCl. Since the oxidation of sulfite by chlorine dioxide is a relatively rapid process, it may also have a great impact on the kinetics of the parent reaction.

The first article in the literature dealing comprehensively with the kinetics and mechanism of the reaction between sulfite and chlorine dioxide was published by Halperin and Taube.[11] The thermodynamically most favorable stoichiometry would be

$$5S(IV) + 2\ {\cdot}ClO_2 + 2H^+ \rightarrow 5SO_4^{2-} + 2Cl^- + H_2O \quad (I)$$

chlorate formation was, however, always detected in appreciable amounts in their experiments. Note that S(IV) stands for all the differently protonated sulfite species, i.e, $[S(IV)] = [H_2SO_3] + [HSO_3^-] + [SO_3^{2-}]$ along this paper. They have also found that the kinetics can be best described by

$$-\frac{d[\cdot ClO_2]}{dt} = k_a[\cdot ClO_2]^2[H_2SO_3] \qquad (1)$$

in strong acidic solution (0.1 M HCl), where k_a decreases as the acidity increases. This fact raises a question about the reactivity of differently protonated S(IV) species. In fact the pH dependence of k_a strongly suggests that the reactivity of HSO_3^- is greater than that of H_2SO_3 toward chlorine dioxide, and still nothing is known about that of SO_3^{2-}.

The stoichiometry and the kinetics of the sulfite−chlorine dioxide was later thoroughly reinvestigated by Suzuki and Gordon[12] in alkaline solutions. Slight stoichiometric excess of sulfite has been applied, the ratio of ($[S(IV)]_0/[\cdot ClO_2]$) was varied between 1.5 and 2.0. Under these circumstances the formation of dithionate was ruled out. Three competitive stoichiometries have been found

$$2{\cdot}ClO_2 + SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + 2ClO_2^- + H_2O \quad (II)$$

$$2{\cdot}ClO_2 + 2SO_3^{2-} + 2OH^- \rightarrow Cl^- + ClO_3^- + 2SO_4^{2-} + H_2O \quad (III)$$

$$2{\cdot}ClO_2 + 3SO_3^{2-} + 2OH^- \rightarrow ClO_2^- + Cl^- + 3SO_4^{2-} + H_2O \quad (IV)$$

It has also been found that the disappearance of chlorine dioxide obeyed a simple second-order kinetics

$$-\frac{d[\cdot ClO_2]}{dt} = k_b[\cdot ClO_2][S(IV)] \qquad (2)$$

They have also noticed that the value of k_b increases with increasing pH; at 10 °C k_b was found to be $7.5 \times 10^5\ M^{-1}\ s^{-1}$ and $1.2 \times 10^6\ M^{-1}\ s^{-1}$ as the pH was adjusted to 8.7 and 10.0, respectively. Moreover, the authors have also reported a slight buffer dependence on k_b. The following mechanism was proposed based on their measurements

$$SO_3^{2-} + {\cdot}ClO_2 \rightarrow {\cdot}SO_3^- + ClO_2^- \qquad (3)$$

$$SO_3^{2-} + {\cdot}ClO_2 \rightarrow SO_4^{2-} + {\cdot}ClO \qquad (4)$$

$${\cdot}SO_3^- + {\cdot}ClO_2 + 2OH^- \rightarrow SO_4^{2-} + ClO_2^- + H_2O \quad (5)$$

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$$\cdot SO_3^{-} + \cdot ClO + 2OH^{-} \rightarrow SO_4^{2-} + OCl^{-} + H_2O \qquad (6)$$

$$SO_3^{2-} + OCl^{-} \rightarrow SO_4^{2-} + Cl^{-} \qquad (7)$$

Note that further reaction of chlorite with S(IV) was not involved since in alkaline solution this reaction is very slow.[13] This mechanism, however, cannot be incorporated with the three competitive stoichiometry, since no chlorate formation is indicated in the mechanism. Stoichiometry II comes forward with addition of eqs 3 and 5, while stoichiometry IV with addition of eqs 4, 6, and 7. Stoichiometry III would easily be interpreted after inclusion of the following step into the mechanism

$$2\cdot ClO + H_2O \rightarrow Cl^{-} + ClO_3^{-} + 2H^{+} \qquad (8)$$

since the appropriate linear combination of eqs 4 and 8 would directly refer to this stoichiometry. The most important conclusion of this work was that formal oxygen transfer from chlorine dioxide to sulfite must occur parallel to a single electron transfer from S(IV) to chlorine dioxide to give the branching stoichiometry.

More recently the electron-transfer process from sulfite to chlorine dioxide has been investigated[14] in 1 M ClO_2^{-} solution. The forward and the reverse rate coefficients of the following equation

$$SO_3^{2-} + \cdot ClO_2 \rightleftharpoons \cdot SO_3^{-} + ClO_2^{-} \qquad (9)$$

was found to be 2.6×10^6 M^{-1} s^{-1} and 1300 M^{-1} s^{-1}, respectively, in huge excess of chlorite (1 M). A very similar value of 2.82×10^6 M^{-1} s^{-1} was used for the forward reaction in the interpretation of pH oscillations found in the chlorite−sulfite system.[15] Furthermore, formation of dithionate was also considered in Frerichs's and co-workers' simulation throughout a fast dimerization of sulfite radical.

To give an adequate answer whether the S(IV)−chlorine dioxide reaction may play significant role describing the kinetics of the parent reaction or not we decided to reinvestigate it in slightly acidic medium.

Experimental Section

Materials. The chlorine dioxide solution was prepared as described previously.[8] The stock solution was kept refrigerated and was protected from light. The purity of the commercially available sodium sulfite (Merck) was checked by standard iodometric titration and was found to be better than 95%, and the main contamination was found to be sulfate. Separate experiment has shown that addition of sulfate disturbs neither the stoichiometry nor the kinetic curves. All the other chemicals were of the highest purity commercially available (sodium acetate, acetic acid). All the solutions were prepared by four times distilled water. Before preparing the sulfite solution the water was even boiled for 20 min and deoxygenated with bubbling N_2. All the solutions used for the kinetic measurements were prethermostated at 25.0 ± 0.1 °C and protected from light. The ionic strength was adjusted to 0.5 M by using 0.5 M sodium acetate. The desired pH was achieved by addition of the appropriate amount of acetic acid.

Methods. The stoichiometry was determined by standard iodometry in excess of sulfite. After mixing the reactants in the desired buffer solution only chloride and chlorate remained since both chlorite and hypochlorous acid react rapidly[13,16] with sulfite and sulfite cannot be oxidized by chlorate in slightly acidic medium, so the unreacted sulfite can easily be determined. In this case the stoichiometric ratio (SR) is calculated by $([S(IV)]_0 - [S(IV)]_\infty)/[\cdot ClO_2]_0$. In excess of chlorine dioxide spectrophotometric measurements were used to calculate SR $= [S(IV)]_0/([\cdot ClO_2]_0 - [\cdot ClO_2]_\infty)$.

TABLE 1: Initial Concentrations of the Reactants

run no.	$[\cdot ClO_2]_0$ (mM)	$[S(IV)]_0$ (mM)	pH
1−7	0.265, 0.395, 0.55, 0.77, 1.035, 1.79, 2.50	0.2	4.55
8−14	0.267, 0.385, 0.55, 0.76, 1.035, 1.84, 2.46	0.3	4.55
15−21	0.29, 0.395, 0.55, 0.765, 1.038, 1.88, 2.46	0.5	4.55
22−28	0.28, 0.395, 0.55, 0.785, 1.035, 1.90, 2.49	0.7	4.55
29−35	0.27, 0.392, 0.55, 0.775, 1.02, 1.88, 2.50	1.0	4.55
36−42	0.28, 0.392, 0.55, 0.77, 1.02, 1.98, 2.54	2.0	4.55
43−49	0.27, 0.396, 0.56, 0.77, 1.02, 1.88, 2.52	3.0	4.55
50−56	0.285, 0.405, 0.565, 0.79, 1.05, 1.88, 2.51	4.0	4.55
57−63	0.275, 0.39, 0.55, 0.77, 1.08, 1.88, 2.57	0.2	4.25
64−70	0.277, 0.385, 0.545, 0.76, 1.07, 1.88, 2.62	0.3	4.25
71−77	0.278, 0.395, 0.55, 0.765, 1.06, 1.88, 2.62	0.5	4.25
78−84	0.27, 0.395, 0.55, 0.785, 1.07, 1.89, 2.63	0.7	4.25
85−91	0.26, 0.385, 0.545, 0.775, 1.06, 1.88, 2.63	1.0	4.25
92−98	0.265, 0.39, 0.54, 0.77, 1.07, 1.88, 2.57	2.0	4.25
99−105	0.26, 0.39, 0.54, 0.77, 1.06, 1.88, 2.58	3.0	4.25
106−112	0.27, 0.395, 0.55, 0.77, 1.07, 1.88, 2.55	4.0	4.25
113−119	0.29, 0.405, 0.548, 0.79, 1.115, 1.89, 2.52	0.2	3.95
120−126	0.29, 0.405, 0.548, 0.78, 1.11, 1.91, 2.64	0.3	3.95
127−133	0.29, 0.405, 0.555, 0.785, 1.10, 1.9, 2.63	0.5	3.95
134−140	0.288, 0.4, 0.55, 0.78, 1.10, 1.85, 2.635	0.7	3.95
141−147	0.285, 0.4, 0.545, 0.78, 1.10, 1.86, 2.62	1.0	3.95
148−154	0.27, 0.395, 0.545, 0.73, 1.07, 1.89, 2.68	2.0	3.95
155−161	0.27, 0.39, 0.545, 0.75, 1.10, 1.88, 2.61	3.0	3.95
162−168	0.27, 0.39, 0.545, 0.75, 1.05, 1.75, 2.60	4.0	3.95
169−175	0.283, 0.385, 0.54, 0.765, 1.07, 1.82, 2.52	0.2	3.65
176−182	0.283, 0.377, 0.533, 0.775, 1.055, 1.84, 2.64	0.3	3.65
183−189	0.282, 0.375, 0.536, 0.765, 1.055, 1.85, 2.63	0.5	3.65
190−196	0.275, 0.38, 0.534, 0.765, 1.05, 1.85, 2.635	0.7	3.65
197−203	0.27, 0.365, 0.53, 0.765, 1.05, 1.82, 2.62	1.0	3.65
204−210	0.25, 0.365, 0.53, 0.73, 1.04, 1.82, 2.68	2.0	3.65
211−217	0.255, 0.365, 0.53, 0.74, 1.0, 1.80, 2.61	3.0	3.65
218−224	0.260, 0.36, 0.53, 0.73, 1.0, 1.75, 2.60	4.0	3.65

For the qualitative determination of the end products, Raman spectroscopy has been used by a Bio-rad Digilab Division dedicated FT-Raman spectrometer with laser type Nd:YVO_4 lasing at 1064 nm. After the reaction was completed, the solution was vacuum-evaporated at 35 °C. The Raman spectrum of the solid material was registered for identification of the dithionate.

The kinetic measurements were carried out by a Hi-Tech SF-61 stopped-flow apparatus attached to a single wavelength spectrophotometer that provides monochromatic light. The reaction was followed at 400 nm where the only absorbing species is chlorine dioxide ($\epsilon_{\cdot ClO_2} = 552$ M^{-1} cm^{-1}). Table 1 summarizes the pH and concentration range of the reactants used in the kinetic experiments.

Data Treatment. Only measurements up to 1.4 absorbance units were used in our analysis, because the relative error of absorbance measurements above this value is unacceptably high. Because each kinetic curve contained 512 data points, the number of points in each run was reduced to 45−50 to avoid unnecessary and time-consuming calculations. The point reduction algorithm was based on the principle of equivalent arclength in order to avoid losing any significant chemical information. Each kinetic curve was repeated at least five times; the average of them was used for the fitting procedure.

The experimental curves were analyzed with the program package ZiTa,[17] developed recently for fitting kinetic data simultaneously. Altogether, 10700 experimental points from the 224 absorbance−time series were used for simultaneous fitting. This method required a new evaluation procedure of the stopped-

TABLE 2: Determination of the Ratio of Consumed S(IV) and $\cdot ClO_2$ in Excess of Sulfite[a]

c_0(S(IV))	$c_0(\cdot ClO_2)$	c_∞(S(IV))	pH	$[S(IV)]_{conc}/[\cdot ClO_2]_{conc}$
3.64	1.91	0.11	4.55	1.85
4.20	1.89	0.53	4.55	1.94
4.76	1.87	1.06	4.55	1.98
5.31	1.86	1.16	4.55	2.23
5.85	1.84	1.29	4.02	2.48
6.37	1.83	2.11	4.55	2.33
6.89	1.81	2.38	4.02	2.49
7.40	1.79	3.19	4.02	2.35
7.90	1.78	3.93	4.55	2.23
8.40	1.76	3.56	4.55	2.75
8.33	2.33	2.95	4.55	2.31
8.26	2.89	2.39	4.55	2.03
8.19	3.44	1.48	4.55	1.95
8.12	3.98	0.64	4.55	1.88
8.05	4.51	0.29	4.55	1.72
7.99	5.03	0.09	4.55	1.57
7.93	5.55	0.04	4.55	1.42
8.47	1.19	4.92	4.55	2.98
8.54	0.60	6.73	4.55	3.02
15.01	1.05	12.08	4.55	2.79
14.23	1.07	11.00	4.05	3.02
13.42	1.08	10.59	4.55	2.62
12.58	1.10	9.66	4.25	2.65
11.72	1.12	8.64	4.02	2.75
10.83	1.14	7.40	3.85	3.01
9.91	1.16	6.73	4.05	2.74

[a] c_∞(S(IV)) is the final concentration of S(IV) calculated from the titration after the reaction is completed. All the concentrations are indicated in mM units.

flow measurements. Details of this method were published previously.[6,18] Absolute and relative average deviations have also been calculated in order to judge between the different models. The criterion of the goodness of fit was to reach the uncertainty of the spectrophotometer (±0.005) in case of the absolute fit and 3% in case of relative fit.

Results

Stoichiometry. Table 2 summarizes the results of the stoichiometric measurements in sulfite excess. The consumed S(IV)/$\cdot ClO_2$ ratio (SR) varies between 1.43 and 3.02; the larger the excess of S(IV) is, the higher this ratio is. Moreover, in a number of cases this ratio exceeds 2.5, which cannot be explained if sulfite is uniquely oxidized to sulfate. As eqs I−IV indicate, this ratio must be between 0.5 and 2.5 if sulfate is the only sulfur-containing end product. Our stoichiometric measurements, however, clearly suggest that, beside sulfate, dithionate should also be present to be responsible for the values of SR found to be higher than 2.5. To strengthen the formation of dithionate among the end products, we have analyzed the Raman spectrum of the vacuum-evaporated solution of the reacted mixtures. The appearance of the characteristic bands of dithionate around 291, 708, and 1100 cm^{-1} strongly supports the result of the classical titration method. Separate experiments have shown that dithionate is not oxidized by chlorine dioxide under our experimental circumstances.

Table 3 summarizes the results of the stoichiometric measurements in chlorine dioxide excess. As it is clearly seen when ($[S(IV)]_0/[\cdot ClO_2]$) ratio is small, the consumed S(IV)/$\cdot ClO_2$ ratio (SR) approaches unity, but increase of the initial concentration ratio of the reactants results in the increase of SR. In some cases, when almost all the chlorine dioxide is consumed, SR slightly exceeds 2.5, supporting again the formation of dithionate. In excess of chlorine dioxide, formation of chlorite is also conceivable; therefore, the end product was analyzed for chlorite contamination after purging the remaining chlorine dioxide from the sample. Only a trace amount (≈0.1%) of the reacted chlorine dioxide is transformed into chlorite; thus, its role is negligible in determining the stoichiometry.

TABLE 3: Determination of the Ratio of Consumed S(IV) and $\cdot ClO_2$ in Excess of Chlorine Dioxide[a]

c_0(S(IV))	$c_0(\cdot ClO_2)$	A_∞	pH	$[S(IV)]_{conc}/[\cdot ClO_2]_{conc}$
0.2	2.50	1.286	4.55	1.18
0.3	2.46	1.234	4.55	1.34
0.5	2.46	1.158	4.55	1.38
0.7	2.49	1.097	4.55	1.39
1.0	2.50	0.989	4.55	1.41
2.0	2.54	0.635	4.55	1.44
3.0	2.52	0.270	4.55	1.48
4.0	2.51	0.020	4.55	1.62
0.2	0.77	0.348	4.25	1.81
0.3	0.76	0.364	4.25	1.94
0.5	0.77	0.334	4.25	2.08
0.7	0.77	0.292	4.25	2.15
1.0	0.77	0.245	4.25	2.21
0.2	0.405	0.170	3.95	2.06
0.3	0.405	0.153	3.95	2.35
0.5	0.405	0.118	3.95	2.62
0.7	0.40	0.075	3.95	2.65
1.0	0.40	0.018	3.95	2.72
0.2	0.54	0.243	3.65	2.00
0.3	0.533	0.221	3.65	2.26
0.5	0.536	0.184	3.65	2.47
0.7	0.534	0.140	3.65	2.50
1.0	0.53	0.091	3.65	2.74

[a] A_∞ is the final absorbance at 400 nm measured after the reaction is completed. All the concentrations are indicated in mM units. The molar absorbance of $\cdot ClO_2$ Is 552 M^{-1} cm^{-1} at this wavelength.

These studies convincingly demonstrate that in chlorine dioxide excess the limiting stoichiometry is

$$2SO_3^{2-} + 2\cdot ClO_2 + H_2O \rightarrow 2SO_4^{2-} + ClO_3^- + Cl^- + 2H^+ \quad (S1)$$

but as the $[S(IV)]_0/[\cdot ClO_2]_0$ ratio increases the following stoichiometry gradually takes over the governing role.

$$6SO_3^{2-} + 2\cdot ClO_2 \rightarrow 4SO_4^{2-} + S_2O_6^{2-} + 2Cl^- \quad (S2)$$

The latter reaction may seem unnecessarily complicated to give sulfate and dithionate, but it is easily understood from our proposed mechanism (see below). The stoichiometry of sulfite−chlorine dioxide reaction at any initial concentration ratios of the reactants can therefore be described by an appropriate linear combination of S1 and S2 in slightly acidic medium.

Initial Rate Studies. Since the only absorbing species in the given wavelength is $\cdot ClO_2$, (d*A*/d*t*) is directly proportional to (d[$\cdot$*ClO*$_2$]/d*t*) former values were used to analyze the initial rates. These studies have revealed that the kinetic order of the reactants are greater than 1. Figure 1 indicates typical kinetic orders of the reactants. The kinetic order of chlorine dioxide varies between 1.03 and 1.22, while that of the sulfite changes between 0.99 and 1.33. The rate of the reaction depends reversely on the H^+ concentration in agreement with earlier studies[11,12] found at very different experimental circumstances.

Proposed Mechanism. The approach used to generate the proposed model resembles more some of the techniques used to construct large models in atmospheric[19] or combustion[20] chemistry than the earlier studies of this system, takes advantage of the significant advancing in computing power. The first, probably the most critical part of this procedure is to choose all the species that may be involved in the chemical model. Of course the reactants, the end products, and the solvent must be included. This group consists of SO_3^{2-}, HSO_3^-, H_2SO_3 (SO_2), $\cdot ClO_2$, Cl^-, ClO_3^-, SO_4^{2-}, $S_2O_6^{2-}$, H^+, and H_2O. Additional intermediates $\cdot SO_3ClO_2^{2-}$, $\cdot SO_3^-$, $\cdot ClO$, Cl_2O_2, HOCl, and ClO_2^- were chosen for the following reasons:

- Several studies of the reactions of chlorine dioxide have suggested an initializing step in which a weak adduct is formed.[6,8,21,22] By analogy, we propose $\cdot SO_3ClO_2^{2-}$.
- Single electron transfer from sulfite to chlorine dioxide is easily conceivable such as in the oxidation of phenol, indoles, and metal complexes by chlorine dioxide.[14,23] Therefore, inclusion of $\cdot SO_3^-$ and ClO_2^- seems plausible.
- Suzuki and Gordon[12] have proven experimentally that in alkaline solution formal oxygen transfer from chlorine dioxide to sulfite plays a significant role in describing their results beside the electron-transfer process. Thus, we included $\cdot ClO$ and its dimeric form Cl_2O_2.
- Since chlorite might also be an intermediate and its reaction with sulfite goes through the intermediate HOCl,[13] this compound was also included among the possible intermediates.

This set of reactants, intermediates and end products leads to 40 plausible mono- or bimolecular steps. Since the initial rate also depends on $[H^+]$, the H^+ and OH^--catalyzed pathways of the 40 reactions were also considered initially. From the 120 initially included steps, the following simple model emerged from the systematic reduction procedure.

$$SO_3^{2-} + H^+ \rightleftharpoons HSO_3^- \qquad (R1)$$

$$SO_3^{2-} + \cdot ClO_2 \rightleftharpoons \cdot SO_3ClO_2^{2-} \qquad (R2)$$

$$\cdot SO_3ClO_2^{2-} \rightarrow SO_4^{2-} + \cdot ClO \qquad (R3)$$

$$2\cdot SO_3ClO_2^{2-} \rightarrow 2SO_4^{2-} + Cl_2O_2 \qquad (R4)$$

$$Cl_2O_2 + H_2O \rightarrow Cl^- + ClO_3^- + 2H^+ \qquad (R5)$$

$$HSO_3^- + \cdot ClO \rightarrow \cdot SO_3^- + HOCl \qquad (R6)$$

$$\cdot ClO_2 + \cdot ClO + H_2O \rightarrow HOCl + ClO_3^- + H^+ \qquad (R7)$$

$$SO_3^{2-} + HOCl \rightarrow SO_4^{2-} + Cl^- + H^+ \qquad (R8)$$

$$2\cdot SO_3^- \rightarrow S_2O_6^{2-} \qquad (R9)$$

The corresponding rate laws are given by either the law of mass action (for equilibria) or by simple first or second-order kinetics (the concentration of water is not included in the rate equations).

Discussion

Step R1 is the simple protonation equilibrium of sulfite. The forward and reverse rate coefficients were fixed to sufficiently high values in such a way that the ratio of them gives the association constant pK = 6.30 of HSO_3^-.[24]

Step R2 is the equilibrium formation of the adduct $\cdot SO_3ClO_2^{2-}$. The rate constants of the forward and reverse reactions can be determined independently, but k_{-2} is in total correlation with k_3 and k_4 (see later). Since step R4 is a second-order process and k_4 correlates with k_{-2}, the diffusion control limit of the bimolecular step (R4) provides an upper limit for the value of k_{-2} found to be 6500 s^{-1}. Our calculations have also revealed that k_{-2} must have a lower limit that was found to be 350 s^{-1}, below which the importance of step R4 is gradually lost and therefore the average deviation between the measured and calculated absorbance would increase significantly. Therefore k_{-2} was fixed to a feasible 1300 s^{-1} value chosen from the following reason. Merényi and co-workers[14] determined the forward and reverse rate of the electron-transfer process from sulfite to chlorine dioxide in alkaline medium at constant $[ClO_2^-]_0$ = 1 M concentration. They have found 2.6×10^6 M^{-1} s^{-1} and 1300 M^{-1} s^{-1} values for the forward and reverse rate coefficients, respectively. Since the concentration of chlorite was not varied in their experiments, it cannot be distinguished unambiguously whether the reverse reaction is a second-order reaction between sulfite radical and chlorite or a simple first-order decomposition of the adduct $\cdot SO_3ClO_2^{2-}$. The adduct formation is preferred from the following reasons:

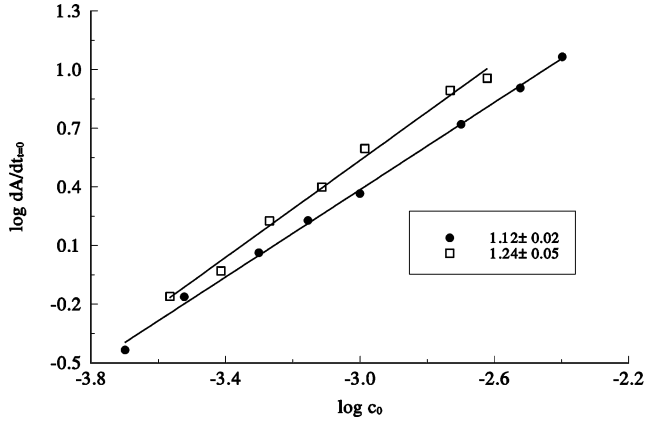


Figure 1. Dependence of the initial rate on the concentration of the reactants. $[S(IV)]_0$ (mM) = 0.7 and pH = 4.55 (□), $[\cdot ClO_2]_0$ (mM) = 2.50 and pH = 3.65 (●). Note furthermore that the latter curve is shifted by −0.1 along *Y*-axis to avoid overlapping of the curves.

- A weak adduct formation between a substrate and chlorine dioxide is generally accepted.[6,8,21,22]
- If single electron transfer occurs, it would yield appreciable amount of dithionate from the recombination of sulfite radical in sulfite excess at alkaline pH. The formation of dithionate, however, was clearly ruled out by Suzuki and Gordon.[12]
- Chlorite formation can easily be taken into account by the following equation that is likely to be hydroxide-catalyzed.

$$\cdot SO_3ClO_2^{2-} + \cdot ClO_2 + H_2O \rightarrow SO_4^{2-} + 2ClO_2^- + 2H^+ \qquad (10)$$

- Experiments carried out by Suzuki and Gordon[12] strongly support this reaction since not only the increase of k_b with increasing $[OH^-]$ can be explained with it, but also the lack of chlorate at higher pH.
- The kinetic orders of the reactants slightly higher than one can easily be taken into consideration by the second-order decomposition of the adduct.

We have calculated $(2.08 \pm 0.13) \times 10^6$ M^{-1} s^{-1} value for the forward rate coefficient, which is in reasonable agreement with the values found in the literature.[14,15]

Any efforts intended to include the direct electron-transfer process

$$SO_3^{2-} + \cdot ClO_2 \rightleftharpoons \cdot SO_3^- + ClO_2^- \qquad (11)$$

that must be augmented with the well-known[13] further oxidation of S(IV) by chlorite, i.e.

$$HSO_3^- + ClO_2^- \rightarrow SO_4^{2-} + HOCl$$

$$v = 5.5[HSO_3^-][ClO_2^-] + 6.26 \times 10^6[HSO_3^-][ClO_2^-][H^+] \quad (12)$$

have failed; we therefore concluded that direct electron transfer is unlikely to occur.

Step R3 is a formal oxygen transfer from chlorine dioxide to sulfite yielding sulfate and chlorine monoxide radical. This formal oxygen transfer process was already proposed by Suzuki and Gordon[12] since significant amount of chlorate was detected in their experiments at alkaline pH. If, however, either from a formal electron-transfer process or from a reversible adduct formation followed by eq 10 only chlorite was formed, there would be no other route for chlorate to form only the sulfite−chlorite reaction. In an alkaline solution, however, no reaction takes place between them, and in acidic solution, no chlorate could be detected among the end products of the reaction.[13] The rate coefficient of this step cannot be determined independently, because it is in complete correlation with the reverse rate constant of the adduct formation in Step R2. This ratio of k_3/k_{-2} was found to be 0.79 ± 0.13.

Step R4 is the second-order decay of the $\cdot SO_3ClO_2^{2-}$ adduct. This step is responsible for the kinetic order of the reactants slightly higher than 1. It is also a possible route for chlorate to form throughout the hydrolysis of Cl_2O_2 and gives back stoichiometry S1. Since k_4 correlates with k_{-2}, only the ratio of $k_4/(k_{-2})^2$ could be calculated, and it was found to be 84.6 ± 3.5 M^{-1} s. We have also tried to neglect the second-order decomposition of the adduct from the model without any success, the average deviation in case of the absolute fit increased dramatically from 0.0054 to 0.0389; thus, we concluded that the second-order decomposition is needed for the adequate fit.

Step R5 is the well-known hydrolysis of Cl_2O_2 into chloride and chlorate that is quite often involved in many of the reactions of chlorite and chlorine dioxide, and it is even central part of general model used to interpret the kinetic behavior of the chlorite-based oscillators.[25] Several other reactions of Cl_2O_2 were also considered to be inserted into the model. The most obvious

$$HSO_3^- + Cl_2O_2 + H_2O \rightarrow SO_4^{2-} + 2HOCl + H^+ \quad (13)$$

was found to be unnecessary to give adequate fit even if it was considered as a proton- or hydroxide-catalyzed path. All the efforts to implant any other reactions of Cl_2O_2 were unsuccessful.

Step R6 is one of the possible routes for $\cdot ClO$ to react. The absolute value of this rate coefficient cannot be determined independently since it is in complete correlation with that of Step R7. Therefore k_7 was fixed to a reasonable fast 10^9 M^{-1} s^{-1} value and k_8/k_7 was found to be $(5.53 \pm 0.41) \times 10^{-2}$. It is also clearly seen that addition of Steps R2, R3, R6, and R9 gives stoichiometry S2, while that of Steps R2, R3, R7, and R8 gives stoichiometry S1.

Step R8 is the well-known rapid oxidation of sulfite by hypochlorous acid. This rate coefficient was fixed to 7.6×10^8 M^{-1} s^{-1}, which was determined by Fogelman et al.[16]

Step R9 is the fast recombination of sulfite radical. The absolute value of this rate coefficient cannot be determined from our experiments; therefore, we fixed it to 3.1×10^8 M^{-1} s^{-1} that was determined by Fischer and Warneck.[26] A very similar value was given by Waygood and McElroy[27] in quite different experimental circumstances. Therefore, we have also tried to take the branching ratio[26] of the recombination into account.

TABLE 4: Fitted and Fixed Rate Coefficients Used in the Fitting Procedure[a]

parameter	value
k_1 (M^{-1} s^{-1})	1.995×10^{10}
k_{-1} (s^{-1})	10^4
k_2 (M^{-1} s^{-1})	$(2.08 \pm 0.13) \times 10^6$
k_{-2} (s^{-1})	1.3×10^3
k_3 (s^{-1})	$(1.02 \pm 0.18) \times 10^3$
k_4 (M^{-1} s^{-1})	$(1.43 \pm 0.58) \times 10^8$
k_5 (s^{-1})	10^2
k_6 (M^{-1} s^{-1})	10^9
k_7 (M^{-1} s^{-1})	$(5.53 \pm 0.41) \times 10^7$
k_8 (M^{-1} s^{-1})	7.6×10^8
k_9 (M^{-1} s^{-1})	3.1×10^8

[a] No error indicates that the value in question was fixed during the fitting procedure. Note that the actual calculations yielded k_3/k_{-2}, $k_4/(k_{-2})^2$ and k_7/k_6.

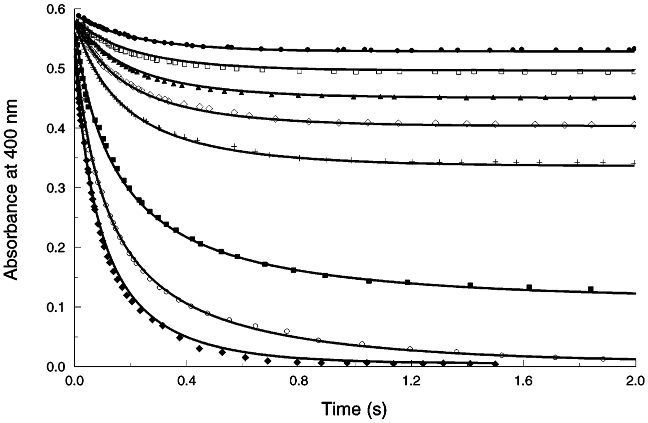


Figure 2. Measured (symbols) and calculated (solid lines) kinetic curves at pH = 3.65 and $[\cdot ClO_2]_0 \approx 0.00075$ M. $[S(IV)]_0$ (mM) = 0.2 (●), 0.3(□), 0.5(▲), 0.7(◇), 1.0(+), 2.0(■), 3.0(○), 4.0(◆).

The average deviation was increased to 0.0065 absorbance unit in case of absolute fit and 3.8% in case of relative fit. Inclusion of the branching ratio means that when the production of dithionate is decreased, so too is the consumed $S(IV)/\cdot ClO_2$ ratio. If, however, we include the following reaction

$$SO_3^{2-} + \cdot SO_3ClO_2^{2-} + 2H^+ \rightarrow S_2O_6^{2-} + \cdot ClO + H_2O \quad (14)$$

fitting its rate coefficient (k_{14}) at a fixed branching ratio value, almost the same average can be reached by adding a fixed and a fitted parameter to the final model (0.006 in case of absolute and 3.4% in case of relative fitting). Since the value of k_{14} is in total correlation with the value of the branching ratio, they cannot be determined independently. The final consequence of this fitting procedure is that if the branching ratio is included then an additional source of dithionate might also have to be taken into consideration (preferably eq 14) for an adequate fit.

Table 4 summarizes the fixed and fitted rate coefficients used in the fitting procedure. Figures 2−4 demonstrate that the model works pretty well. The average deviation between the measured and calculated data was found to be 0.0054 absorbance units in case of absolute fit and 3.2% in case of relative fit, which we believe is close to the experimentally achievable limit of error.

Conclusions

Despite the fact that formation of chlorate, chloride, chlorite (only in alkaline solution), sulfate, and dithionate might make the sulfite−chlorine dioxide reaction quite complex, the mechanism turned out to be very simple indeed, which can easily be

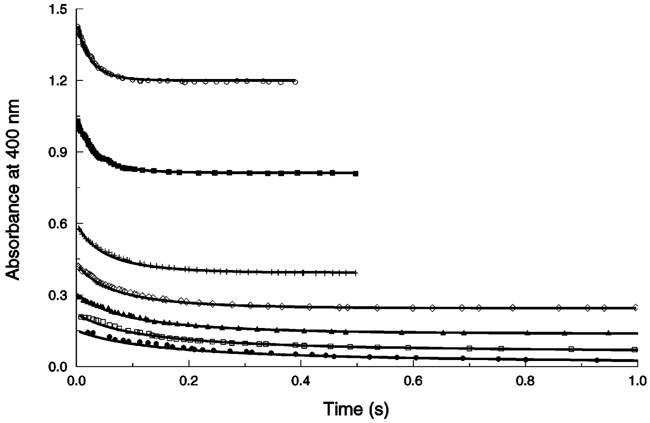


Figure 3. Measured (symbols) and calculated (solid lines) kinetic curves at pH = 4.25 and $[S(IV)]_0 = 0.0007$ M. $[\cdot ClO_2]_0$ (mM) = 0.27 (●), 0.395 (□), 0.55 (▲), 0.77 (◇), 1.07 (+), 1.89 (■), 2.63 (○).

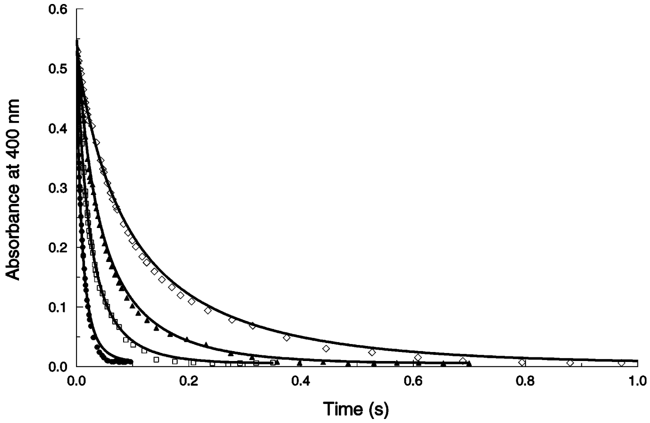
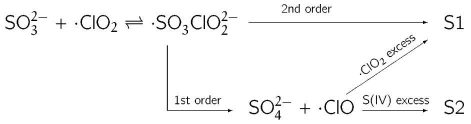


Figure 4. Measured (symbols) and calculated (solid lines) kinetic curves at $[S(IV)]_0 = 0.004$ M and $[\cdot ClO_2]_0 \approx 0.00105$ M. pH = 4.55 (●), 4.25 (□), 3.95 ▲), 3.65 (◇).

SCHEME 1



visualized by Scheme 1. Formation of an adduct $\cdot SO_3ClO_2^{2-}$ has been proposed to initiate the reaction. Further reactions of this adduct yield the final products throughout a mixed first- and second-order decomposition. The second-order decomposition of the intermediate uniquely leads to stoichiometry S1. The first-order decomposition leads to the reactive ·ClO species (formal oxygen transfer) of which further reactions with the reactants yield the branching stoichiometry. High excess of chlorine dioxide also leads to stoichiometry S1, while high excess of sulfite shifts the stoichiometry toward S2. In other words it means that S1 can be reached if either the excess of chlorine dioxide or the product of the concentration of the reactants is high; otherwise stoichiometry S3 rules. Direct electron transfer from sulfite to chlorine dioxide is not likely to happen because there would be no plausible explanation for the kinetic order slightly higher than 1 with respect to both reactants and for the OH^- dependence of k_b in alkaline solution far from the pK_a of HSO_3^-. Instead of direct electron transfer therefore, eq 10 is suggested that involves the possibility of the explanation of the observed characteristics of the kinetic curves. Unfortunately, the rate coefficient of this step cannot be estimated from the present experiments; it would require further extension of pH-dependence studies as well as changing the buffer components. Changing the buffer components, however, may establish the appearance of general hydroxide catalysis in this system, the phenomenon which was already mentioned by Suzuki and Gordon.[12]

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Supporting Information Available: Files containing the measured and calculated absorbances for all the 224 kinetic curves are available free of charge via Internet at http://pubs.acs.org.

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