Revisiting the Kinetics and Mechanism of the Tetrathionate−Hypochlorous Acid Reaction in Nearly Neutral Medium[†]

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The tetrathionate−hypochlorous acid reaction has been investigated in nearly neutral medium at $I = 0.5$ M ionic strength and $T = 25.0 \pm 0.1$ °C in dihydrogen-phosphate−hydrogen-phosphate buffer by UV−vis spectrophotometry. In excess of hypochlorous acid, the stoichiometry was found to be $S_4O_6^{2-} + 7HOCl + 3H_2O \rightarrow 4SO_4^{2-} + 7Cl^- + 13H^+$, but in excess of tetrathionate colloidal sulfur precipitates. On the basis of the simultaneous evaluation of the kinetic curves, a nine-step kinetic model with four fitted and five fixed rate coefficients is proposed. Analogous oxidation reactions of tetrathionate are also compared and discussed.

Introduction

The chlorite−thiosulfate reaction represents the lone non-BZ type reaction among the chlorite-driven chemical oscillators[1] that exhibits several nonlinear dynamical phenomena such as the appearance of complex periodic and aperiodic oscillations in CSTR,[2] extreme sensitivity to fluctuations in batch conditions,[3] and generation of front reaction in thin tubes.[4] Although these observations have been known for more than two decades, no accepted mechanism of the chlorite−thiosulfate reaction has been presented so far that is capable of even a qualitative explanation of the wide variety of dynamical behaviors mentioned above. It is, however, not surprising if one takes the particular complexity of the reaction into account. At least three long-lived intermediates are formed during the reaction, tetrathionate, hypochlorous acid, and chlorine dioxide, that can further react with not only the reactants but also each other making the reaction extremely complicated. The last two decades have witnessed the elucidation of the kinetics and mechanism of several subsystems of the parent reaction such as the hypochlorous acid−chlorite,[5,6] thiosulfate−chlorine dioxide,[7] tetrathionate−chlorine dioxide,[8] and tetrathionate−hypochlorous acid[9] systems. The latter study convincingly proved that a long-lived intermediate was formed in the tetrathionate−hypochlorous acid reaction in slightly alkaline medium. The surprising result of that paper was that the intermediate cannot be determined unambiguously in slightly alkaline medium based on the simultaneous evaluation of the kinetic curves. Half a century ago, Awtrey and Connick proposed that $S_2O_3I^-$ and its analogues $S_2O_3Cl^-$ should have a relatively long lifetime,[10] therefore $S_2O_3Cl^-$ was suggested to be the long-lived intermediate in the tetrathionate−hypochlorous acid reaction. Our recent paper, however, has shown that it is not necessary to assign a relatively long lifetime to $S_2O_3I^-$ in the iodine−tetrathionate reaction,[11] and a reasonable kinetic model was proposed to be capable of a sound explanation of the long-awaited question raised by Awtrey and Connick about the unexpected iodide dependence of the apparent rate coefficient; therefore, it may indirectly question $S_2O_3Cl^-$ to be the long-lived intermediate in the tetrathionate−hypochlorous reaction. Moreover, our recent paper has shown that though $S_2O_3Br^-$ plays a key role as an intermediate in the tetrathionate−bromine reaction responsible for the formation of pentathionate it cannot have a long lifetime.[12] Moreover, the latter reaction has the surprising characteristic that apparently partial reduction of tetrathionate occurs by the strong oxidizing agent bromine eventually resulting in a formation of colloidal sulfur at a longer time scale. These new results and the uncertainty of $S_2O_3Cl^-$ being a long-lived intermediate prompted us to reinvestigate the tetrathionate−hypochlorous acid reaction in a nearly neutral medium. This investigation was explicitly requested to understand the HOCl-catalyzed pathway of the chlorite−tetrathionate reaction more thoroughly.[13] Moreover, as mentioned before, this reaction also plays a significant role in determining the kinetics and mechanism of the chlorite−thiosulfate reaction, and therefore its mechanism is indispensable for the quantitative description of the parent reaction.

Experimental Section

Materials and Buffers. Hypochlorous acid stock solution was prepared as described elsewhere.[5] All the other chemicals were of the highest purity commercially available—potassium tetrathionate (Fluka), sodium chloride, sodium dihydrogen-phosphate, disodium hydrogen-phosphate (Reanal)—and were used without further purification. All the stock solutions were prepared from ion exchanged and four times distilled water. The concentration of the stock hypochlorous acid solution was checked by standard iodometric titration prior to each experiment.

Dihydrogen-phosphate−hydrogen-phosphate buffer was used to maintain the pH between 5.64 and 7.06 taking the pK_a of dihydrogen-phosphate as 6.59.[14] It raised a question about using constant ionic strength or constant total phosphate (sum of the concentration of the buffer components is constant) concentration. The constant ionic strength approach was used as Table 1 shows the composition of the buffers at different pHs resulting in a constant ionic strength adjusted to 0.5 M by the buffer components. The pK_a of hypochlorous acid was adopted as 7.36 determined previously.[9]

The kinetics and mechanism of the title reaction were studied at the following concentration ranges: $[S_4O_6^{2-}]_0 = 0.1-0.85$ mM,

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[†] This paper is dedicated to the memory of Dénes Varga who suddenly passed away during the preparation of this manuscript.

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TABLE 1: Composition of the Buffer Components at Different pHs

pH	$[H_2PO_4^-]_0$/M	$[HPO_4^{2-}]_0$/M
7.07	0.05	0.15
6.59	0.125	0.125
6.11	0.25	0.08333
5.89	0.3125	0.0625
5.64	0.375	0.04167

TABLE 2: Measured and Calculated Molar Absorbance[a]

wavelength (nm)	$\varepsilon_{S_4O_6^{2-}}$	ε_{HOCl}	ε_{OCl^-}	$\varepsilon_{HS(OH)}$	$\varepsilon_{HS(OH)}$[b]
260	555	42.2	106	623 ± 31	374 ± 14
265	417	33.6	152	469 ± 24	314 ± 11
270	309	28.4	205	353 ± 20	267 ± 10
275	226	26.1	256	262 ± 16	227 ± 8
280	162	25.6	300	189 ± 14	189 ± 7
285	114	25.8	334	126 ± 11	153 ± 5

[a] Molar absorbances are given in M^{-1} cm^{-1} unit. [b] These values were determined in the tetrathionate−bromine system.[12]

$T^0_{Cl(I)} = 0.88-8.2$ mM, $[Cl^-]_0 = 0-18.0$ mM, pH = 5.64, 5.89, 6.11, 6.59, and 7.06, where $T^0_{Cl(I)} = [HOCl]_0 + [OCl^-]_0$. Altogether, 102 kinetic runs at different initial concentrations were used for data evaluation. The exact compositions of all the kinetic runs are listed in the Supporting Information.

Methods and Instrumentation. The reaction was followed by a Zeiss S10 diode array spectrophotometer at 260−500 nm wavelength range. The kinetic measurements were carried out in a standard 1 cm quartz cuvette equipped with a Teflon cap and a magnetic stirrer. The buffer solution was delivered first, followed by the hypochlorous acid solution (also containing the corresponding buffer). Then the spectrum of this solution was recorded to determine the initial concentration of hypochlorous acid. Finally, the necessary amount of tetrathionate was introduced from a fast delivery pipet to start the reaction.

Data Treatment. The spectra of the reactants are highly overlapping, therefore no wavelength can be selected where any of the absorbing species have exclusive contribution to the measured absorbance. Thus, six different wavelengths (between 260 and 290 nm in every 5 nm) have been chosen for the evaluation procedure to characterize the reaction. Table 2 shows the molar absorbance of the reactants measured independently as well as that of the absorbing species calculated from the fitting procedure. The experimental curves were evaluated simultaneously by the ZiTa program package.[15] The sum of squares of the deviations between the measured and calculated absorbances was selected as the parameter to be minimized. Our quantitative criterion for an acceptable fit was that the average deviation for the absolute fit approached 0.005 absorbance unit, which is close to the uncertainty of the spectrophotometer. Since each kinetic curve contained at least 300 data pairs, the number of points in each run was reduced to 40−80 to avoid unnecessary time-consuming calculations. The essence of this method has already been described elsewhere.[16] Altogether more than 30 000 experimental points from 612 kinetic series (6 × 102 absorbance-time series) were used for the simultaneous evaluation.

In excess of tetrathionate, colloidal sulfur precipitation occurs. Since colloidal sulfur particles cannot be taken into consideration as a specific entity having a characteristic absorption spectrum, those parts of the kinetic curves were simply truncated where an absorbance increase could be observed at a higher wavelength (500 nm). Typically, it meant that the kinetic curves were cut off around 50−600 s depending on the initial concentration of the reactants (see later).

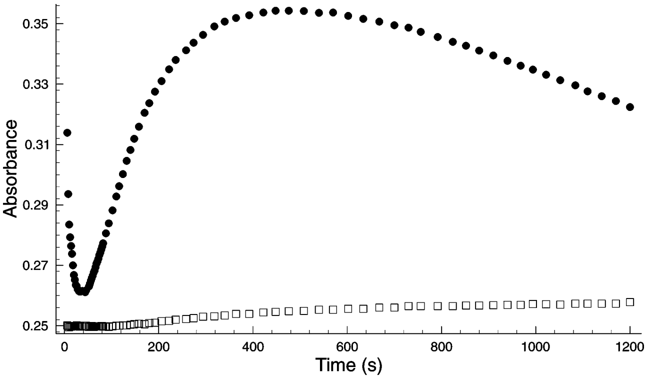

Figure 1. Measured absorbances at two different wavelengths at $[S_4O_6^{2-}]_0 = 0.85$ mM and $[Cl(I)]_0 = 2.9$ mM, pH = 5.64. Wavelength (nm) = 260 (●), 500 (☐). Note that the measured absorbances at 500 nm are shifted along the *y*-axis by 0.25 absorbance units to see the trends better.

Results

MRA Studies. To determine the number of absorbing species, matrix rank analysis (MRA) has been carried out[17] on only those parts of the absorbance−time series where no contribution to the absorption can be observed due to the light reflectance on the colloidal sulfur particles. These studies clearly revealed four absorbing species indicating that an extra absorbing species was formed beside the reactants in excess of tetrathionate. It should be emphasized again that this species must have a characteristic absorption (see later) and is probably responsible for the formation of colloidal sulfur at the later stages of the reaction. For the sake of completeness, matrix rank analysis has also been carried out on the absorbance−time series including the later phase of the reaction. It was found that at least six absorbing species are required for the quantitative description of the kinetic curves. However, one of the "absorbing" species has to be the colloidal sulfur, the species that cannot be taken into account as a special entity having constant molar absorbance as it coagulates. We therefore concluded that the later phase of the measured absorbance−time curves is not suitable for quantitative data analysis, and only qualitative considerations may be taken into account.

Characteristics of the Kinetic Curves. Tetrathionate is completely oxidized to sulfate in excess of hypochlorous acid as observed earlier.[9,18]

$$S_4O_6^{2-} + 7HOCl + 3H_2O \rightarrow 4SO_4^{2-} + 7Cl^- + 13H^+ \tag{1}$$

In excess of tetrathionate, however, an absorbing species is formed with a relatively long lifetime. Figure 1 shows the absorbance−time traces at two different wavelengths. As seen, the intermediate formed in the first stage of the reaction gradually disappears; meanwhile, an absorbance increase can be observed at longer wavelengths suggesting the formation of colloidal sulfur. Therefore, the light reflections on the colloid sulfur particles resulted in a significant contribution to the light absorption. It clearly suggests two important facts: on one hand, the light absorbing long-lived intermediate cannot be the elementary sulfur, and on the other hand, the later stages of the absorbance−time curves have to be eliminated from the evaluational procedure since the colloid sulfur particles cannot be taken into account as a special entity having constant molar absorbance. As a result, time points up to 50−600 s, depending

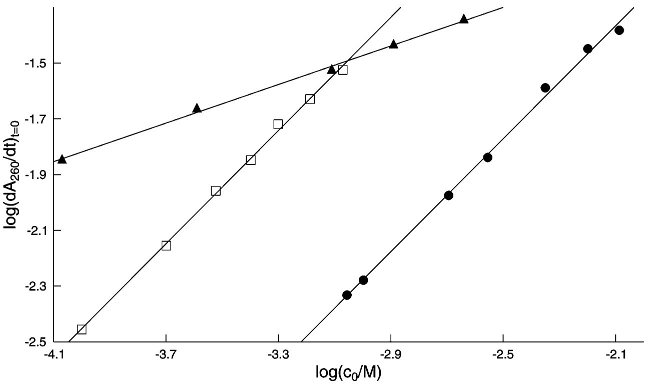

Figure 2. Calculated initial rates at 260 nm with changing tetrathionate (□) and $T_{Cl(I)}$ (●) concentration and pH (▲). Conditions are as follows: (□) $[Cl(I)]_0 = 2.8$ mM, pH = 7.07; (●) $[S_4O_6^{2-}]_0 = 0.4$ mM, pH = 7.07; (▲) $[Cl(I)]_0 = 2.9$ mM, $[S_4O_6^{2-}]_0 = 0.4$ mM. Note that the pH values are shifted along the *x*-axis by 3 units to see the trends better. The calculated slopes are 1.02 ± 0.02 (□), 1.01 ± 0.02 (●), and 0.35 ± 0.01 (▲), respectively.

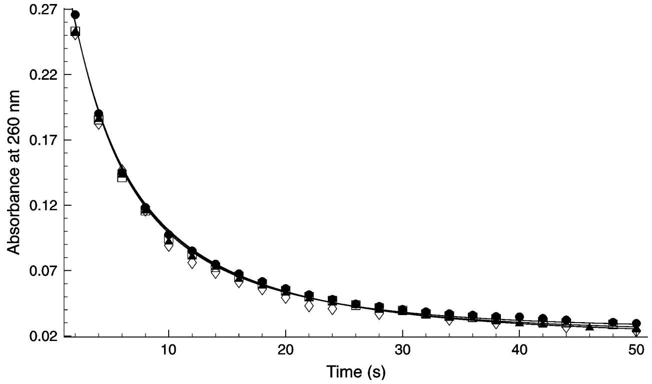

Figure 3. Measured (symbols) and calculated absorbances (solid lines) at different initial chloride concentrations. Conditions: pH = 5.64, $[S_4O_6^{2-}]_0 = 0.4$ mM, $T^0_{Cl(I)} = 2.9$ mM. $[Cl^-]_0$ (M) = 0.001 (●), 0.003 (□), 0.007 (▲), 0.01 (◇).

on the initial concentrations of the reactants, were used in the final evaluational procedure. Separate experiments showed that hydrogen-sulfide is also formed besides sulfate and elementary sulfur as an end product of the reaction in accordance with the analogous tetrathionate−bromine reaction.[12] It suggests that the underlying chemistry of the oxidation of the tetrathionate ion by an inorganic halogen-containing strong oxidizing agent must be similar.

Figure 2 shows the initial rate studies to determine the formal kinetic order of the reactants. As seen, the reaction is perfectly first order with respect to the reactants (i.e., tetrathionate and $T_{Cl(I)}$), but we found the formal kinetic order of the hydrogen ion to be significantly lower than unity, strongly suggesting the possibility of a complex kinetics. Figure 3 shows, however, that the chloride ion has negligible effect on the kinetics within the concentration range studied in contrast to other oxychlorine oxidation reactions, where the otherwise sluggish chloride ion acts as an efficient catalyst.[6,8,16]

Proposed Kinetic Model. As a starting point, to build up the kinetic model, we have chosen the following set of species that are very likely to participate in the reaction mechanism. This set consists of the reactants tetrathionate and hypochlorous acid as well as hypochlorite, the products sulfate, chloride, sulfur, and hydrogen sulfide, and finally the intermediates such as hydrogen-sulfite, pentathionate, $S_2O_3Cl^-$, $S_2O_3OH^-$, $S_4O_6Cl^-$, $S(OH)_2$, and HS(OH) and the species H^+, OH^-, and H_2O that are always present in aqueous medium. After that, all the possible mono- and bimolecular steps of these species were considered along with their H^+- and OH^--catalyzed pathways. During the fitting procedure, the steps whose rate coefficient became insensitive for the average deviation were omitted step by step. This method has been applied successfully in several cases of our previous work.[8,19] After long but straightforward systematic reduction, the following model has emerged.

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \tag{E1}$$

$$S_4O_6^{2-} + HOCl \rightleftharpoons S_4O_6Cl^- + OH^- \tag{R1}$$

$$S_4O_6Cl^- + H_2O \rightarrow S_2O_3Cl^- + S_2O_3OH^- + H^+ \tag{R2}$$

$$S_2O_3OH^- + HOCl + H_2O \rightarrow 2HSO_3^- + Cl^- + 2H^+ \tag{R3}$$

$$S_4O_6^{2-} + S_2O_3Cl^- + H_2O \rightarrow S_5O_6^{2-} + SO_4^{2-} + Cl^- + 2H^+ \tag{R4}$$

$$OCl^- + S_2O_3Cl^- + 2H_2O \rightarrow 2HSO_3^- + 2Cl^- + 2H^+ \tag{R5}$$

$$HSO_3^- + HOCl \rightarrow SO_4^{2-} + Cl^- + 2H^+ \tag{R6}$$

$$S_5O_6^{2-} + 4H_2O \rightarrow 2HS(OH) + 2SO_4^{2-} + H_2S + 2H^+ \tag{R7}$$

$$HS(OH) + HOCl \rightarrow S(OH)_2 + Cl^- + H^+ \tag{R8}$$

$$2S(OH)_2 \rightarrow HS(OH) + HSO_3^- + H^+ \tag{R9}$$

The rapid de- and reprotonation process E1 was taken into account with known equilibrium constant to follow the slight change in pH during the reaction. This acid dissociation equilibrium may be regarded as an auxiliary process necessary for the detailed calculation, but it is not a central part of the proposed model. Table 3 contains the fitted and fixed kinetic parameters used in the simultaneous evaluation of the kinetic curves at six different wavelengths. The average deviation was found to be 0.0043 absorbance unit indicating a sound description of the measured curves by the proposed model.

Discussion

Step R1 is a formal Cl^+ transfer from hypochlorous acid to one of the inner sulfur atoms of tetrathionate producing $S_4O_6Cl^-$ and hydroxide ion. This step is the analogy of the initiative step of the corresponding tetrathionate−iodine[11] and tetrathionate−bromine[12] reactions. We found that the rate coefficient of the forward reaction (k_{R1}) can be determined independently from our experiments, but the rate coefficient of the backward reaction is in total correlation with k_{R2}; therefore, only their ratio could be calculated. Only a lower limit of 10^9 M^{-1} s^{-1} can be given for k_{R-1}; any higher value would result in the same final average deviation. As seen, the rate of the back reaction is proportional to the concentra-

TABLE 3: Fitted and Fixed Rate Coefficients of the Proposed Kinetic Model[a]

step	rate equation	parameter	reference
R1	$k_{R1}[S_4O_6^{2-}][HOCl]$	101 ± 3 M^{-1} s^{-1}	this work
(R − 1)	$k_{R-1}[S_4O_6Cl^-][OH^-]$	10^9 M^{-1} s^{-1}	this work
R2	$k_{R2}[S_4O_6Cl^-]$	54.6 ± 1.2 s^{-1}	this work
R3	$k_{R3}[S_2O_3OH^-][HOCl]$	≥ 6000 M^{-1} s^{-1}	this work
R4	$k_{R4}[S_4O_6^{2-}][S_2O_3Cl^-]$	≥ 5000 M^{-1} s^{-1}	this work
R5	$k_{R5}[OCl^-][S_2O_3Cl^-]$	$(5.26 \pm 0.48) \times 10^4$ M^{-1} s^{-1}	this work
R6	$k_{R6}[HSO_3^-][HOCl]$	7.6×10^8 M^{-1} s^{-1}	ref 21
R7	$(k_{R7} + k_{R7}'[OH^-])[S_5O_6^{2-}]$	0.0132 s^{-1}, 1.92×10^9 M^{-1} s^{-1}	ref 12
R8	$k_{R8}[HS(OH)][HOCl][H^+]$	$(1.47 \pm 0.11) \times 10^8$ M^{-2} s^{-1}	this work
R9	$k_{R9}[S(OH)_2]^2$	≥ 1000 M^{-1} s^{-1}	this work

[a] Note that only the ratios of k_{R2}/k_{R-1} and k_{R5}/k_{R4} can be determined from our experiments.

tion of the hydroxide ion resulting in a slight pH-dependence of the reaction at a certain pH range where the rate of step R2 and the backward reaction of step R1 are comparable. Once the pH decreases, this effect becomes negligible meaning that pH affects the overall reaction throughout the retardation effect of the hydroxide ion on step R1 as well as the greater reactivity of hypochlorous acid than the hypochlorite ion toward tetrathionate. Furthermore, the value of k_{R1} determined here ($k_{R1} = 101 \pm 3$ M^{-1} s^{-1}) is in reasonably good agreement with the value (32.4 M^{-1} s^{-1}) obtained previously[10] at different experimental conditions.

Step R2 is the hydrolysis of $S_4O_6Cl^-$ into $S_2O_3Cl^-$ and $S_2O_3OH^-$ that probably proceeds via the splitting of the inner S−S bond of the adduct. The possible structures of these molecules were already predicted in our previous paper[9] as O_3SSCl^- and O_3SSOH^-, respectively; however, calculation of the relative energies of several different isomers of $S_2O_3OH^-$ by different theoretical calculation methods indicated that it is difficult to decide which of these isomers is the most stable one.[20] As shown before, the rate coefficient k_{R2} cannot be determined individually, and only the ratio of k_{R2}/k_{R-1} can be calculated from our experiments. We have found this ratio to be $(5.46 \pm 0.12) \times 10^{-8}$ M.

Step R3 is a fast oxidation of $S_2O_3OH^-$ by hypochlorous acid leading to hydrogen-sulfite. Although k_{R3} cannot be determined directly from our experiments, a lower limit could be given as $k_{R3} \geq 6000$ M^{-1} s^{-1}. This step is responsible for the fast removal of $S_2O_3OH^-$ keeping its concentration low enough to have any significant contribution to the measured absorbances. It should also be noted that step R4 can readily be substituted with

$$S_2O_3OH^- + OCl^- + H_2O \rightarrow 2HSO_3^- + Cl^- + H^+ \tag{2}$$

reaction having a rate coefficient k_2 higher than 2×10^5 M^{-1} s^{-1}. Therefore, we concluded that the calculation process requires only the fast oxidation of $S_2O_3OH^-$ by either hypochlorous acid or hypochlorite ion. Since at our experimental condition HOCl is the predominant form of Cl(I) and HOCl is usually more reactive toward sulfur-containing oxyanions, we rather tend to include the oxidation of $S_2O_3OH^-$ by hypochlorous acid in the proposed kinetic model.

Step R4 is responsible for the formation of the short-lived intermediate pentathionate that was already proposed previously.[9] In that work at alkaline solution, however, we were not able to calculate the rate coefficient of this reaction. At nearly neutral solution, we found that the rate coefficient of this reaction (k_{R4}) is in total correlation with k_{R5}, and therefore only their ratio could be calculated. Nevertheless, based upon our calculation process we could set up a lower limit of 5000 M^{-1} s^{-1} for k_{R4} above which the same average deviation is obtained between the measured and calculated data.

Step R5 is the oxidation of $S_2O_3Cl^-$ by the hypochlorite ion leading to hydrogen-sulfite and chloride ions. As mentioned above, the exact value of the rate coefficient k_{R5} cannot be determined, and only the ratio of k_{R5}/k_{R4} could be calculated from our experiments. We found this ratio to be (10.5 ± 0.10). One might argue that this process can also be substituted with the following reaction

$$HOCl + S_2O_3Cl^- + 2H_2O \rightarrow 2HSO_3^- + 2Cl^- + 3H^+ \tag{3}$$

but our calculation process has revealed that including eq 3 instead of step R5 leads to 0.0064 average deviation. Although in itself this average deviation may also be regarded as acceptable, the systematic deviation encountered between the measured and calculated data at higher pHs along with the increase in the average deviation suggests that step R5 is rather involved in the proposed model than eq 3.

Step R6 is the well-known rapid oxidation of hydrogen-sulfite by hypochlorous acid. The rate coefficient of this reaction was determined[21] previously to be 7.6×10^8 M^{-1} s^{-1}, and therefore we fixed this value during the calculation process.

Step R7 is the well-known degradation of pentathionate. Of course k_{R7} and k_{R7}' cannot be calculated from our experiments, and these values were directly taken from our previous work as fixed parameters.[12] As seen, k_{R7}' in itself is enough to provide that pentathionate can only be a short-lived intermediate at our experimental circumstances, thus k_{R7} is kept in the proposed model for the sake of completeness. It also means that steps R4 and R7 can be replaced by the following equation not involving pentathionate as a short-lived intermediate in the kinetic model without any change in the average deviation

$$S_4O_6^{2-} + S_2O_3Cl^- + 5H_2O \rightarrow 3SO_4^{2-} + 2HS(OH) + H_2S + Cl^- + 4H^+ \tag{4}$$

On one hand, this reaction looks unnecessarily complicated, and it is difficult to compare the proposed kinetic model with that of the analogous tetrathionate−bromine system. Therefore, we are inclined to keep steps R4 and R7 in the final model.

Step R8, the oxidation of HS(OH) by hypochlorous acid, has not been proposed yet. This prevents the concentration of HS(OH) to build up as long as HOCl is present in the solution. The rate coefficient (k_{R8}) can readily be determined from our experiments as $(1.47 \pm 0.11) \times 10^8$ M^{-2} s^{-1}. The necessity of

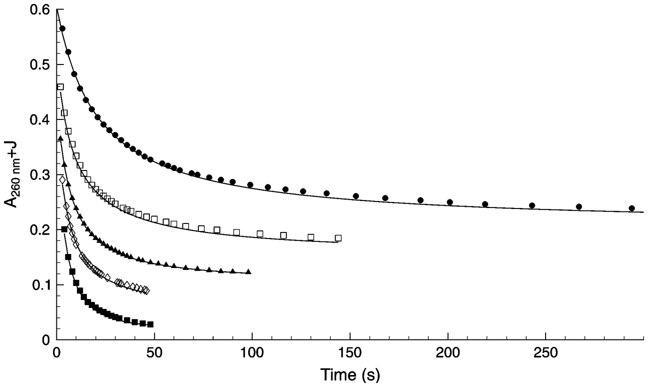

Figure 4. Measured (symbols) and calculated absorbances (solid lines) at pHs. Conditions: $[S_4O_6^{2-}]_0 = 0.4$ mM, $T^0_{Cl(I)} = 2.9$ mM. pH = 7.07 (●), 6.59 (□), 6.11 (▲), 5.89 (◇), 5.64 (■). Note that the curves are shifted by $J = 0.2$ (●), 0.15 (□), 0.1 (▲), 0.05 (◇), and 0.0 (■) absorbance units to see the trend better, respectively.

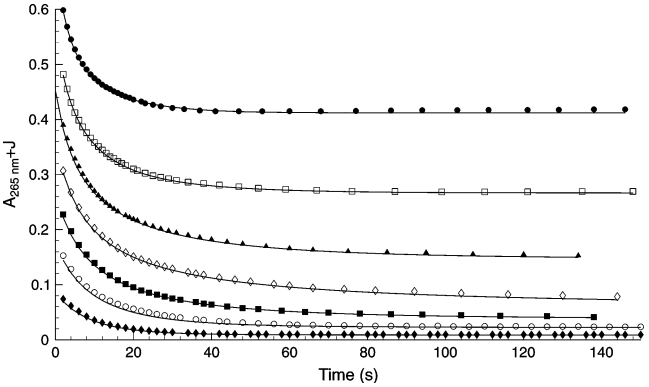

Figure 5. Measured (symbols) and calculated absorbances (solid lines) at different tetrathionate concentrations. Conditions: pH = 6.59, $T^0_{Cl(I)} = 2.8$ mM. $[S_4O_6^{2-}]_0$ (mM) = 0.85 (●), 0.65 (□), 0.5 (▲), 0.4 (◇), 0.3 (■), 0.2 (○), 0.1 (◆). Note that the curves are shifted by $J = 0.2$ (●), 0.15 (□), 0.1 (▲), 0.05 (◇), 0.0 (■), −0.05 (○), and −0.1 (◆) absorbance units to see the trend better, respectively.

the hydrogen dependence of this step was also checked, and it was found that the average deviation increases to 0.0058 absorbance units if this step is independent of pH. It may as well indicate that the fit is acceptable, but careful inspection of the fitted curves showed that the majority of this increase belongs to the kinetic curves measured at larger tetrathionate excess resulting in a systematic error between the measured and calculated kinetic curves. Therefore, it is thought that the role of step R8 is firmly established in the proposed kinetic model. It is also interesting to compare the molar absorbances of HS(OH) determined here with the previously calculated ones in the analogous tetrathionate−bromine system.[12] As seen in Table 2, there is a considerable difference between them. Presently, we are unable to give a proper explanation for this deviation. However, it seems to be quite possible that HS(OH) may be involved in a protonation equilibrium. This possibility along with the fact of the quite different experimental conditions in pH used here (nearly neutral) and at the tetrathionate−bromine system (strong acidic) might explain that the difference stems from the spectral difference of the protonated and the deprotonated form of HS(OH). Careful inspection of the calculated molar absorbance data reveals that if this assumption is valid then the protonated and the deprotonated form of HS(OH) should have an isosbestic point at 280 nm indicated by the calculations. Further investigations are in need to clarify this effect.

Step R9 is a fast process and was already proposed by Wagner and Schreier.[22] Its rate coefficient cannot be calculated from our measurements. We could set only a lower limit for k_{R9} to be 1000 M^{-1} s^{-1} not to accumulate $S(OH)_2$ in a significant amount. Any value higher than that will lead to the same final results.

Figures 4−6 show a set of the measured and fitted kinetic data of representative absorbance−time series with varying the initial concentration of the reactants. They clearly indicate that the proposed model is capable of providing a good description of the kinetic data. The Supporting Information contains all the measured and calculated absorbance−time curves at 280 nm.

Conclusion

The kinetics and the mechanism of the tetrathionate−hypochlorous acid have been investigated in nearly neutral media. The former suggestion is that eventually elementary sulfur precipitates in excess of tetrathionate and the role of $S_2O_3Cl^-$ have been reinforced, but the sulfur precipitation is now explained through the formation of the short-lived intermediate pentathionate followed by its disproportionation, not the direct hydrolytic decomposition of $S_2O_3Cl^-$ suggested earlier.[9] The results presented here are in complete harmony with the other oxidation reactions of tetrathionate with iodine and bromine. As seen, all these reactions start with the attack of the oxidizing agent to the inner sulfur atoms of tetrathionate followed by the bond cleavage. In other words, the initiating equilibrium in all these cases is a formal X^+ transfer from the oxidizing agent to one of the inner sulfurs of tetrathionate. Depending on the oxidizing agent in the case of X_2 and HOX, respectively, either a halide ion or a hydroxide ion is also involved in this equilibrium resulting in a retarding effect of this species on the overall reaction rate. This effect, however, strongly depends on the reactivity of this ion.

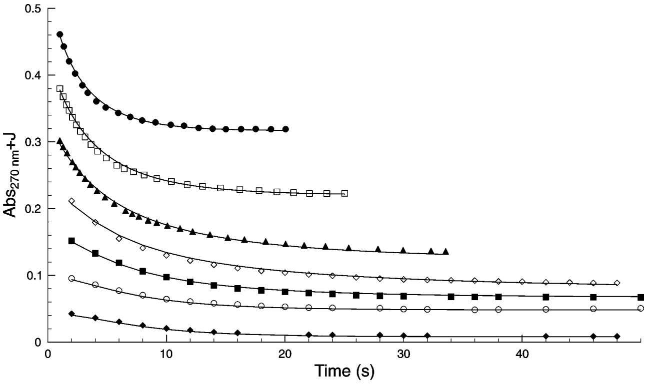

Figure 6. Measured (symbols) and calculated absorbances (solid lines) at different Cl(I) concentrations. Conditions: pH = 6.11, $[S_4O_6^{2-}]_0 = 0.4$ mM. $T^0_{Cl(I)}$ (mM) = 6.15 (●), 4.73 (□), 3.26 (▲), 2.11 (◇), 1.48 (■), 0.88 (○), 0.64 (◆). Note that the curves are shifted by $J = 0.2$ (●), 0.15 (□), 0.1 (▲), 0.05 (◇), 0.0 (□), −0.05 (○), and −0.1 (◆) absorbance units to see the trend better, respectively.

It should also be mentioned that the roles of $S_2O_3Cl^-$ and $S_2O_3OH^-$ can be completely commutable. If we replace step R3 by the oxidation of $S_2O_3Cl^-$ by hypochlorous acid (see: eq 3), which also involves replacement of steps R4 and R5 by the corresponding equations

$$S_4O_6^{2-} + S_2O_3OH^- \rightarrow S_5O_6^{2-} + SO_4^{2-} + H^+ \qquad (5)$$

and

$$OCl^- + S_2O_3OH^- + H_2O \rightarrow 2HSO_3^- + Cl^- + H^+ \quad (6)$$

then exactly the same results can be calculated with the same parameters and the average deviation. At this point, we are unable to distinguish between these mathematically equivalent possibilities.

It should also be emphasized, however, that the present model works up to the time point of the appearance of precipitation, and it is still unable to predict the slower phase of the reaction, where elementary sulfur precipitates possibly from HS(OH). Since colloidal sulfur cannot be taken into account as a special entity having constant molar absorbance during the coagulation process, it is not expected to evaluate this part of the kinetic curves by a simultaneous evaluation procedure.

Finally, it is strongly hoped that the refinement of the kinetic model of the tetrathionate−hypochlorous acid reaction may also contribute to the elucidation of kinetics and mechanism of the fascinating chlorite−thiosulfate reaction as well as to the deeper understanding of the nature of spatiotemporal structures arising in the chlorite−tetrathionate reaction in which the title reaction may also play a central role.

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Supporting Information Available: Table containing the conditions of each kinetic run and figures containing the measured and fitted data. This material is available free of charge via the Internet at http://pubs.acs.org.

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