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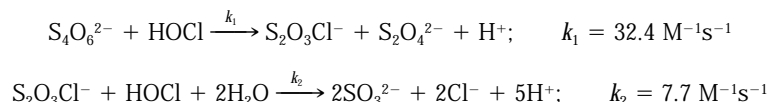**86** PUBLICATIONS **1,453** CITATIONS

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Kinetics and Mechanism of the Reaction between Hypochlorous Acid and Tetrathionate Ion

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ABSTRACT: The reaction has been studied spectrophotometrically monitoring the absorbance in the 240–400 nm wavelength range. The spectra of the reactants, intermediates, and products in this system are overlapping; thus special programs [1,2] have been used (and tested) to unravel the kinetics and mechanism of the reaction. The stoichiometry of the reaction in excess hypochlorous acid is $S_4O_6^{2-} + 7HOCl + 3H_2O \rightarrow 4SO_4^{2-} + 7Cl^- + 13H^+$. Various experiments are presented to show that—in excess tetrathionate—the reaction produces a light-absorbing intermediate identified as $S_2O_3Cl^-$. The intermediate slowly hydrolyzes into sulfur and sulfate and it yields pentathionate in excess tetrathionate. The rate-determining steps and their rate constants are

$$S_4O_6^{2-} + HOCl \xrightarrow{k_1} S_2O_3Cl^- + S_2O_4^{2-} + H^+; \qquad k_1 = 32.4 \ M^{-1}s^{-1}$$

$$S_2O_3Cl^- + HOCl + 2H_2O \xrightarrow{k_2} 2SO_3^{2-} + 2Cl^- + 5H^+; \qquad k_2 = 7.7 \ M^{-1}s^{-1}$$

The further oxidation of $S_2O_4^{2-}$ and SO_3^{2-} by HOCl to sulfate are fast processes. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 395–402, 2000

INTRODUCTION

Chlorite–thiosulfate reaction exhibits the most exotic dynamical behaviour found among the chlorite-driven chemical oscillators [3]. A mechanism has been proposed to interpret extreme sensitivity to stirring rate and the apparent role of internal fluctuations in determining the course of the reaction [4]. The explanation of exotic dynamical feature requires the detailed knowledge of all the conceivable subsystems of chlorite–thiosulfate reaction. A reasonable mechanism has been proposed for the reaction between hypochlorous acid and chlorite ion [5]. A tentative model, explaining the formal ten-order rate equation has been suggested for the tetrathionate–chlorite system [6]. Hypochlorous acid is one of the possible intermediates of the chlorite–thiosulfate and tetrathionate–chlorite systems. Therefore, in order to unravel the mechanistic details of the chlorite–thiosulfate reaction, we have investigated the kinetics of the tetrathionate–hypochlorous acid reaction.

The overlapping spectra of the reactants in the near

UV range prevented the precise examination of the kinetics of this reaction so far. Peintler et al. [1] have recently developed a computational technique (matrix rank analysis (MRA) and calculation of the residual curves) for evaluation of the spectrophotometric measurements when direct concentration determination of the reactants and/or the products is not possible. The new method provides the number of the independent absorbing species. Besides, it gives valuable information on the intermediate without assuming any chemical model!

Finally, by combining MRA with supplementary experimental information and with rigorous fitting of the primary measured experimental data, a probable model may be obtained both mathematically and chemically. This procedure will also be illustrated through the evaluation of the tetrathionate–hypochlorous acid reaction. The kinetics of the system has not yet been studied.

EXPERIMENTAL SECTION

Materials

All chemicals were the highest purity commercially available and were used without further purification. The purity of potassium-tetrathionate was checked by standard bromatometric titration and found to be better than 99.5%. HOCl solution was prepared as described [7] earlier. The concentration of the HOCl was checked by iodometric titration each day, and the solution was stored in the dark at 5°C. The chloride contamination of the stock solution was checked by 0.5 M silver-nitrate solution. The stock solutions were not used for over a week. All solutions were prepared by using deionized distilled water prepared by the Milli-Q water purification system. The stock solutions were freshly prepared for each series of experiments.

Buffers

The equilibrium measurements were carried out between the pH range of 5.9–7.6, adjusted by $H_2PO_4^-$/HPO_4^{2-} buffer. The ionic strength was kept at 1.0 M by $NaClO_4$, and the solutions were thermostatted at 25.0 $\pm$ 0.3°C. A mixed buffer, $H_2PO_4^-$/HPO_4^{2-}/HCO_3^-/CO_3^{2-}, was used to maintain the pH between 8.2 and 9.0 to ensure sufficient buffer capacity to compensate the proton formation during the reaction (see Eq. (1) later). The reason for the pH increase in the case of kinetic measurements was to slow the reaction down so that it could be followed by a commercial diode-array spectrophotometer.

Methods and Instrumentation

Fourteen different samples were prepared to study the stoichiometry of the reaction at different concentration ratios and at different pH values. After 24 hours, the reacted samples were analyzed by standard analytical procedures, which included iodometry and spectrophotometry.

Solutions for equilibrium measurements were prepared in a 10-mm quartz cuvette equipped with a teflon cap and magnetic stirrer. The buffer solution was introduced first, then the HOCl stock solution, from a fast-delivery pipette under continuous stirring. The mean of the 10 recorded spectra on a Zeiss S10 diode-array spectrophotometer was used for evaluation. The spectra were recorded at nine different pH values. The concentration of hypochlorous acid was determined independently by standard iodometry.

Solutions for the kinetic runs were prepared in the same quartz cuvette. After the buffer solution, the tetrathionate stock solution and finally the hypochlorous acid stock solution were introduced under continuous stirring. The reaction was monitored for up to 6000 seconds. Altogether, 137 kinetic runs were executed within the pH-range 8.20–9.00 in the interval of 0.065–0.66 mM for $[S_4O_6^{2-}]_0$ and in the interval of 0.845–3.17 mM for $[HOCl]_0$.

DATA TREATMENT

The experimental data measured up to 1.4 absorbance units only have been used for the evaluation of the equilibria and kinetic runs because the relative error of absorbance measurements significantly increases above this limit. The protonation constant of hypochlorite ion was calculated by PSEQUAD [8] at a 240–360 nm wavelength range.

The evaluation of kinetic runs started with the matrix rank analysis (MRA) on the absorbance–time data series to determine the number of absorbing species. First of all, the MRA and the residual analysis [1] were executed on each kinetic run separately. Then, handling together all the kinetic experiments in one matrix at different initial concentrations and pH (each run contains 47–50 time points on nine selected wavelengths), MRA was also carried out. The basis of wavelength selection will be explained later.

The kinetic experiments were analyzed by the recently developed program package ZiTa [2]. Altogether, 55,116 experimental points of 137 absorbance–time series on nine different wavelengths were used for the fitting. Two criteria were applied to select between the different models: the minimum number

of the fitting parameter and a qualitative agreement with the most important characteristics of the experimental curves.

RESULTS

pK Calculations and the Spectra

The evaluation of kinetic measurements requires exact pK_a of the hypochlorous acid at the given experimental conditions and the molar absorbances of OCl^- and HOCl at the 240–360 nm wavelength range. The recorded spectra of HOCl solutions at different pHs are seen in Figure 1.

The molar absorbances of HOCl and OCl^- calculated by PSEQUAD can be seen in Figure 2, together with the spectrum of $S_4O_6^{2-}$ and the intermediate (see later). The average deviation between the measured and calculated spectra is 0.0026 absorbance unit, and $pK_a = 7.36 \pm 0.01$ was given by the program. The pK_a and the molar absorbances are in good agreement with the data of Adam et al. [9], taking into account the different experimental conditions.

Stoichiometry

In excess hypochlorous acid the stoichiometry can be described by the following simple equation:

$$S_4O_6^{2-} + 7HOCl + 3H_2O \longrightarrow$$
$$4SO_4^{2-} + 7Cl^- + 13H^+ \quad (1)$$
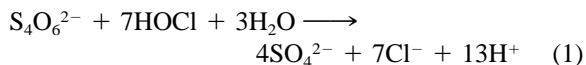
as the spectra of the reacted samples completely agreed with the spectra of HOCl and OCl^- calculated from equation (1) and the pH. The measurements in
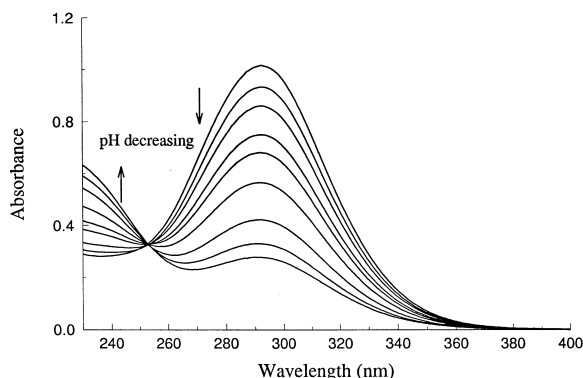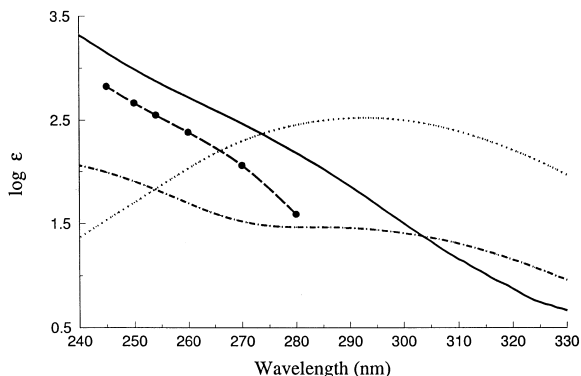
Figure 2 Spectra of $S_4O_6^{2-}$ (solid line), HOCl (dot-dashed line), and OCl^- (dotted line) and the fitted molar absorbances of the intermediate (●) at the six wavelengths.

excess tetrathionate, however, unambiguously indicated that another absorbing species had to be taken into account since the spectra of reacted samples were significantly different from the spectra of the remaining concentration of tetrathionate calculated.

MRA Studies

It is obvious that at least three absorbing species exist, namely, $S_4O_6^{2-}$, HOCl, OCl^-. At constant pH, however, the last two are indistinguishable for MRA because of the constant $[HOCl]/[OCl^-]$ ratio, which has to satisfy the equilibrium constant. Therefore, a simple MRA study on an absorbance matrix at given pH and initial tetrathionate and hypochlorous acid concentration should lead to two absorbing species if there is/are no accumulated intermediate(s) in detectable absorbance contribution(s). At first sight, no characteristic feature can be found on the primary measured absorbance surface, which would suggest more than two absorbing species (see Fig. 3).

In spite of that, in almost half (62 out of 137) of the kinetic curves, a third non-zero element of the diagonal appears with greater than 0.01 absolute value. Since the error of the absorbance measurements with Zeiss S10 is definitely less than 0.01 absorbance unit, this deviation clearly indicates the formation of a third absorbing species. The results of MRA analysis of each reaction surface were completed by handling together all the measured kinetic curves at different initial concentration of reagents and pH but only at nine selected wavelengths. The result unambiguously confirmed that all the 55,116 experimental points cannot be described by three but can be described by four absorbing species. The method of the wavelength selection involved 245 and 292 nms, where the $S_4O_6^{2-}$ and OCl^- have absorption maxima in the

Figure 1 The recorded spectra of the hypochlorous acid solution at different pHs. The pH of the solutions were the following: 5.85; 6.09; 6.45; 6.67; 6.91; 7.09; 7.32; 7.53; 7.68. $[HOCl]_0 = 4.646 \times 10^{-3}$ M.

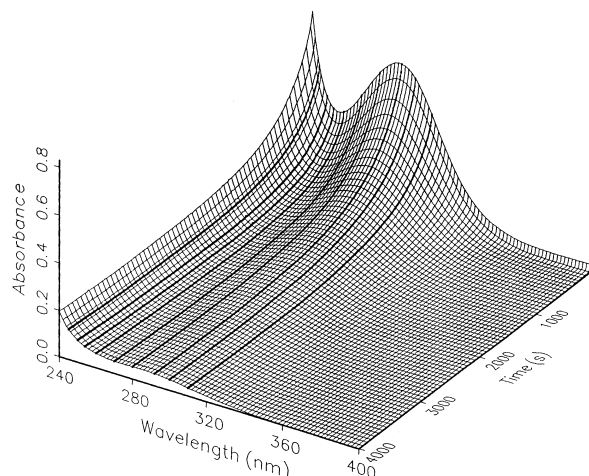**Figure 3**   Typical absorbance surface in the reaction between tetrathionate and hypochlorous acid. $[S_4O_6^{2-}]_0 = 3.5 \times 10^{-4}$ M, $[HOCl]_0 = 2.21 \times 10^{-3}$ M, pH = 8.60. The fitting procedure was executed on the boldface printed wavelengths.

245–400 nm range, respectively, and the isobestic point of the hypochlorite–hypochlorous acid system at 254 nm (see Fig. 1). The 245–310 nm range was divided almost uniformly. Nine different wavelengths were selected altogether: 245, 250, 254, 260, 270, 280, 292, 300, and 310 nms.

The residual absorbance of the third and fourth absorbing species for each individual kinetic run (137) was also calculated. The results are seen in Figure 4a
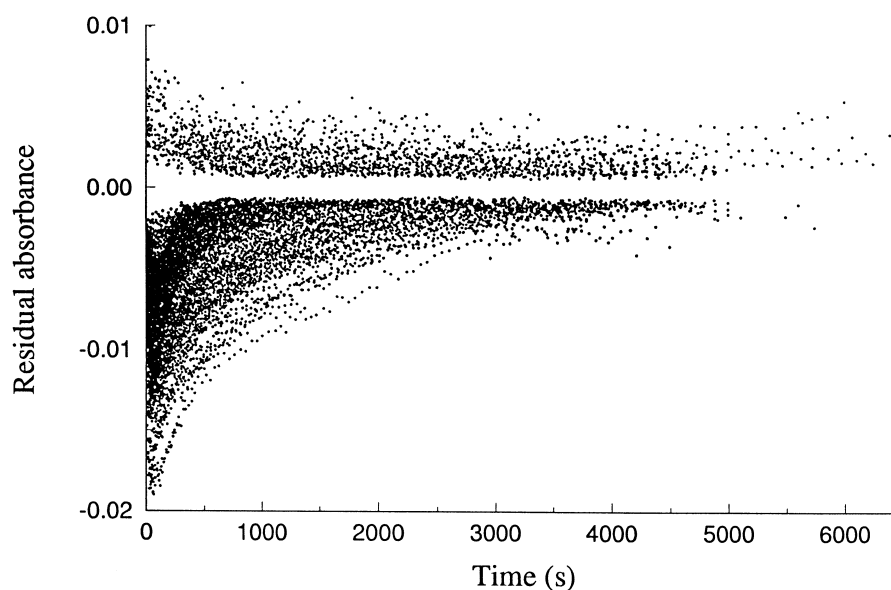
and 4b. It is seen in these figures that the kinetic curves can only be described within experimental error with three absorbing species. The OCl^- and HOCl are indistinguishable in the case of individual evaluation; therefore, the third species may only be an intermediate.

Formal Kinetics

Our first attempt to evaluate the kinetic experiments was based upon the simple stoichiometric equation (1) and the following rate law:

$$v_1 = \frac{d[S_4O_6^{2-}]}{dt} = \frac{1}{7}\frac{d[HOCl]}{dt}$$
$$= -k[S_4O_6^{2-}][HOCl] \quad (2)$$

The standard deviation was found to be 0.0141, much higher than acceptable. The presence of the intermediate was formally interpreted as follows. An unknown intermediate with an average oxidation state (x) was supposed, where x changes from 3 to 5.5 in steps of 0.5. In other words, we divide the basic stoichiometric equation into two consecutive reactions. In the first process 1 mole $S_4O_6^{2-}$ consumes ($2x - 5$) mole HOCl during formation of a long-lived intermediate, in which the average oxidation number of sulfur is x. In the second reaction, this intermediate consumes the rest of HOCl ($3 - 0.5x$) to give the $1:7$ $[S_4O_6^{2-}]/$ $[HOCl]$ ratio. So the calculations were carried out by the following stoichiometric equations and rate laws:
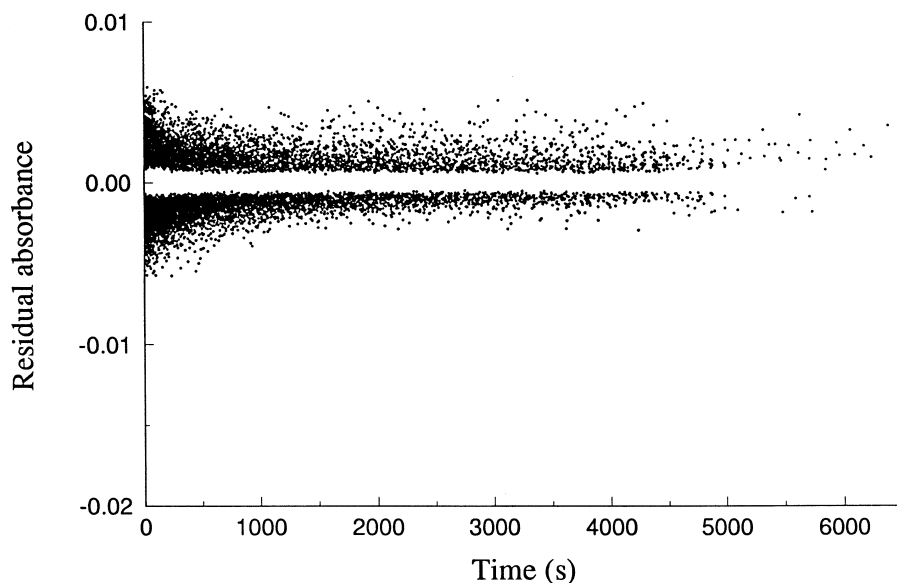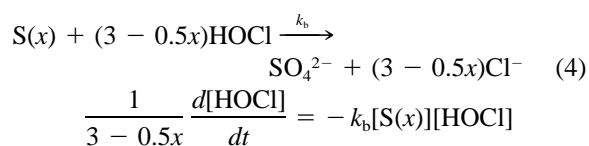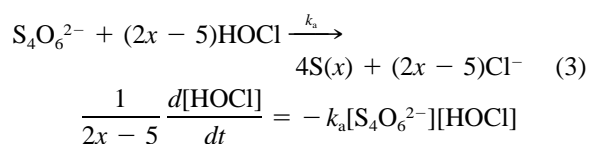

Figure 4a   Residual curves of the third absorbing species at each kinetic run (137).

Figure 4b   Residual curves of the fourth absorbing species at each kinetic run (137).

$$S_4O_6{}^{2-} + (2x - 5)\text{HOCl} \xrightarrow{k_a}$$
$$4S(x) + (2x - 5)\text{Cl}^- \quad (3)$$
$$\frac{1}{2x - 5}\frac{d[\text{HOCl}]}{dt} = -k_a[S_4O_6{}^{2-}][\text{HOCl}]$$

$$S(x) + (3 - 0.5x)\text{HOCl} \xrightarrow{k_b}$$
$$SO_4{}^{2-} + (3 - 0.5x)\text{Cl}^- \quad (4)$$
$$\frac{1}{3 - 0.5x}\frac{d[\text{HOCl}]}{dt} = -k_b[S(x)][\text{HOCl}]$$

Note that the arrangement of the stoichiometric equations is incomplete since the composition of the intermediate is unknown. It may contain an arbitrary number of oxygens with -2, Cl with -1, and H with $+1$ oxidation number. Only two kinetic parameters (k_a, k_b) and the molar absorbance of $S(x)$ in the selected wavelengths were necessary in the fitting procedure. These calculations showed that the intermediate does not absorb light significantly over 280 nm. Therefore, its molar absorbances were taken into consideration as zero over this wavelength. The surprising result of this evaluation was that this huge experimental data set can be described by two kinetic parameters and six molar absorbances of the intermediate. The oxidation number of sulfur in the intermediate, however, cannot be decided unambiguously, since the fitting parameters in the case of $x = 4, 4.5, 5, 5.5$ are 0.0063, 0.0054, 0.0050, and 0.0052, respectively. The calculated spectra of the intermediate, of course, significantly differ

in the four different fitting procedures, but none of them was similar to the spectra of sulfur chlorides or to the sulfur-oxygen containing anions.

These calculations clearly indicate that any of the appropriately selected intermediates leads to almost the same average absorbance deviation! So it should be emphasized that the rigorous fitting procedure in itself is not worth much without sufficient additional experimental information.

Identification of the Intermediate

A number of well-established analytical procedures [10] have been carried out to identify the intermediate. On the basis of these experiments, the intermediate is characterized as follows:
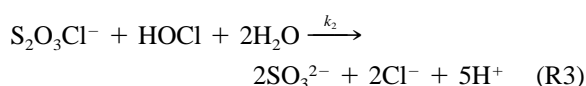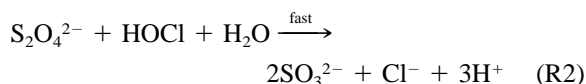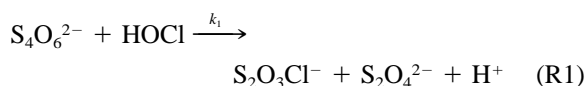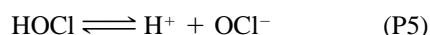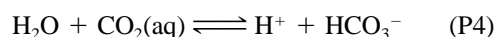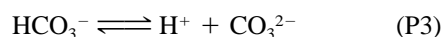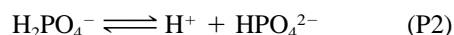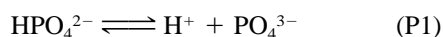
- It cannot be oxidized by iodine.
- Its hydrolysis yields sulfur precipitate—the lower the pH, the faster the appearance of sulfur precipitation—and its slow reaction with the excess tetrathionate yields pentathionate.
- The lifetime of the intermediate is much longer than those of the known sulfur chlorides or sulfur oxychlorides in aqueous solution.

It was convincingly proven by Awtrey and Connick [11] that the oxidation of thiosulfate by iodine proceeds through an intermediate, $S_2O_3I^-$, and—in the presence of chloride—$S_2O_3Cl^-$ is also formed. They

found that the rate constant of the hydrolysis of these anions are on the order of 10^{-3} min^{-1}. In spite of the relatively high hydrolytic stability, no known salts of these anions have been prepared yet. To summarize, it seems to be logical to consider $S_2O_3Cl^-$ to be the long-lived intermediate of the tetrathionate–hypochlorous acid reaction.

Proposed Mechanism

Based on the previous considerations, the following mechanism is proposed:

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad (P1)$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad (P2)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad (P3)$$

$$H_2O + CO_2(aq) \rightleftharpoons H^+ + HCO_3^- \qquad (P4)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (P5)$$

$$S_4O_6^{2-} + HOCl \xrightarrow{k_1}$$
$$S_2O_3Cl^- + S_2O_4^{2-} + H^+ \quad (R1)$$

$$S_2O_4^{2-} + HOCl + H_2O \xrightarrow{fast}$$
$$2SO_3^{2-} + Cl^- + 3H^+ \quad (R2)$$

$$S_2O_3Cl^- + HOCl + 2H_2O \xrightarrow{k_2}$$
$$2SO_3^{2-} + 2Cl^- + 5H^+ \quad (R3)$$

$$SO_3^{2-} + HOCl \xrightarrow{fast} SO_4^{2-} + Cl^- + H^+ \quad (R4)$$

DISCUSSION

The fast protonation and deprotonation processes (equilibria P1–P5) were taken into account with known equilibrium constants in order to follow the slight change of pH during the reaction. These are regarded as auxiliary processes, necessary for the calculations, but they are not part of the proposed model.

Step (R1) is the initial elementary reaction of our model. This process probably takes place through a transient species (Structure I).
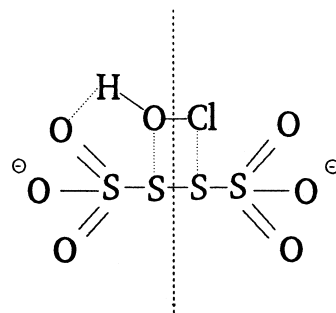

Structure I

Fogelman et al. [12] proposed a similar transient in the sulfite–hypochlorous acid system. It is established in their work that the sulfur atom can be attacked either by the chlorine atom of hypochlorous acid or by the oxygen atom of hypochlorite ion. The huge difference between the rate coefficients of SO_3^{2-}=HOCl and SO_3^{2-}=OCl$^-$ reactions is explained by a shift in mechanism from oxygen atom transfer for OCl$^-$ to Cl$^+$ transfer for HOCl. In the tetrathionate–hypochlorous acid system the attack of chlorine and oxygen of hypochlorous acid can take place simultaneously on the partially positively charged inner sulfurs of tetrathionate. Splitting of the S—S and O—Cl bonds of the long-lived transient adduct forms $S_2O_3Cl^-$. The other product—which resembles dithionite—is instantaneously oxidized to sulfate through sulfite. Step (R3) is the oxidation of $S_2O_3Cl^-$ (Structure II) by hypochlorous acid yielding SO_3^{2-} first, which is oxidized further in a well-known fast reaction. [12,13] The supposed structure of this compound is the following [11]:
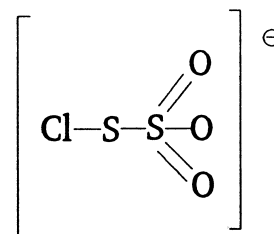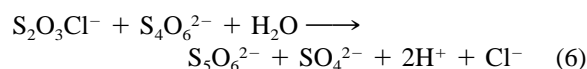

Structure II

In our kinetic timescale, the key species, $S_2O_3Cl^-$, is an end product in excess tetrathionate. Its relatively slow hydrolysis yields sulfur precipitation:

$$S_2O_3Cl^- + H_2O \longrightarrow$$
$$SO_4^{2-} + S + 2H^+ + Cl^- \quad (5)$$
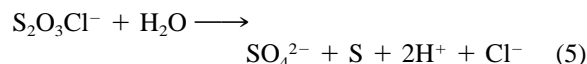
Its reaction with tetrathionate gives pentathionate by the following equation:

$$S_2O_3Cl^- + S_4O_6^{2-} + H_2O \longrightarrow$$
$$S_5O_6^{2-} + SO_4^{2-} + 2H^+ + Cl^- \quad (6)$$

At lower pH, $S_2O_3Cl^-$ is protonated, which accelerates the decomposition into sulfur, sulfate, and chloride ions, as observed in unbuffered and slightly buffered media. Equations (5) and (6) explain the behavior of the system at lower pH region and in a longer timescale; therefore, they are only mentioned for the sake of completeness. The calculated rate constants are

$$k_1 = 32.4 \pm 0.5 \text{ M}^{-1}\text{s}^{-1}, \qquad k_2 = 7.7 \pm 0.3 \text{ M}^{-1}\text{s}^{-1}$$

The molar absorbances of the intermediate above 280 nm are seen in Figure 2. By the help of eight fitted parameters (two rate constants and six molar absorbances), the average deviation between the measured and calculated data is 0.0054 absorbance unit. Typical experimental and calculated kinetic curves are illustrated in Figure 5. This agreement and lack of systematic deviations support the correctness of our proposed mechanism. In the sense of equations (3) and (4), the reaction may be characterized by the following two mechanistic steps:

$$H_2O + S_4O_6^{2-} + 4HOCl \longrightarrow$$
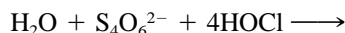
$$2SO_4^{2-} + S_2O_3Cl^- + 3Cl^- + 6H^+ - \frac{d[S_4O_6^{2-}]}{dt}$$

$$= -\frac{1}{4}\frac{d[HOCl]}{dt} = 32.4 \ [S_4O_6^{2-}][HOCl] \quad (7)$$

$$2H_2O + S_2O_3Cl^- + 3HOCl \longrightarrow$$
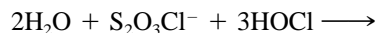
$$2SO_4^{2-} + 4Cl^- + 7H^+ - \frac{d[S_2O_3Cl^-]}{dt}$$

$$= -\frac{1}{3}\frac{d[HOCl]}{dt} = 7.7 \ [S_2O_3Cl^-][HOCl] \quad (8)$$

It is interesting to note that the average oxidation number of the sulfur-containing species is 4.5 on the right-hand side of equation (7) and the calculated curves completely agree with those calculated from equations (3) and (4), with $x = 4.5$.

CONCLUSIONS

The results presented show that the reaction between tetrathionate and hypochlorous acid takes place through an intermediate $S_2O_3Cl^-$. In tetrathionate excess, this ion is one of the end products on our timescale ($t \leq 2$ h), which very slowly hydrolyzes in alkaline solution. Further work for the preparation of some salt of this anion is in progress in our laboratory.

Another important conclusion from our work is that using the most rigorous computational procedures, even the overlapping spectra of reactants, intermediates, and products may be used for gaining kinetic information. However, even these methods are unable to distinguish between the different possible pathways
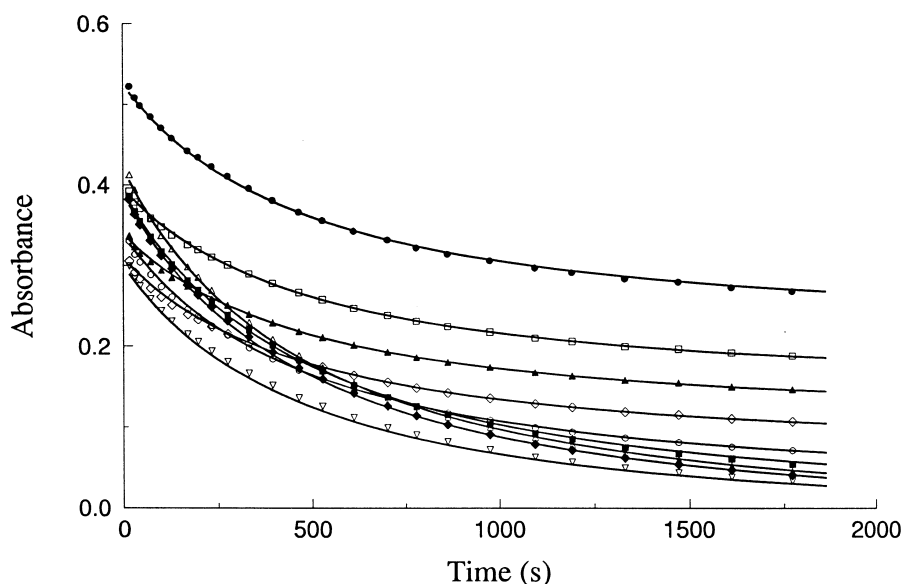
Figure 5 Measured (symbols) and calculated (solid lines) kinetic curves. Initial concentrations are $[S_4O_6^{2-}]_0 = 3.39 \times 10^{-4}$ M, $[HOCl]_0 = 1.27 \times 10^{-3}$ M, pH = 8.60; 245 (●), 250 (□), 254 (▲), 260 (◇), 270 (○), 280 (■), 292 (△), 300 (◆), 310 (▽) nms.

if the structure of the differential equations describing the processes is similar.

Supplementary Material Available

Figures containing sets of absorbance vs. time measured and fitted curves for all the 137 kinetic runs take up about 70 pages. They can be downloaded through anonymous FTP or by WWW at ftp://ftp.jate.u-szeged.hu/pub/chem/pgabor/hote.exe.

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