Simultaneous Evaluation of Different Types of Kinetic Traces of a Complex System: Kinetics and Mechanism of the Tetrathionate−Bromine Reaction

Dénes Varga[†,‡] **and Attila K. Horváth***[,†]

Department of Chemistry, University of Pécs, Ifjúság útja 6, H-7624 Pécs, Hungary

Received: March 23, 2009; Revised Manuscript Received: July 14, 2009

The bromine−tetrathionate reaction has been studied in the presence of phosphoric acid/dihydrogen phosphate buffer at $T = 25 \pm 0.1$ °C and at $I = 0.5$ M ionic strength with both stopped-flow technique and a conventional diode array spectrophotometer. The stoichiometry of the reaction was found to be $S_4O_6^{2-} + 7Br_2 + 10H_2O \rightarrow 4SO_4^{2-} + 14Br^- + 20H^+$ in bromine excess, but no unambiguous stoichiometry can be established in tetrathionate excess because elementary sulfur as well as hydrogen sulfide are also present in appreciable amounts besides the major product sulfate. It has also been shown that the reaction has two well-separable kinetic phases in an excess of tetrathionate. Rapid disappearance of bromine was observed in the early stage of the reaction followed by a much slower spectral change in the UV region that can be attributed to the disappearance of an absorbing species having much stronger light absorption than that of tetrathionate in the given wavelength range. Two different types of kinetic curves measured by two different instruments have been evaluated simultaneously that led us to suggest and discuss a 10-step model.

Introduction

Tetrathionate ion is known as one of the most stable low valence sulfur-containing compounds obtained through the oxidation of thiosulfate leading to sulfate in neutral and slightly acidic media. Its formation as a long-lived key intermediate in the oxidation reactions of thiosulfate is often accompanied by the appearance of wide variety of nonlinear dynamical phenomena. It has been recently shown that electrochemical oxidation of thiosulfate leads to the formation of not only tetrathionate but also higher polythionates in an oscillatory fashion.[1] Moreover, oxidation of thiosulfate by hypochlorous acid also eventually gives an appreciable amount of polythionates and sulfur precipitation in slightly acidic media.[2] The most studied chemical system involving the oxidation of thiosulfate in which tetrathionate plays an important role is the thiosulfate−chlorite reaction, which shows multistability, complex periodic and aperiodic oscillation in a continuously stirred tank reactor (CSTR), and a fluctuation and stirring rate effect in batch.[3−6] Unfortunately, the kinetics and mechanism of the chlorite−thiosulfate reaction is still a mystery, and no quantitative description can therefore be offered for the explanation of such a wide variety of dynamical behavior. The last two decades have, however, witnessed considerable efforts to unravel the kinetics and mechanism of reaction of tetrathionate with several different oxidizing agents such as hydrogen peroxide,[7] hypochlorous acid,[8] chlorine dioxide,[9] and chlorite[10] that may help to contribute to a better understanding of the dynamical behavior of the chlorite−thiosulfate parent reaction. In most of these systems the highly overlapping spectra of the reactants and the end products prevent the usage of simplified evaluation techniques—such as the initial rate studies and the individual exponential curve fitting method—to obtain reliable kinetic models; therefore, the choice of the simultaneous curve fitting method is more preferred. The advantages of this method have recently been summarized in our previous paper,[11] though in the case of evaluation of overlapping spectra sometimes no unambiguous kinetic model can be offered even with the simultaneous curve fitting method. This situation occurred in case of the tetrathionate−hypochlorous acid system, where a couple of mathematically equivalent but chemically different models were proposed.[8] At that time it was supposed that a long-lived intermediate was formed ($S_2O_3Cl^-$) during the reaction based on the early observations of Awtrey and Connick[12] who assigned a relatively long lifetime to $S_2O_3I^-$ and $S_2O_3Cl^-$ species. It was concluded from the experimental observations that iodine slowly disappeared in the thiosulfate−iodine reaction in an excess of iodine after the first very rapid stage.[13] Tetrathionate can, however, further react with iodine in a relatively slow autoinhibitory reaction because the iodide ion formed during the oxidation process retards the reaction significantly,[13,14] therefore, it is not necessary to suppose a long-lived intermediate whose further reaction is responsible for the slow reduction of iodine. Furthermore, it was also demonstrated that no absorbing species was accumulated in appreciable amounts. Nevertheless, our paper also provided a reasonable answer[14] to the question about the unexpected but experimentally found iodide dependence of the rate coefficient of the rate law suggested by Awtrey and Connick. To obtain more reliable information about the possible role of the $S_2O_3X^-$ species (where X can be any halogen), we decided to investigate the analogous tetrathionate−bromine reaction. Thorough survey of the literature indicated no detailed investigation on the kinetics and mechanism of this reaction. Recent renewed interest of further conversion of thiosulfate and/or polythionates in microbiology,[15−18] geochemistry,[19] and leaching processes[20] also justifies an investigation leading to a deeper understanding of the redox chemistry of tetrathionate.

Experimental Section

Materials and Buffers. Bromine stock solution was prepared by distilling bromine (Sigma-Aldrich) into 0.01 M H_3PO_4

---

* E-mail: horvatha@gamma.ttk.pte.hu.

[†] University of Pécs.

[‡] This paper is dedicated to the memory of Dénes Varga, who suddenly deceased during the preparation of this manuscript.

10.1021/jp9026089 CCC: $40.75

solutions. All the other chemicals were of the highest purity commercially available—potassium tetrathionate (Fluka), sodium bromide, sodium dihydrogen phosphate, phosphoric acid (Reanal)—and were used without further purification. The purity of the commercially available tetrathionate was checked by the following procedure. First, the S(IV) and thiosulfate contamination was examined by standard triiodide solution. If the solution turned out to be sulfite and thiosulfate free then the weighed amount of tetrathionate was oxidized by bromine in excess followed by purging the remaining bromine by N_2 gas. The liberated proton was titrated against standard sodium hydroxide solution. The purity of tetrathionate was found to be better than 99.5%. All the stock solutions were prepared from ion-exchanged and four-times-distilled water. The concentration of the stock bromine solution was checked by standard iodometric titration prior to each experiment.

Phosphoric acid−dihydrogen-phosphate buffer was used to maintain the pH between 2.10 and 3.80. The ionic strength was kept constant at 0.5 M with sodium dihydrogen phosphate as a buffer component, and the pH of the solution was adjusted with the desired amount of phosphoric acid, taking the $\mathrm{p}K_\mathrm{a}$ of phosphoric acid as 1.80.[21]

To study the first kinetic stage of the reaction, the following concentration ranges were used: $[\mathrm{S_4O_6^{2-}}]_0 = 0.001-0.008$ M, $T^0_{\mathrm{Br_2}} = 0.0028-0.0075$ M, $[\mathrm{Br^-}]_0 = 0-0.2$ M, pH = 2.10, 2.80, 3.80, where $T^0_{\mathrm{Br_2}} = [\mathrm{Br_2}]_0 + [\mathrm{Br_3^-}]_0$. Altogether 76 concentration−time series were used for data evaluation. When the slower part of the reaction was studied at the same pHs, the initial tetrathionate and bromine concentrations were kept in the ranges of 0.167−1.33 mM and 0.25−1.1 mM, respectively. Twenty different initial concentration ratios at three different pHs were used to investigate the reaction in such a way that tetrathionate was always maintained in excess. The exact concentrations of each kinetic run are seen in the Supporting Information.

Methods and Instrumentation. ***Stoichiometric Studies.*** In an excess of bromine the stoichiometry of the reaction was established by simple iodometric and acid−base titrations. In the case of iodometric titration, iodide was added to the solution and the iodine formed from the remaining amount of bromine was titrated with standard thiosulfate solution.

Kinetic Studies. The first relatively fast kinetic phase of the title reaction was measured by a Hi-Tech SF-61 stopped-flow apparatus attached to a single wavelength spectrophotometer that provides monochromatic light. The reaction was followed at 460 nm, the isosbestic point of $\mathrm{Br_2-Br_3^-}$ system. The measured absorbances were converted into total bromine concentration according to the molar absorbances of bromine and tribromide at this wavelength (see Supporting Information, $\varepsilon_{\mathrm{Br_2}} = \varepsilon_{\mathrm{Br_3^-}} = 81\ \mathrm{M^{-1}\ cm^{-1}}$). The reaction becomes too fast to be measured conveniently at pseudo-first-order conditions; thus, an improved calibration and use of a stopped-flow spectrophotometer has been used to unravel the kinetics and mechanism of the title reaction. The application and the essence of this method have already been published elsewhere.[22,23]

In an excess of tetrathionate, the reaction was also followed by Zeiss S10 diode array spectrophotometer at 260−600 nm wavelength range. The kinetic measurements were carried out in a standard 1 cm quartz cuvette equipped with a Teflon cap and magnetic stirrer. The buffer solution was delivered first, followed by the bromine solution (also containing the corresponding buffer). Then the spectrum of this solution was recorded to determine the initial concentration of bromine. Finally, the necessary amount of tetrathionate was introduced from a fast delivery pipet to start the reaction. Separate experiments showed that the loss of bromine was always less than 6% in such an experimental protocol.

Data Treatment. Seven different wavelengths (between 260 and 290 nm in every 5 nm) have been chosen for the evaluation procedure in the case of the diode array spectrophotometer to gain as much information about the end products as possible. The experimental curves measured by the stopped-flow apparatus and by the diode array spectrophotometer were then evaluated simultaneously by the ZiTa program package.[24] Because two different types of kinetic data (absorbance−time and concentration−time series) were evaluated simultaneously, a relative fitting procedure has been chosen to minimize the average deviation between the measured and calculated data. A relative fitting procedure means that the difference between the measured and calculated quantities are divided by the largest change in the experimental value for each kinetic curve and the sum of squares of average deviation obtained this way is minimized.

Because each kinetic curve contained at least 300 data pairs, the number of points in each run was reduced to 40−50 to avoid unnecessary time-consuming calculations. The essence of this method has already been described elsewhere.[10] Altogether more than 22000 experimental points from 496 kinetic series (76 concentration−time and 7 × 60 absorbance−time series) were used for the simultaneous evaluation. Our quantitative criterion for an acceptable fit was that the average deviation for the relative fit approach 6%, which is close to the experimentally achievable limit of error, taking the maximum loss of bromine into consideration.

In an excess of tetrathionate, colloidal sulfur precipitation occurs (see description below). Because colloidal sulfur particles cannot be taken into consideration as a specific entity having a characteristic absorption spectrum, therefore we decided to remove those parts of the kinetic curves, where absorbance increase can be observed at longer wavelengths. The "absorbance" change measured at longer wavelength can be attributed to the colloidal sulfur particles because on one hand the reflection of the analyzing light on the particles fails to reach the detector and on the other hand none of the sulfur-containing species has an absorption at 600 nm. Typically it meant that the kinetic curves were truncated at around 300 s, depending on the initial concentration of the reactants.

Results

Preliminary Observations. Figure 1 shows a typical kinetic run in an excess of tetrathionate measured by the diode array spectrophotometer. It clearly indicates that bromine is consumed within the time of mixing the reactants in the cuvette, but significant changes can be observed in the UV range lasting for approximately 10 min. Moreover, comparing the initial spectra of the reactants with the spectrum of the reacting mixture clearly indicates that a species having a much stronger absorbance band than that of tetrathionate in the given spectral range accumulates in a detectable amount. Although it is well-known that tribromide ion has a very intense absorbance band[25] in the UV range ($\lambda_{\mathrm{max}} = 266$ nm, $\varepsilon = 39900\ \mathrm{M^{-1}\ cm^{-1}}$), as Figure 1 indicates tribromide ion cannot be responsible for this effect, because the measured absorbance is zero at the first experimental time point at the 460 nm (isosbestic point of $\mathrm{Br_2-Br_3^-}$ system). A reasonable explanation would, however, be the formation of higher polythionates or other polysulfide species that has a much stronger absorbance band in the UV range than that of tetrathionate.[26] At first sight, the idea that oxidation of tetrathionate by a strong oxidizing agent leads to the formation of higher

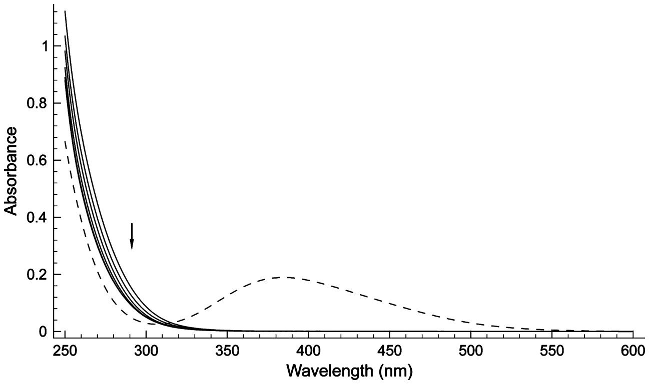

Figure 1. Time-resolved spectral changes in the tetrathionate−bromine reaction in an excess of tetrathionate after the fast disappearance of bromine in the absence of initially added bromide ion. The initial concentrations are as follows: $[S_4O_6^{2-}]_0 = 0.001$ M, $T^0_{Br_2} = 0.001$ M, $[Br^-]_0 = 0$ M, and pH = 2.80. The dashed line indicates calculated initial spectrum of the reactants supposing no reaction at all. The time-resolved spectra (solid lines) were taken at $t = 5$, 25, 45, 95, 195, and 495 s. The arrow indicates the direction of change in the absorbance at the time interval given above.

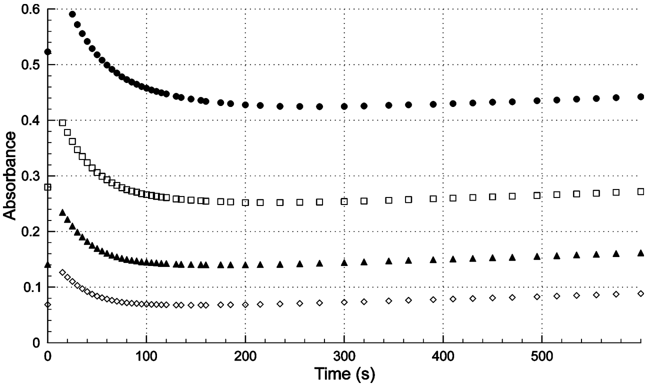

Figure 2. Typical absorbance change at four different wavelength. $[S_4O_6^{2-}]_0 = 1.33 \times 10^{-3}$ M, $T^0_{Br_2} = 1.1 \times 10^{-3}$ M, $[Br^-]_0 = 0$ M, pH = 2.08. λ (nm) = 270 (●), 280 (□), 290 (▲), 300 (◊). Note that absorbance at $t = 0$ values are calculated from the initial concentrations of the reactants.

polythionates or polysulfides may seem surprising, but recent studies have already shown this phenomenon in the case of oxidizing thiosulfate.[1,2] Further discussion about the formation of the relatively long-lived intermediate will be discussed later. The appearance of polythionates or polysulfides also complicates the stoichiometry of the reaction in an excess of tetrathionate because several other sulfur-containing species may also be formed. Separate experiments confirmed the formation of hydrogen sulfide by its characteristic odor as well as by the formation of a brownish black lead sulfide precipitate after adding lead nitrate to the solution. For the sake of completeness, it should be noted that the majority of the precipitation is due to the formation of white lead sulfate. Besides hydrogen sulfide, however, we ruled out the formation of thiosulfate, because addition of Fe^{3+} to the reacting solution does not give the characteristic purple color of the ferric(III) thiosulfato complex that gradually fades away after approximately 1 min upon its formation. It is also well-known that degradation of polythionates leads to the formation of S(IV) species.[27,28] Moreover, at a huge excess of tetrathionate after the rapid disappearance of bromine, the solution becomes pale yellow depending on the excess of tetrathionate, suggesting the formation of some polysulfide species[29] from which elementary sulfur also precipitates. Figure 2 shows a typical measured absorbance−time profile at the later stages of the reactions in an excess of tetrathionate measured at several different wavelengths. As seen, the intermediate formed in the first rapid stage of the reaction disappears, but after a couple of minutes, a slow but steady absorbance increase can be observed; meanwhile, the solution gradually becomes opalescent, suggesting the formation of colloidal sulfur. It should be emphasized that the appearance of a wide variety of sulfur-containing compounds is definitely the consequence of the reaction because the tetrathionate solution is stable under these experimental conditions.

Stoichiometry. Iodometric titration showed that the stoichiometry of the reaction can be characterized in an excess of bromine as follows:

$$S_4O_6^{2-} + 7Br_2 + 10H_2O \rightarrow 4SO_4^{2-} + 14Br^- + 20H^+ \tag{1}$$

This stoichiometry was also verified in absence of buffer by simple acid−base titration. The results are summarized in Table 1. In excess of tetrathionate, however, our attempt to establish a uniform stoichiometry failed. This fact is not surprising if one takes the number of different sulfur-containing species detected in an excess of tetrathionate into account.

TABLE 1: Determination of the Stoichiometry in an Excess of Bromine[a]

pH	$[S_4O_6^{2-}]_0$, M	$[Br_2]_0$, M	$[Br_2]_\infty$, M	$[H^+]_\infty$, M	SR_1	SR_2
3.8	0.001	0.04	0.0331	−	6.90	−
3.8	0.0015	0.04	0.0293	−	7.13	−
3.8	0.002	0.04	0.0258	−	7.10	−
3.8	0.003	0.04	0.01915	−	6.95	−
3.8	0.005	0.04	0.0049	−	7.02	−
2.8	0.001	0.04	0.0328	−	7.20	−
2.8	0.0015	0.04	0.0294	−	7.07	−
2.8	0.002	0.04	0.0262	−	6.90	−
2.8	0.003	0.04	0.01915	−	6.95	−
2.8	0.005	0.04	0.00475	−	7.05	−
−[b]	0.001	0.04	−	0.0202	−	20.2
−[b]	0.0015	0.04	−	0.0300	−	20.0
−[b]	0.002	0.04	−	0.0398	−	19.9
−[b]	0.003	0.04	−	0.0597	−	19.9
−[b]	0.005	0.04	−	0.1005	−	20.1

[a] SR_1 and SR_2 are defined as the $([Br_2]_0-[Br_2]_\infty)/[S_4O_6^{2-}]_0$ and $[H^+]_\infty/[S_4O_6^{2-}]_0$ ratios. [b] Without buffer.

MRA Studies. To determine the number of absorbing species, matrix rank analysis (MRA)[30] has been executed on all the measured series simultaneously where the measured values did not exceed 1.0 absorbance unit. Those time points where absorbance increase could be observed at longer wavelenghts (500−600 nm) due to the light reflection on colloidal sulfur particles have been eliminated from the evaluation. It typically meant that time points up to 300−600 s were taken into account depending on the initial concentration of the reactants. This study has clearly revealed three independent absorbing species, namely tetrathionate, a color intermediate, and "sulfur". The present study is, however, unable to distinguish between the possible forms of "sulfur" that may be HS(OH), etc., from which the gradual sulfur precipitation occurs. The polysulfide species as a form of "sulfur", however, can clearly be ruled out because acidification of polysulfide solution immediately leads to the formation of elementary sulfur precipitation.

Proposed Kinetic Model. Early Stage: The method leading to the best fitting model has already been published elsewhere.[9,10,23,31,32] The most critical part of this procedure is to choose the set of species involved in the mono- and bimolecular reactions. This group consists of $S_4O_6^{2-}$, Br_2, Br^-, Br_3^-, SO_4^{2-}, H_2O, H^+, and

P(x), where P(x) is a sulfur-containing end product at the stopped-flow time scale, but it is an intermediate at longer periods. Further discussion on P(x) will be continued later in this paper. Additionally the $S_4O_6Br^-$, $S_2O_3Br^-$, $S_2O_3OH^-$, HSO_3^- intermediates have also been chosen for the following reasons:

- The role of $S_4O_6I^-$ and $S_2O_3I^-$ has already been well-established in the tetrathionate−iodine reaction.[13,14] By analogy one can assume that the corresponding bromine-containing species may also be involved in the tetrathionate−bromine reaction.
- The $S_2O_3OH^-$ species is a well-known key intermediate of the tetrathionate−hydrogen peroxide reaction[7] as well as the tetrathionate−iodine reaction.[13,14] Therefore, it must also be included as an intermediate of the tetrathionate−bromine reaction.

To set up the initial kinetic model as a first step, all the conceivable mono- and bimolecular reactions of these species were considered along with their H^+- and OH^--catalyzed pathways, meaning that more than 100 reactions were included in the start of the evaluational process. By eliminating the processes step by step that do not have any effect on the quality of fit we finally arrive at the core of the kinetic model in which all the steps are necessary for description of the kinetic data for the early stage of the reaction. After this long, but straightforward, calculation procedure, the following kinetic model emerged

$$H^+ + H_2PO_4^- \rightleftharpoons H_3PO_4 \tag{E1}$$

$$Br_2 + Br^- \rightleftharpoons Br_3^- \tag{R1}$$

$$S_4O_6^{2-} + Br_2 \rightleftharpoons S_4O_6Br^- + Br^- \tag{R2}$$

$$S_4O_6Br^- + H_2O \rightarrow S_2O_3Br^- + S_2O_3OH^- + H^+ \tag{R3}$$

$$S_4O_6Br^- + Br^- \rightarrow 2S_2O_3Br^- \tag{R4}$$

$$S_2O_3Br^- + Br_2 + 3H_2O \rightarrow 2HSO_3^- + 3Br^- + 4H^+ \tag{R5}$$

$$S_2O_3Br^- + Br_3^- + 3H_2O \rightarrow 2HSO_3^- + 4Br^- + 4H^+ \tag{R6}$$

$$S_2O_3OH^- + Br_2 + 2H_2O \rightarrow 2HSO_3^- + 2Br^- + 3H^+ \tag{R7}$$

$$HSO_3^- + Br_2 + H_2O \rightarrow 2Br^- + SO_4^{2-} + 3H^+ \tag{R8}$$

$$S_4O_6^{2-} + S_2O_3Br^- + H_2O \rightarrow P(x) + Br^- + 2H^+ + ySO_4^{2-} \tag{R9}$$

where y can be 1, 2, or 3.

The average deviation was found to be 4.6% for the 76 concentration−time series with six fitted rate coefficients in the case of only the stopped-flow measurements. The final results of the calculation can be seen in the fourth column of Table 2.

Later Kinetic Stage: As seen in Figure 2, the reaction has a slower kinetic phase in an excess of tetrathionate. To evaluate the second kinetic stage, all the kinetic parameters determined from the first stage of the reaction were fixed. It means that P(x) formed in step R9 can only be treated as an intermediate over a longer time scale. Decay of P(x) results in formation of another absorbing species—most probably it is HS(OH)—from which elementary sulfur gradually precipitates. The simplicity of the kinetic curves suggests that the description of the second kinetic phase requires only two fitted rate coefficients (the OH^- dependent and independent R10) and 2 × 7 molar absorbances of P(x) and HS(OH) at seven different wavelengths.

$$P(x) \rightarrow (3 - y)SO_4^{2-} + 2HS(OH) + H_2S \tag{R10}$$

The average deviation was found to be 4.8% for the 7 × 60 absorbance−time series in the case of evaluating only the later stage of the reaction. The final results (rate coefficients and molar absorbances) can be found in the last column of Tables 2 and 3, respectively.

Evaluation of Two Kinetic Stages Simultaneously: As seen, evaluation of the two distinct, well-separable kinetic phases led to a reasonable kinetic model for both stages. The connection between them is the color intermediate P(x) formed in step R9. Although there are two types of kinetic traces (concentration−time for the first phase and absorbance−time for the second phase), the comprehensive program package ZiTa[24] is capable of determining the rate coefficients of the combined system, evaluating different types of the kinetic curves simultaneously. The results of the simultaneous evaluation can be seen in Tables 2 and 3; the average deviation was found to be 4.9%. It is clear that the kinetic parameters and the molar absorbances determined from the two different calculation procedures agree well within their standard deviation. Therefore, it is concluded that the parameter set obtained from both evaluational procedures is reliable and consistent. Nevertheless, the powerful ability of the comprehensive program package ZiTa to determine the kinetic parameters of an unknown system is also highlighted.

Discussion

The rapid de- and reprotonation process E1 was taken into account with a known equilibrium constant[21] to follow the change in pH during the reaction especially at pH = 3.8, where the phosphate buffer has weak capacity ($pK_{E1} = 1.80$). 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.

Step R1 is the well-known formation of tribromide ion. This equilibrium is established rapidly; therefore, the fast forward ($k_{R1} = 1.81 \times 10^9$ M^{-1} s^{-1}) and the reverse ($k_{-R1} = 10^8$ s^{-1}) rate coefficients of step R1 were fixed during the calculation to give the known formation constant of tribromide ion as 18.1 M^{-1}.[33]

Step R2 is a formal Br^+ transfer from bromine to one of the inner sulfur atoms of tetrathionate. The back reaction was found to be fast; any value higher than $k_{-R2} = 10^7$ M^{-1} s^{-1} would lead to the same final result. Therefore, we fixed it to $k_{-R2} = 10^7$ M^{-1} s^{-1}. The forward reaction (k_{R2}) is, however, in total correlation with k_{-R2}; therefore, only the ratio of $k_{R2}/k_{-R2} = K_{R2} = 1.68 \pm 0.26$ could be determined. Figure 3 shows the first rapid stage of the reaction as the initial concentration of tetrathionate varies. As one can see at $t = 0$ s, the concentration of bromine significantly decreases with increasing tetrathionate concentration, apparently indicating that the $K_{R2} = k_{R2}/k_{-R2}$ value would be determined by a simple linear fit of the measured bromine concentration at $t = 0$ s plotting against the inverse of initial tetrathionate concentration (see Supporting Information). However, it would only be true if the decrease of the bromine

TABLE 2: Fitted and Fixed Rate Coefficients of the Proposed Kinetic Model[a]

step	rate equation	parameter[b]		
		simultaneous	SF	S10
R1	$k_{R1}[Br_2][Br^-]$ (M^{-1} s^{-1} × 10^{-9})	1.81	1.81	−
(−R1)	$k_{-R1}[Br_3^-]$ (s^{-1})	10^8	10^8	−
R2[c]	$k_{R2}[S_4O_6^{2-}][Br_2]$ (M^{-1} s^{-1} × 10^{-7})	1.68 ± 0.26	2.11 ± 0.49	−
(−R2)	$k_{-R2}[S_4O_6Br^-][Br^-]$ (M^{-1} s^{-1})	10^7	10^7	−
R3	$k_{R3}[S_4O_6Br^-]$ (s^{-1})	141 ± 13	121 ± 12	−
R4	$k_{R4}[S_4O_6Br^-][Br^-]$ (M^{-1} s^{-1} × 10^{-3})	8.83 ± 1.64	5.87 ± 0.90	−
R5	$k_{R5}[S_2O_3Br^-][Br_2]$ (M^{-1} s^{-1} × 10^{-5})	2.27 ± 0.20	1.80 ± 0.30	−
R6	$k_{R6}[S_2O_3Br^-][Br_3^-]$ (M^{-1} s^{-1} × 10^{-6})	1.03 ± 0.33	1.72 ± 0.82	−
R7	$k_{R7}[S_2O_3OH^-][Br_2]$ (M^{-1} s^{-1})	10^9	10^9	−
R8	$k_{R8}[HSO_3^-][Br_2]$ (M^{-1} s^{-1})	3 × 10^8	3 × 10^8	−
R9	$k_{R9}[S_4O_6^{2-}][S_2O_3Br^-]$ (M^{-1} s^{-1} × 10^{-5})	1.82 ± 0.32	1.98 ± 0.60	−
R10	$k_{R10}[P(x)]$ (s^{-1} × 10^2)	1.33 ± 0.10	−	1.32 ± 0.10
R10′	$k'_{R10}[H^+]^{-1}$ $[P(x)]$ ($M \cdot s^{-1}$ × 10^5)	1.92 ± 0.22	−	1.93 ± 0.23

[a] No error indicates that the value in question was fixed during the fitting procedure. [b] The value of the rate coefficients determined from only the first kinetic phase (SF), the second kinetic phase (S10), and simultaneously (simultaneous) from both measurements, respectively. [c] Note that the k_{R2}/k_{-R2} ratio can only be determined from the experiments.

TABLE 3: Measured and Calculated Molar Absorbance[a] **of the Absorbing Species Used in the Fitting Procedure**

λ (nm)	P(x)		HS(OH)			
	simultaneous[c] ε_{calcd}	S10[c] ε_{calcd}	simultaneous ε_{calcd}	S10 ε_{calcd}	$S_4O_6^{2-}$ ε_{measd}	$S_5O_6^{2-}$ ε_{measd}[b]
260	2034 ± 44	2033 ± 42	374 ± 14	375 ± 12	552	2100
265	1724 ± 37	1724 ± 36	314 ± 11	314 ± 11	416	1800
270	1439 ± 31	1439 ± 30	267 ± 10	267 ± 10	309	1500
275	1174 ± 25	1174 ± 24	227 ± 8	227 ± 8	225	1150
280	936 ± 20	936 ± 19	189 ± 7	189 ± 6	161	940
285	727 ± 15	727 ± 14	153 ± 6	153 ± 5	112	720
290	549 ± 12	549 ± 11	122 ± 5	122 ± 4	76.3	544

[a] Molar absorbances are given in the M^{-1} cm^{-1} unit. [b] See ref 26. [c] Molar absorbance determined from only the second kinetic phase (S10) and simultaneously (simultaneous) from both measurements, respectively.

concentration in the dead-time of the stopped-flow instrument is solely due to the rapid establishment of equilibrium R2. Partial contribution of the extent of the reaction to the concentration decrease of bromine during the dead-time cannot be ruled out; therefore, we do not have solid basis to determine K_{R2} by this way.

Similar initiating process was proposed in the corresponding tetrathionate−iodine reaction[13,14] with two important differences. First, the forward reaction of the initiating equilibrium could be calculated independently; second, k_{R2} is many orders of magnitude lower in case of the tetrathionate−iodine reaction than that of the present one. It directly indicates that the initiating equilibrium is not shifted as much to the left in the tetrathionate−bromine reaction. Also taking into consideration that the formation constant of tribromide ion is more than 1 order of magnitude lower than that of the triiodide ion, it directly means that the inhibitory effect of halide ion cannot be so pronounced as that observed in the latter system. The inhibitory or more precisely the autoinhibitory effect of bromide ion in the tetrathionate−bromine reaction is illustrated in Figure 4.

A reaction similar to step R3 was already suggested to take place in the tetrathionate−iodine system.[13,14,34] By analogy one can assume that $S_4O_6Br^-$ formed in the initiating equilibrium reacts with water to produce $S_2O_3Br^-$ and $S_2O_3OH^-$ by splitting the inner sulfur bond. Our fitting procedure has provided a value of (141 ± 13) s^{-1} for the rate coefficient of step R3. Omitting this step from the proposed model would yield a 26% average deviation from which we concluded this step to be essential for the quantitative description of the simultaneous evaluation of the kinetic curves.

A similar process to step R4 has recently been proposed in the tetrathionate−iodine reaction to explain the iodide dependence of the kinetic curves. The reaction proposed here is the bromine analogy of that reaction, which proceeds via the attack of bromide ion on the empty inner sulfur of $S_4O_6Br^-$ followed by splitting of the S−S bond of the intermediate. As a result, $S_4O_6Br^-$ is converted to $S_2O_3Br^-$ that can either be oxidized by bromine eventually to sulfate or can react with tetrathionate to produce the absorbing intermediate P(x). The necessity of this step can be supported by the fact that its elimination would result in a significant increase in the average deviation (8.0%). The majority of the increase in the average deviation arises from the difference between the measured and calculated curves in the presence of initially added bromide ion; therefore, we concluded that this step is essential for quantitative description of the kinetic curves.

Step R5 is the oxidation of $S_2O_3Br^-$ by bromine yielding sulfite and bromide ions. The individual rate coefficient k_{R5} was found to be (2.27 ± 0.20) × 10^5 M^{-1} s^{-1}. Omitting this step from the final model would increase the average deviation to 6.2%, indicating systematic deviation between the measured and calculated data in the absence of initially added bromide ion; therefore, we found the role of this step to also be important in the final model.

Step R6 is the oxidation of $S_2O_3Br^-$ by tribromide ion yielding sulfite and bromide ions. It is interesting to note that this is the only reaction of tribromide ion which is necessary for fitting the kinetic data. It plays a significant role at a larger initial bromide concentration and eventually helps to use up the total bromine amount more quickly. Although elimination of this step from the final model increases the average deviation from 4.9% to only 5.9%, systematic deviation can be observed between the measured and calculated data at high initial bromide concentration in the stopped-flow time-scale; therefore, we

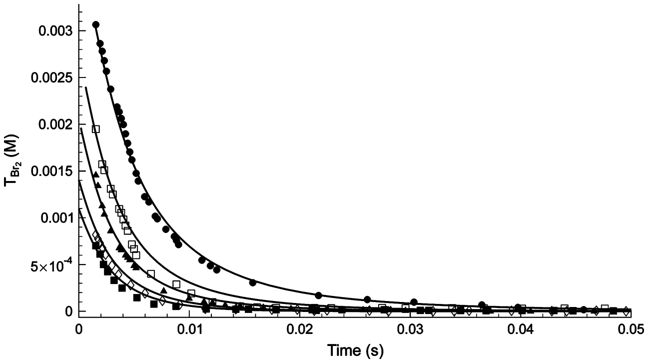

Figure 3. Measured (symbols) and calculated (solid lines) kinetic curves at different tetrathionate concentrations in the early stage of the reactions. $T^0_{Br_2} = 0.006$ M, pH = 2.08, $[Br^-]_0 = 0$ M. $[S_4O_6^{2-}]_0$/M = 0.002 (●), 0.003 (□), 0.004 (▲), 0.006 (◇), 0.008 (■).

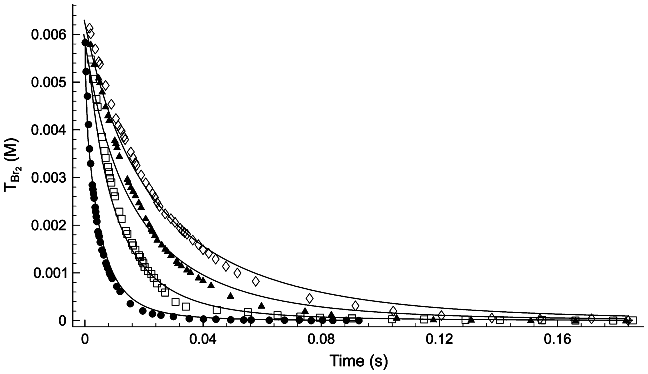

Figure 4. The disappearance of total bromine ($T_{Br_2} = [Br_2] + [Br_3^-]$) in presence of initially added bromide ion in the early stage of the reaction. $[S_4O_6^{2-}]_0 = 0.002$ M, $T^0_{Br_2} = 0.007$ M, pH = 2.80. $[Br^-]_0$/M = 0 (●), 0.04 (□), 0.12 (▲), 0.2 (◇). Measured and calculated curves are indicated by symbols and solid lines, respectively.

concluded this step to be necessary for quantitative description of the kinetic data.

Step R7 is also a rapid reaction that converts $S_2O_3OH^-$ into HSO_3^-. The individual rate coefficient of k_{R7} cannot be determined from our experiments. Any value higher than 10^8 M^{-1} s^{-1} leads to the same final results, which means that this rate coefficient has to be near to the diffusion control limit. Therefore, we have set k_{R7} to an arbitrary but reasonable value of 10^9 M^{-1} s^{-1}.

Step R8 is a very rapid oxidation of hydrogen sulfite by bromine. The analogous hydrogen sulfite−iodine reaction was studied by Yiin and Margerum,[35] who determined its rate coefficient to be 3.1×10^9 M^{-1} s^{-1}. Because bromine is a more powerful oxidizing agent than iodine, the rate coefficient of the hydrogen sulfite−bromine reaction is expected to be higher than that of the previous reaction. Troy and Margerum[36] also determined the rate constant between sulfite and hypobromite ion to be 1.0×10^8 M^{-1} s^{-1}, suggesting that the rate coefficient of the bromine-S(IV) reaction must be higher than that. Therefore, we fixed $k_{R8} = 5 \times 10^9$ M^{-1} s^{-1} during the fitting procedure, though the calculation requires only a value higher than 10^8 M^{-1} s^{-1} for k_{R8}.

Step R9 is responsible for the formation of the colored sulfur-containing intermediate P(x). As Figure 5 clearly indicates, the first phase of the reaction is basically independent of pH in the pH range studied; therefore, the rate equations of steps R1−R9 cannot have $[H^+]$ or $[OH^-]$ dependent terms. The surprising result of our calculation is, however, that the formal oxidation number of sulfur in P(x) cannot be determined unambiguously. Any appropriately chosen sulfur-containing species will lead to the same average deviation, meaning that we do not have a solid basis to differentiate among the possible forms of P(x) by the simple evaluation procedures. This situation has already been reported in the tetrathionate−hypochlorous acid reaction.[8] As a result, we may easily interpret our results by using three different feasible possibilities for the intermediate P(x) as if it was pentathionate, $S_4O_2OH^-$, or S_3^{2-}.

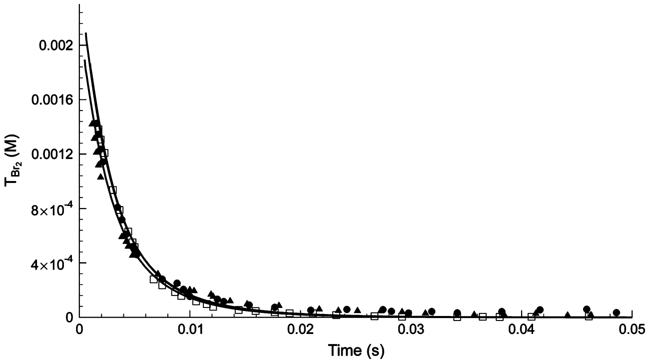

Figure 5. Measured (symbols) and calculated (solid lines) kinetic curves at different pHs in the early stage of the reaction. $[S_4O_6^{2-}]_0 = 0.006$ M, $T^0_{Br_2} = 0.006$ M, $[Br^-]_0 = 0$ M. pH = 2.08 (●), 2.80 (□), 3.80 (▲).

P(x) as pentathionate: If we suppose that the intermediate P(x) is pentathionate, then R9 must be modified as

$$S_4O_6^{2-} + S_2O_3Br^- + H_2O \rightarrow S_5O_6^{2-} + SO_4^{2-} + Br^- + 2H^+ \quad (2)$$

Although this step is not an elementary reaction, one may easily suggest reasonable consecutive elementary processes to decompose it as follows:

$$S_4O_6^{2-} + S_2O_3Br^- \rightarrow S_5O_6^{2-} + SO_3Br^- \quad (3)$$

$$SO_3Br^- + H_2O \rightarrow SO_4^{2-} + Br^- + 2H^+ \quad (4)$$

where eq 3 is the rate-determining step.

A reaction similar to eq 2 has already been proposed in the kinetic model of the thiosulfate−hypochlorous acid reaction;[2] hence, by analogy we may propose this reaction as a source of pentathionate in the reaction studied. Formation of pentathionate during the oxidation of tetrathionate by a strong oxidizing agent such as bromine may seem to be astonishing, but several pieces of indirect evidence can be aligned to support this fact. First, as mentioned above, Figure 1 clearly shows the formation of an absorbing intermediate having a much stronger absorption band in the UV range than that of tetrathionate. Second, Table 3 indicates a considerably good agreement between the calculated molar absorbance of pentathionate compared with the values measured by independent research more than 40 years ago.[26] Third, not only chemical but also electrochemical oxidation of thiosulfate leads to the formation of pentathionate as shown by other researchers recently.[1]

P(x) as $S_4O_2OH^-$: Supposing that P(x) is $S_4O_2OH^-$, then R9 may be modified as

$$S_4O_6^{2-} + S_2O_3Br^- + 2H_2O \rightarrow S_4O_2OH^- + 2SO_4^{2-} + Br^- + 3H^+ \quad (5)$$

This reaction can also be decomposed into an elementary reaction such as

$$S_4O_6^{2-} + S_2O_3Br^- \rightarrow S_6O_9^{2-} + Br^- \quad (6)$$

$$S_6O_9^{2-} + H_2O \rightarrow SO_4^{2-} + S_5O_6OH^- + H^+ \quad (7)$$

$$S_5O_6OH^- + H_2O \rightarrow SO_4^{2-} + S_4O_2OH^- + 2H^+ \quad (8)$$

where eq 6 is the rate-determining step. As mentioned previously, this possibility also leads to the same final result. The reason why alternative solutions are presented for P(x), although pentathionate seems to be a very reasonable suggestion, can be understood based on the rate coefficients of step R10 (see later).

P(x) as S_3^{2-}: Supposing that the polysulfide species is the intermediate P(x), then Step R9 has to be modified as

$$S_4O_6^{2-} + S_2O_3Br^- + 3H_2O \rightarrow 3SO_4^{2-} + Br^- + 6H^+ + S_3^{2-} \quad (9)$$

This reaction is also a complex one that can be decomposed into elementary processes via eqs 6−8 supplemented by

$$S_4O_2OH^- + H_2O \rightarrow SO_4^{2-} + S_3^{2-} + 3H^+ \quad (10)$$

Step R10 is responsible for the degradation of the intermediate formed in step R9. As Figure 6 suggests, the slower kinetic phase of the reaction clearly depends on pH: the lower the acidity, the faster the disappearance of the intermediate. Our predicted values of k_{R10} and k'_{R10} means that the half-life of the intermediate is between 6 and 52 s under our experimental conditions and cannot be longer than 1 min. The feasibility of P(x) to be pentathionate is in question because it is well-known that only the alkaline decomposition of pentathionate proceeds very quickly;[37] under mild acidic conditions, pentathionate is believed to be adequately stable. Again if we consider that P(x) is pentathionate, $S_4O_2OH^-$, or S_3^{2-}, then step R10 can be rewritten as

$$S_5O_6^{2-} + 4H_2O \rightarrow 2SO_4^{2-} + 2HS(OH) + H_2S + 2H^+ \quad (11)$$

or

$$S_4O_2OH^- + 3H_2O \rightarrow SO_4^{2-} + 2HS(OH) + H_2S + H^+ \quad (12)$$

or

$$S_3^{2-} + 2H_2O + 2H^+ \rightarrow 2HS(OH) + H_2S \quad (13)$$

respectively.

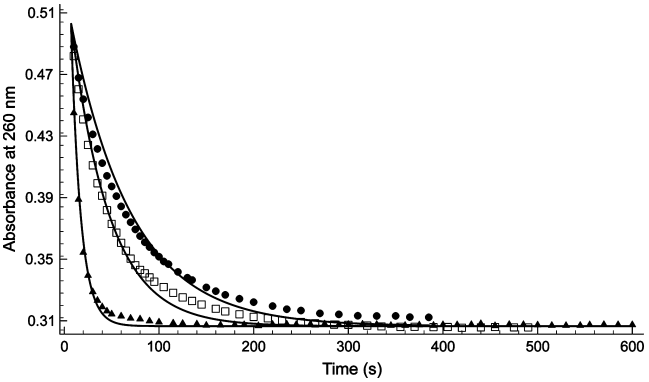

Figure 6. Measured (symbols) and calculated (solid lines) kinetic curves in the later stage of the reaction at different pHs in an excess of tetrathionate after the disappearance of bromine. $[S_4O_6^{2-}]_0 = 6.67 \times 10^{-4}$ M, $T^0_{Br_2} = 7.0 \times 10^{-4}$ M, $[Br^-]_0 = 0$ M. pH = 2.08 (●), 2.80 (□), 3.80 (▲).

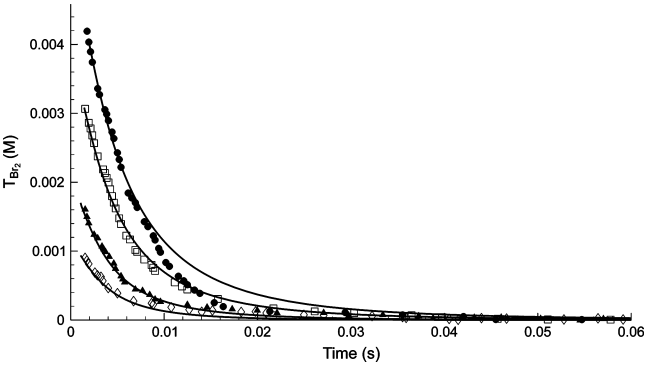

Figure 7. Measured (symbols) and calculated (solid lines) kinetic curves at different bromine concentrations in the early stage of the reactions. $[S_4O_6^{2-}]_0 = 0.002$ M, pH = 2.08, $[Br^-]_0$ (M) = 0. $T^0_{Br_2}$/M = 0.0028 (●), 0.004 (□), 0.006 (▲), 0.0072 (◇).

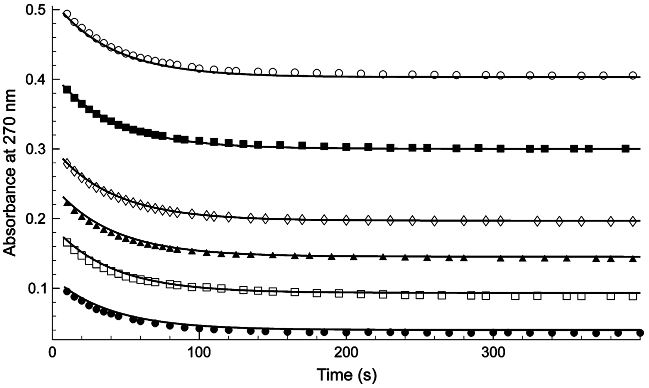

Figure 8. Measured (symbols) and calculated (solid lines) kinetic curves in the later stage of the reaction at different tetrathionate concentrations after the disappearance of bromine. pH = 2.80, $T^0_{Br_2} = 4.0 \times 10^{-4}$ M. $[S_4O_6^{2-}]_0$ (mM) = 0.167 (●), 0.333 (□), 0.500 (▲), 0.667 (◇), 1.00 (■), 1.33 (○).

Tables 2 and 3 summarize the fitted and fixed rate coefficients, as well as the molar absorbances used in the simultaneous evaluation procedure. Figures 3−9 clearly demonstrate that the model is capable of providing an acceptable description of the experimental data over wide concentration ranges of the reactants. The average deviation between the measured and calculated data was found to be 4.9%, which is close to the experimentally achievable limit of error. One must also question which of the above-mentioned intermediates is more likely to be P(x). From a mathematical point of view, no decision can

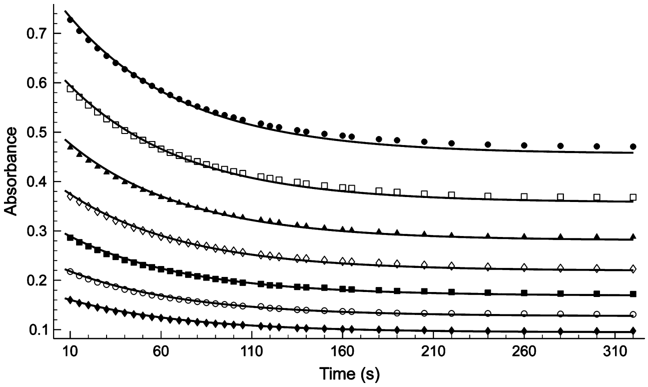

Figure 9. Measured (symbols) and calculated absorbances (solid lines) at different wavelengths in the later stage of the reaction. pH = 2.08, $[S_4O_6^{2-}]_0 = 1.00 \times 10^{-3}$ M, $T^0_{Br_2} = 1.1 \times 10^{-3}$ M, $[Br^-]_0 = 0$ M. Wavelengths (nm) = 260 (●), 265 (□), 270 (▲), 275 (◇), 280 (■), 285 (○), 290 (♦).

be made; however, chemically the most feasible choice seems to be pentathionate if one compares the calculated and the independently measured molar absorbance of pentathionate (see Table 3) despite the fact that pentathionate is considerably less stable than expected under our experimental conditions. It is, however, easily conceivable that one of the products H_2S, HS(OH), or Br^- catalyzes the decomposition of pentathionate, making its lifetime much shorter under the present experimental conditions than in pure water.

It should also be noticed that the decomposition of HS(OH) must also be taken into consideration at a longer time scale as Figure 2 indicates. A feasible possibility would be

$$\mathrm{HS(OH)} \rightarrow \mathrm{H_2O} + \mathrm{S_{col}} \qquad (14)$$

the process indicating the formation of colloidal sulfur. In this case, however, one should consider colloidal sulfur as an additional "absorbing" species having molar absorbances subject to alteration as sulfur particles coagulate. From a standpoint of narrow experimental information (i.e., neglecting the later phase of the kinetic curves measured over approximately 5 min) and because this species cannot be considered as a specific entity having a characteristic absorption spectrum, we did not include this process in the proposed kinetic model.

Conclusion

This paper intends to elucidate the kinetics and the mechanism of the tetrathionate−bromine reaction for the first time. The reaction turned out to be quite complex, especially in an excess of tetrathionate, because besides sulfate various sulfur-containing products such as hydrogen sulfide, polysulfides, and elementary sulfur were produced from further reactions of the key intermediate P(x). It was clearly demonstrated that the reaction has two well-separable kinetic phases in an excess of tetrathionate. The reaction starts with a relatively fast disappearance of bromine that can be measured by stopped-flow technique followed by a much slower kinetic stage that can be investigated by conventional spectrophotometry in which, besides the formation of sulfite, hydrogen sulfide, and polysulfides, elementary sulfur precipitates from the decomposition of the intermediate P(x). The calculated spectra indirectly suggest that P(x) is most probably pentathionate but other possibilities cannot be ruled out unambiguously. As far as we know, this is the first trial in the literature in which simultaneous evaluation of the kinetic curves is applied in two different types of kinetic curves (absorbance−time and concentration−time series) measured by two different instruments, indicating the power of the comprehensive program package ZiTa[24] in unraveling the kinetics and mechanism of an unknown system. Taking the complexity of this system into consideration, we find the result presented here quite promising; therefore, the use of the simultaneous curve-fitting method to determine the kinetics and the mechanism of an unknown system is strongly recommended.

The present study may be helpful as well to understand the intimate details of the reaction of tetrathionate, a compound that is involved in many complex chemical systems exhibiting temporal and spatial nonlinear dynamical behavior as well as in microbiological, geochemical, and leaching processes.

Acknowledgment. This work was supported by the Hungarian Research Fund (OTKA) grant no. K68172. A.K.H. is grateful for the financial support of the János Bolyai Research Scholarship of the Hungarian Academy of Sciences. The authors are indebted to Professor István Nagypál for his valuable suggestions after he read the manuscript.

Supporting Information Available: A table containing the conditions of each kinetic run and additional information on the molar absorbance of the Br_2/Br_3^- system. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Du, Z.; Gao, Q.; Lu, Y.; Wang, J. *J. Phys. Chem. B* **2006**, *110*, 26098.

(2) Varga, D.; Horváth, A. K.; Nagypál, I. *J. Phys. Chem. B* **2006**, *110*, 2467.

(3) Orbán, M.; DeKepper, P.; Epstein, I. R. *J. Phys. Chem.* **1982**, *86*, 431.

(4) Orbán, M.; Epstein, I. R. *J. Phys. Chem.* **1982**, *86*, 3907.

(5) Maselko, J.; Epstein, I. R. *J. Chem. Phys.* **1984**, *80*, 3175.

(6) Nagypál, I.; Epstein, I. R. *J. Phys. Chem.* **1986**, *90*, 6285.

(7) Voslar, M.; Matejka, P.; Schreiber, I. *Inorg. Chem.* **2006**, *45*, 2824.

(8) Horváth, A. K.; Nagypál, I. *Int. J. Chem. Kinet.* **2000**, *32*, 395.

(9) Horváth, A. K.; Nagypál, I.; Epstein, I. R. *J. Phys. Chem. A* **2003**, *107*, 10063.

(10) Horváth, A. K.; Nagypál, I.; Epstein, I. R. *Inorg. Chem.* **2006**, *45*, 9877.

(11) Kormányos, B.; Horváth, A. K.; Peintler, G.; Nagypál, I. *J. Phys. Chem. A* **2007**, *111*, 8104.

(12) Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 1341.

(13) Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4546.

(14) Kerek, A.; Horváth, A. K. *J. Phys. Chem. A* **2007**, *111*, 4235.

(15) Hazeu, W.; van der Vegte, W. H. B.; Bos, P.; van der Pas, R. K.; Kuenen, J. G. *Arch. Microbiol.* **1988**, *150*, 574.

(16) Wentzien, S.; Sand, W.; Albertsen, A.; Steudel, R. *Arch. Microbiol.* **1994**, *161*, 116.

(17) Yong, K.; Kamimura, K.; Sugio, T. *J. Biosci. Bioeng.* **2000**, *90*, 193.

(18) Dam, B.; Mandal, S.; Ghosh, W.; Gupta, S. K. D.; Roy, P. *Res. Microbiol.* **2007**, *158*, 330.

(19) Druschel, G. K.; Hamers, R. J.; Banfield, J. F. *Geochim. Cosmochim. Acta* **2003**, *67*, 4457.

(20) Jeffrey, M. I.; Brunt, S. D. *Hydrometallurgy* **2007**, *89*, 52.

(21) *IUPAC Stability Constant Database*; Royal Society of Chemistry: London, 1992−1997.

(22) Peintler, G.; Nagy, A.; Horváth, A. K.; Körtvélyesi, T.; Nagypál, I. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2575.

(23) Horváth, A. K.; Nagypál, I. *J. Phys. Chem. A* **1998**, *102*, 7267.

(24) Peintler, G. ZiTa, version 5.0; a comprehensive program package for fitting parameters of chemical reaction mechanism; Attila József University, Szeged, Hungary, 1989−1998.

(25) Wang, T. X.; Kelley, M. D.; Cooper, J. N.; Beckwidth, R. C.; Margerum, D. W. *Inorg. Chem.* **1994**, *33*, 5872.

(26) Schmidt, M.; Sand, T. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1173.

(27) Foerster, F.; Centner, K. *Z. Anorg. Chem.* **1926**, *157*, 45.

(28) Fava, A.; Bresadola, S. *J. Am. Chem. Soc.* **1955**, *77*, 5792.

(29) Mao, S.; Gao, Q.; Wang, H.; Zheng, J.; Epstein, I. R. *J. Phys. Chem. A* **2009**, *113*, 1231.

(30) Peintler, G.; Nagypál, I.; Jancsó, A.; Esptein, I. R.; Kustin, K. *J. Phys. Chem. A* **1997**, *103*, 8013.

(31) Horváth, A. K.; Nagypál, I.; Peintler, G.; Epstein, I. R.; Kustin, K. *J. Phys. Chem. A* **2003**, *107*, 6966.

(32) Horváth, A. K.; Nagypál, I. *J. Phys. Chem. A* **2006**, *110*, 4753.

(33) Tóth, Z.; Fábián, I. *Inorg. Chem.* **2000**, *39*, 4608.

(34) Dodd, G.; Griffith, R. O. *Trans. Faraday Soc.* **1949**, *45*, 546.

(35) Yiin, B. S.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 1559.

(36) Troy, R. C.; Margerum, D. W. *Inorg. Chem.* **1991**, *30*, 3538.

(37) Wagner, H.; Schreier, H. *Phosphorus Sulfur* **1978**, *4*, 281.

JP9026089