Kinetics and Mechanism of the Oxidation of Tetrathionate by Iodine in a Slightly Acidic Medium

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The iodine−tetrathionate reaction has been reinvestigated spectrophotometrically at $T = 25.0 \pm 0.1$ °C and at an ionic strength of 0.5 M adjusted by sodium acetate as a buffer component in both the absence and presence of the iodide ion in the pH range of 4.25−5.55. The reaction was found to be independent of pH within the range studied, and it was clearly demonstrated that the reaction proceeds via an intermediate $S_4O_6I^-$ formed in a pre-equilibrium. Iodide dependence of the kinetic curves strongly suggests that the iodide ion has to be involved in this equilibrium. Further reactions of the intermediate, including its hydrolysis and reaction with iodide, leads to the strict stoichiometry characterized by $S_4O_6^{2-} + 7I_2 + 10H_2O \rightarrow 4SO_4^{2-} + 14I^- + 20H^+$. A seven-step kinetic model with three fitted kinetic parameters is suggested and discussed. A rate equation is also derived from which a sound explanation of the iodide dependence of the apparent rate coefficient is presented. Furthermore, it has also been pointed out that formation of the triiodide ion alone is not sufficient to take the retardation effect of the iodide ion into account quantitatively.

Introduction

The iodine−thiosulfate reaction is one of the most widely used titrimetric methods for chemical analysis.[1] The reaction is very rapid, and its stoichiometry is well-established. In high excess of iodide ion, the reaction leads exclusively to the tetrathionate ion, but a low level of iodide ion permits a significant source of sulfate ion besides tetrathionate.[2] This is why the kinetics and mechanism of this reaction have been of interest for decades. Several authors have found independently[3−6] that the reaction must proceed via formation of an intermediate postulated to be $S_2O_3I^-$. In thiosulfate excess, this intermediate reacts further with thiosulfate yielding tetrathionate and iodide ions, but in iodine excess the intermediate is oxidized by iodine further to sulfate ion.[6] It has also been noted[6] that this intermediate has a surprisingly long lifetime if no thiosulfate is present; the rate coefficient of its first-order hydrolytic decomposition in aqueous solution is on the order of 10^{-5} s^{-1}. The kinetic role of the analogs of $S_2O_3I^-$ like $S_2O_3Cl^-$ and $S_2O_3OH^-$ has been established recently in the tetrathionate−hypochlorous acid[7] and tetrathionate−hydrogen peroxide[8] reactions. Scheper and Margerum have pointed out by pulse-accelerated flow studies that $I_2S_2O_3^{2-}$ also plays an important role in determining the kinetics of the iodine−thiosulfate reaction.[9] This adduct is in a rapid equilibrium with $S_2O_3I^-$, but only the latter species is kinetically active to give tetrathionate with another thiosulfate ion. Furthermore, at low iodide concentration the source of sulfate formation[6] is explained by the following stoichiometry:

$$S_2O_3I^- + 3I_3^- + 5H_2O \rightarrow 2SO_4^{2-} + 10I^- + 10H^+ \quad (1)$$
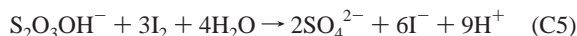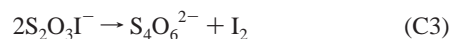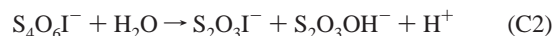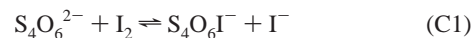
In addition, iodine itself can slowly oxidize the tetrathionate ion further to the sulfate ion.[5,10] Awtrey and Connick have established[10] the following rate law for the iodine−tetrathionate reaction

$$-\frac{d([I_2] + [I_3^-])}{dt} = k_a \frac{[S_4O_6^{2-}][I_2]}{[I^-]} \quad (2)$$

that can be derived from the following mechanism

$$S_4O_6^{2-} + I_2 \rightleftharpoons S_4O_6I^- + I^- \quad (C1)$$

$$S_4O_6I^- + H_2O \rightarrow S_2O_3I^- + S_2O_3OH^- + H^+ \quad (C2)$$

$$2S_2O_3I^- \rightarrow S_4O_6^{2-} + I_2 \quad (C3)$$

$$S_2O_3I^- + 3I_2 + 5H_2O \rightarrow 2SO_4^{2-} + 7I^- + 10H^+ \quad (C4)$$

$$S_2O_3OH^- + 3I_2 + 4H_2O \rightarrow 2SO_4^{2-} + 6I^- + 9H^+ \quad (C5)$$

where step C1 is a rapid equilibrium and step C2 is the rate-determining process. Steps C4 and C5 were taken into consideration to account for the proper stoichiometry of the reaction. From Awtrey and Connick's measurements at an ionic strength of $I = 0.05$ M and at very low initial iodide concentration, only $K_{C1}k_{C2} = 5.5 \times 10^{-5}$ s^{-1} could be determined. The value of $K_{C1}k_{C2}$ in the case of high initial iodide concentration was, however, found to be roughly half of the previous value. Despite all of their efforts, no unambiguous explanation could be given for this difference most probably because of the lack of computational techniques based on nonlinear curve fitting. They have also supposed that in certain experimental circumstances at least one long-lived intermediate may be accumulated, but no unambiguous evidence was presented. The difficulties of this system can be reflected by their own words "...It is therefore concluded that the system is more complicated than was assumed...Clearly this is not a unique explanation, and considerably more research is needed to test its validity. These results

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TABLE 1: Initial Composition of the Kinetic Runs

no.	$[I_2]_0 \times 10^{-4}$ M	$[S_4O_6^{2-}]_0 \times 10^{-4}$ M	$[I^-]_0$ (mM)	pH
1−7	1.14, 1.74, 3.02, 4.25 6.13, 8.52, 10.49	0.7	0	4.55
8−14	4.49	0.3, 0.4, 0.6, 0.7, 1.0, 1.4, 2.0	0	4.55
15−18	6.4	0.7	0.1, 0.3, 0.5, 0.9	4.55
19−22	4.4	2.0	0.1, 0.3, 0.5, 0.9	4.55
23−29	1.04, 1.78, 2.95, 4.20 6.04, 8.37, 10.48	0.7	0	4.25
30−36	4.90	0.3, 0.4, 0.6, 0.7, 1.0, 1.4, 2.0	0	4.25
37−40	5.95	0.7	0.1, 0.3, 0.5, 0.9	4.25
41−42	4.1	2.0	0.5, 0.9	4.55
43−49	1.26, 1.91, 3.25, 4.56 6.43, 9.00, 9.92	0.7	0	5.25
50−56	4.55	0.3, 0.4, 0.6, 0.7, 1.0, 1.4, 2.0	0	5.25
57−60	6.18	0.7	0.1, 0.3, 0.5, 0.9	5.25
61−64	4.16	2.0	0.1, 0.3, 0.5, 0.9	5.25
65−71	1.26, 1.89, 3.20, 4.47 6.33, 8.84, 9.66	0.7	0	5.55
72−78	4.49	0.3, 0.4, 0.6, 0.7, 1.0, 1.4, 2.0	0	5.55
79−82	6.81	0.7	0.1, 0.3, 0.5, 0.9	5.55
83−86	4.63	2.0	0.1, 0.3, 0.5, 0.9	5.55
87−93	1.05, 1.70, 2.88, 4.06 5.65, 7.26, 8.22	0.7	0	4.85
94−100	4.45	0.3, 0.4, 0.6, 0.7, 1.0, 1.4, 2.0	0	4.85
101−104	6.62	0.7	0.1, 0.3, 0.5, 0.7	4.85
105−107	6.50	0.7	1.0, 1.4, 2.0	4.85
108−111	4.41	2.0	0.1, 0.3, 0.5, 0.7	4.85
112−114	4.35	2.0	1.0, 1.4, 2.0	4.85

are being reported now because further work could not be carried out at this time." A very important result of their paper, however, must be indisputably emphasized, namely, the establishment of a $S_4O_6I^-$ intermediate based on the systematic change of the apparent rate coefficient obtained from the integrated rate expression.

Experimental

Reagents and Apparatus. All of the chemicals were of the highest purity commercially available (potassium tetrathionate, iodine, potassium iodide, sodium acetate, acetic acid) and were used without further purification. Four times distilled water was used to prepare all of the stock solutions.

Acetic acid−acetate buffer was used to maintain the pH between 4.25 and 5.55. The ionic strength was kept constant at 0.5 M with sodium acetate as a buffer component, and the pH of the solution was adjusted by adding the desired amount of acetic acid taking the pK_a of acetic acid as 4.55. The initial concentrations of the reactants were varied in the ranges of 0.103−1.049 mM, 0.03−0.2 mM, and 0−2.00 mM in the case of iodine, tetrathionate, and iodide, respectively. The composition of the 114 different runs is collected in Table 1.

Methods. The kinetic measurements were carried out in a standard 1 cm quartz cuvette equipped with a Teflon cap and a magnetic stirrer. The stock solutions of tetrathionate, iodine, and iodide also contained all of the buffer components. First, the iodine and, if necessary, the iodide solution were delivered into the cuvette. The spectrum of the solution was registered from which the precise initial concentration of the iodine and triiodide can be determined. Finally, the tetrathionate solution was added from a fast delivery pipet to start the reaction. After starting the reaction, the cuvette was sealed carefully with Parafilm at the Teflon cap in order to minimize the loss of iodine. The reaction was followed by a Zeiss Specord S10 diode array spectrophotometer within the 400−600 nm wavelength range excluding ultraviolet light to avoid the photochemical decomposition of tetrathionate.[11]

Data Teatment. MRA studies[12] have been executed on absorbance−time series in the wavelength range of 400−600 nm. It clearly indicated that no other absorbing species is present besides iodine and triiodide in the wavelength range in question. Therefore, the isosbestic point of the triiodide−iodine system (468 nm) has been chosen for the evaluation procedure. The experimental curves were analyzed with the program package ZiTa.[13] Altogether, 5700 experimental points from 114 absorbance−time series (each contained 50 points) were used for simultaneous fitting. 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 approaches 0.004 absorbance units, which is close to the uncertainty of the spectrophotometer.

Results

Stoichiometry. Several analytical methods, including gravimetry and iodometry, have confirmed, in agreement with previous studies,[10,14] that the only sulfur-containing product of the reaction is the sulfate ion. Therefore, the stoichiometry of the reaction is characterized by the following equation:

$$S_4O_6^{2-} + 7I_2 + 10H_2O \rightarrow 4SO_4^{2-} + 14I^- + 20H^+ \quad (3)$$

Proposed Kinetic Model. As a starting point, we have undertaken the simultaneous fitting of the 114 kinetic curves with a rate equation being first-order with respect to both reactants with stoichiometry 3 along with the rapid equilibrium formation of triiodide ion

$$I_2 + I^- \rightleftharpoons I_3^- \quad (4)$$

with the well-known rate coefficients of the forward and reverse reactions.[15,16] If one assumes that iodine is the reactive species toward tetrathionate, then this equilibrium might explain the iodide inhibition observed in the kinetic curves. The agreement
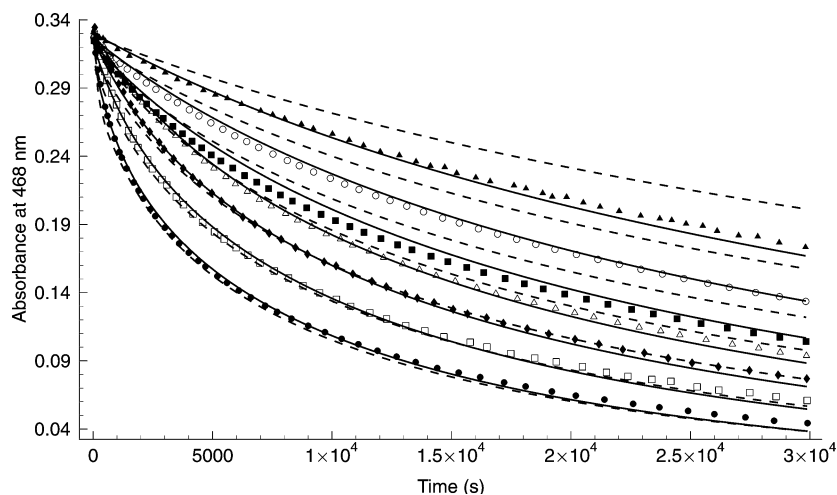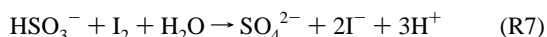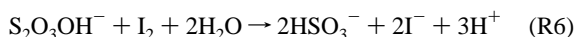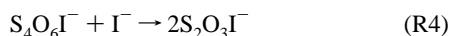
Oxidation of Tetrathionate by Iodine

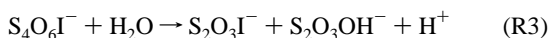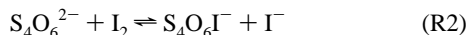*J. Phys. Chem. A, Vol. 111, No. 20, 2007* **4237**

Figure 1. Measured (symbols) and calculated (dashed lines) kinetic curves at the wavelength of 468 nm with neglecting step R4. Solid lines correspond to the fitted kinetic curves with the proposed model. $[S_4O_6^{2-}]_0 = 0.2$ mM, $[I_2]_0 = 0.44$ mM, pH = 4.85, $[I^-]_0 = 0.1(\bullet)$, $0.3(\square)$, $0.5(\blacklozenge)$, $0.7(\triangle)$, $1.0(\blacksquare)$, $1.4(\bigcirc)$, $2.0(\blacktriangle)$ mM.

between the measured and fitted data, however, was extremely poor; the value of 0.0348 absorbance units as an average deviation was unacceptably high. Comparison of the measured and calculated curves has revealed two systematic deviations. On the one hand, the change of absorbance (change of the total iodine concentration) is faster at the early stages of the reaction and slower at the later stages of the reaction and, on the other hand, increase of the iodide concentration retards the reaction much stronger than the simplified model predicts. It clearly indicated that an intermediate must be taken into consideration and iodide must be involved in other process(es) than the formation of the triiodide ion. This conclusion has already been drawn convincingly by Awtrey and Connick.[10] After carrying out the fitting procedure with the kinetic model including steps C1−C5, the average deviation between the measured and calculated curves was found to be 0.0076 absorbance units. After careful inspection, no systematic deviation was encountered between the measured and predicted absorbance values if no iodide ion was initially present in the system; but at high iodide excess the model still predicted a slower decrease in absorbance than was detected experimentally. Therefore, further reactions of the intermediate with the iodide ion were also considered. After several trials, the following model was suggested to describe the kinetics of the iodine−tetrathionate reaction:

$$I_2 + I^- \rightleftharpoons I_3^- \tag{R1}$$

$$S_4O_6^{2-} + I_2 \rightleftharpoons S_4O_6I^- + I^- \tag{R2}$$

$$S_4O_6I^- + H_2O \rightarrow S_2O_3I^- + S_2O_3OH^- + H^+ \tag{R3}$$

$$S_4O_6I^- + I^- \rightarrow 2S_2O_3I^- \tag{R4}$$

$$S_2O_3I^- + I_2 + 3H_2O \rightarrow 2HSO_3^- + 3I^- + 4H^+ \tag{R5}$$

$$S_2O_3OH^- + I_2 + 2H_2O \rightarrow 2HSO_3^- + 2I^- + 3H^+ \tag{R6}$$

$$HSO_3^- + I_2 + H_2O \rightarrow SO_4^{2-} + 2I^- + 3H^+ \tag{R7}$$

Discussion

Step R1 is the fast equilibrium formation of triiodide studied by several authors.[15,16] The rate coefficient of the forward and

reverse reaction was set to $k_{R1} = 5.7 \times 10^9$ M^{-1} s^{-1} and $k_{-R1} = 8.5 \times 10^6$ s^{-1} to give log $\beta_{I_3^-} = 2.83$, where $\beta_{I_3^-}$ is the formation constant of triiodide ion.[18]

Step R2 was already suggested by Awtrey and Connick as a formal I+ transfer from iodine to one of the inner sulfurs of tetrathionate ion.[10] This process was treated as a fast equilibrium shifted far to the left, but the authors were not able to assign any value to the equilibrium constant. We have also started the fitting procedure supposing the back reaction to be rapid. Because any high value of k_{-R2} leads to the same final fit, k_{-R2} was set to 10^7 M^{-1} s^{-1}. It was found that the value of k_{-R2} is in total correlation with k_{R3} and k_{R4}, but k_{R2} can be determined independently if k_{-R2} is fixed. Further analysis about the value of k_{-R2} will be detailed later. The final fitting procedure has yielded a value of 1.92 ± 0.06 M^{-1} s^{-1} for k_{R2}. The reason that k_{R2} is not in correlation with other parameters can be understood easily from the rate equation derived from the proposed kinetic model (see later).

Step R3 was also assumed in the early work of Awtrey and Connick.[10] Although the rate law given by them provided no information about the products of this reaction, they were assumed to be $S_2O_3I^-$ and $S_2O_3OH^-$. This hypothesis was well-supported by Dodd and Griffith,[5] who have shown that the iodine−tetrathionate reaction produced a catalyst for the azide−iodine reaction. It is known that $S_2O_3I^-$ is such a catalyst.[3,5] Our fitting procedure has provided a value of (214 ± 7) s^{-1} for the rate coefficient of step R3. Total correlation between parameters k_{-R2} and k_{R3} means that $k_{R3}/k_{-R2} = (2.14 \pm 0.07) \times 10^{-5}$ M could actually be determined from our work. From this value, one can easily calculate $K_{R2}k_{R3}$ to be $(4.11 \pm 0.19) \times 10^{-5}$ s^{-1}, where $K_{R2} = k_{R2}/k_{-R2}$. Comparison of this value with the $K_{C1}k_{R2} = (3.4-5.5) \times 10^{-5}$ s^{-1} determined by Awtrey and Connick[10] in the absence and presence of the iodide ion shows excellent agreement apart from the different experimental circumstances. The following possibility has also been examined and found to replace step R3 successfully:

$$S_4O_6I^- + 2H_2O \rightarrow 2S_2O_3OH^- + I^- + 2H^+ \tag{5}$$
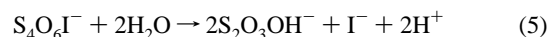
Step R4, which has not been proposed so far, probably proceeds via the attack of another iodide ion to the empty inner sulfur of $S_4O_6I^-$ followed by splitting of the S−S bond of the intermediate. As a result of this process, $S_4O_6I^-$ is converted to

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

step	rate equation	parameter	reference
(R1)	k_{R1} [I$_2$][I$^-$]	5.7×10^9 M^{-1} s^{-1}	refs 15,16
(−R1)	k_{-R1} [I$_3^-$]	8.5×10^6 s^{-1}	refs 15,16
(R2)	k_{R2} [S$_4$O$_6^{2-}$][I$_2$]	1.92 ± 0.06 M^{-1} s^{-1}	this work
(−R2)	k_{-R2} [S$_4$O$_6$I$^-$][I$^-$]	10^7 M^{-1} s^{-1}	this work
(R3)	k_{R3} [S$_4$O$_6$I$^-$]	214 ± 7 s^{-1}	this work
(R4)	k_{R4} [S$_4$O$_6$I$^-$][I$^-$]	$(1.28 \pm 0.03) \times 10^5$ M^{-1} s^{-1}	this work
(R5)	k_{R5} [S$_2$O$_3$I$^-$][I$_2$]	$6 \times 10^5 \gg k_{R5}$/M^{-1} s^{-1} $\geq 10^2$	this work
(R6)	k_{R6} [S$_2$O$_3$OH$^-$][I$_2$]	$\geq 10^2$ M^{-1} s^{-1}	this work
(R7)	k_{R7} [HSO$_3^-$][I$_2$]	3.1×10^9 M^{-1} s^{-1}	ref 17

[a] No error indicates that the value in question was fixed during the fitting procedure.

S$_2$O$_3$I$^-$ that can be rapidly oxidized further with iodine to the sulfite ion. To show the necessity of this process in describing the iodide dependence of the experimental curves, we have also tried to fit our data (on all the 114 experimental curves) while neglecting step R4. The final result has yielded a 0.006 absorbance unit average deviation between the measured and calculated data and introduced a systematic deviation especially at high initial iodide concentrations (see: Figure 1). Any trial to replace this step by another reaction has failed to explain the iodide dependence of the kinetic curves. Therefore, we concluded this step to be necessary for the adequate description of the iodide dependence of the kinetic curves. Its rate coefficient (k_{R4}) was found to be $(1.28 \pm 0.03) \times 10^5$ M^{-1} s^{-1}. Because k_{R4} is in total correlation with k_{-R2}, the ratio $k_{R4}/k_{-R2} = (1.28 \pm 0.03) \times 10^{-2}$ could be determined from our experiments and in fact the reaction is governed by the balance of $K_{R2}k_{R3}$ and $K_{R2}k_{R4} = (2.46 \pm 0.10) \times 10^{-2}$ M^{-1} s^{-1}. It should also be mentioned that the back reaction of step R4 was also considered in the final fitting procedure. We have found that inserting the back reaction slightly decreased the average deviation from 0.0039 absorbance units to 0.0038, giving a reasonable $k_{-R4} = (1.50 \pm 0.36) \times 10^7$ M^{-1} s^{-1} if k_{R5} was fixed to 3×10^4 M^{-1} s^{-1}, but introduced a total correlation between parameters k_{R5} and k_{-R4}. It actually means that we were able to calculate only the ratio of $k_{-R4}/k_{R5}^2 = (1.67 \pm 0.40) \times 10^{-2}$ M^{-1} s^{-1}. Because the average deviation decreased slightly within the experimentally achievable limit of error, this process can only be regarded as a hypothetical step.

One might argue that if this reaction may proceed via the formation of S$_4$O$_6$I$_2^{2-}$ followed by splitting S−S bond to give

S$_2$O$_3$I$^-$, then it is not necessary to suppose the formation of S$_4$O$_6$I$^-$ and the initiating step can be written as

$$S_4O_6^{2-} + I_2 \rightleftharpoons S_4O_6I_2^{2-} \quad (6)$$

followed by

$$S_4O_6I_2^{2-} \rightleftharpoons 2S_2O_3I^- \quad (7)$$
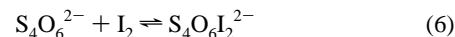
Although this suggestion looks quite reasonable, it would clearly mean that the iodide inhibition of the model is uniquely connected to the triiodide formation. This process alone, however, is not able to explain the iodide inhibition of the kinetic curves. In support of this fact, we have carried out additional fitting (on all 114 experimental curves) in which steps R2 and R4 were replaced by eqs 6 and 8 and found an unacceptably high average deviation (0.047 absorbance unit!). This additional fitting also supports the fact that the iodide ion has to be included in the initiating equilibrium. Therefore, if the attack of iodine starts with an adduct formation, S$_4$O$_6$I$_2^{2-}$ (eq 5), then it must be followed by the cleavage of the iodide ion first:

$$S_4O_6I_2^{2-} \rightleftharpoons S_4O_6I^- + I^- \quad (8)$$
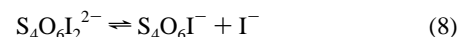
As a result, our K_{R2} value must be the product of K_6 and K_8 and the formation of S$_2$O$_3$I$^-$ would only follow eq 8. Our measurements, however, do not provide any experimental evidence to divide step R2 into two equilibria even if it really occurs in this way; therefore, we decided not to include them in the proposed model.

Step R5 is the fast oxidation of S$_2$O$_3$I$^-$ by iodine yielding sulfite and iodide ions. The individual rate coefficient of this step cannot be determined from our experiments. If k_{-R4} (second-order decomposition of S$_2$O$_3$I$^-$ to give S$_4$O$_6$I$^-$ and iodide ion) is not included in the final model, then any value higher than 10^2 M^{-1} s^{-1} for k_{R5} leads to the same calculated kinetic curves. If, however, k_{-R4} is included then the value of k_{R5} cannot be higher than 6×10^5 M^{-1} s^{-1} because k_{-R4} would exceed the diffusion control limit. Therefore, independent measurement of the rate coefficient of step R5 would resolve the question of whether the hypothetically mentioned back reaction of step R4 can be confirmed or not. Unfortunately, neither the rate coefficient of step R5 is available from the
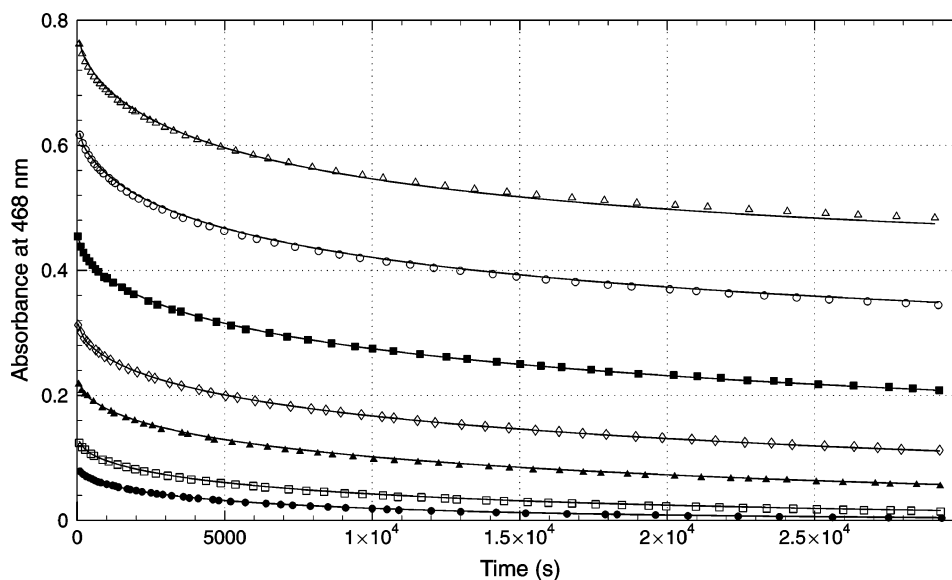

Figure 2. Measured (symbols) and calculated (solid lines) kinetic curves at the wavelength of 468 nm. [S$_4$O$_6^{2-}$]$_0$ = 0.07 mM, [I$^-$]$_0$ = 0 mM, pH = 4.55, [I$_2$]$_0$ = 0.114(●), 0.174(□), 0.302(▲), 0.425(◇), 0.613(■), 0.852(○), 1.049(△) mM.
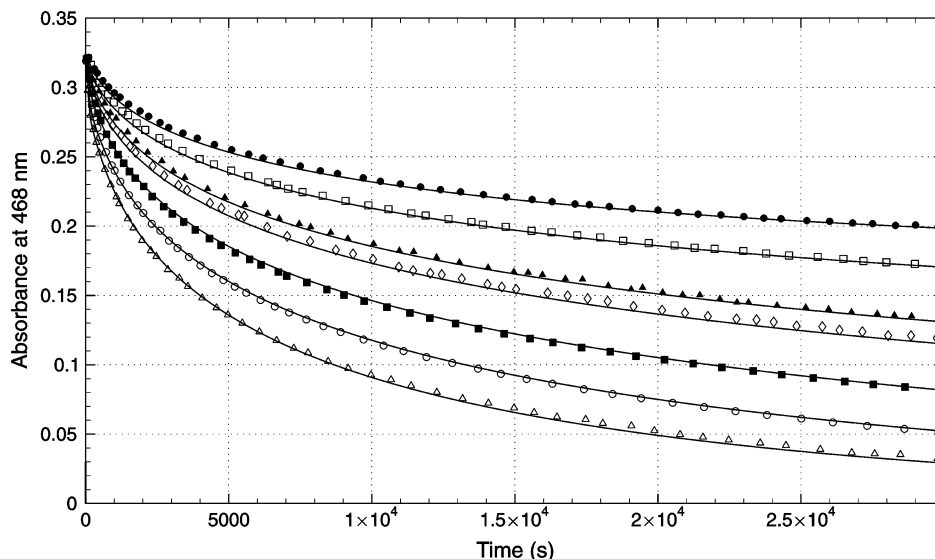
Figure 3. Measured (symbols) and calculated (solid lines) kinetic curves at the wavelength of 468 nm. $[I_2]_0 = 0.449$ mM, $[I^-]_0 = 0$ mM, pH = 5.55, $[S_4O_6^{2-}]_0 = 0.03(\bullet)$, $0.04(\square)$, $0.06(\blacktriangle)$, $0.07(\diamond)$, $0.1(\blacksquare)$, $0.14(\bigcirc)$, $0.2(\triangle)$ mM.
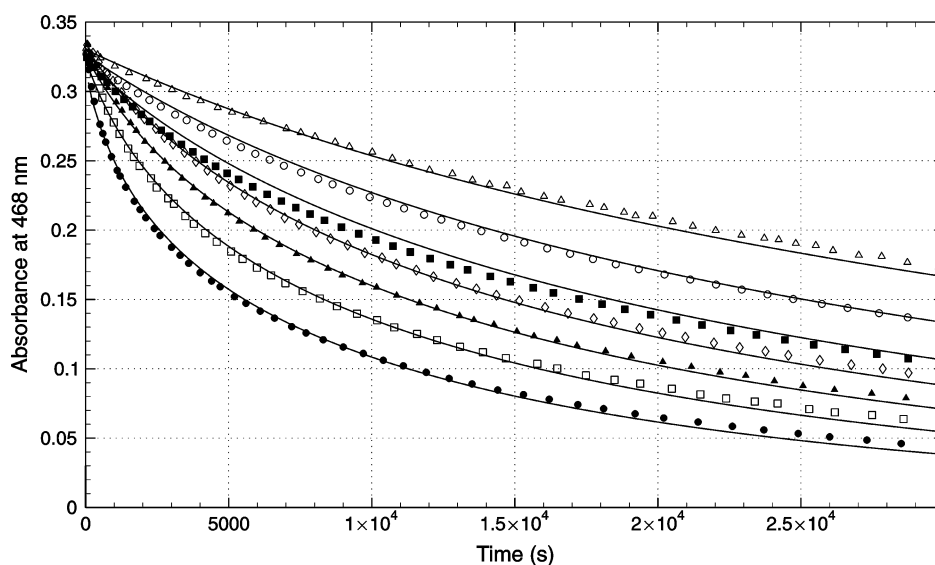

Figure 4. Measured (symbols) and calculated (solid lines) kinetic curves at the wavelength of 468 nm. $[I_2]_0 = 0.435$ mM, $[S_4O_6^{2-}]_0 = 0.2$ mM, pH = 4.85, $[I^-]_0 = 0.1(\bullet)$, $0.3(\square)$, $0.5(\blacktriangle)$, $0.7(\diamond)$, $1.0(\blacksquare)$, $1.4(\bigcirc)$, $2.0(\triangle)$ mM.

literature nor can it be expected to be determined because of the difficulty of preparation of $S_2O_3I^-$. Therefore, for lack of independent experimental confirmation we would tend to not include the back reaction of step R4 into the final model. For the sake of completeness, the hydrolysis of $S_2O_3I^-$ was also considered

$$S_2O_3I^- + H_2O \rightarrow S_2O_3OH^- + I^- + H^+ \qquad (9)$$

but was found to be unnecessary if step R5 is included. Replacing step R5 with eq 9 could, however, be done successfully, and the same can be said about k_9 as was discussed about k_{R5}. It has to be a fast reaction $k_9 \geq 0.1$ s^{-1}, but inclusion of k_{-R4} introduces total correlation between parameters k_9 and k_{-R4}, which would result in an upper limit of $k_9 = 80$ s^{-1} for the rate coefficient of the spontaneous hydrolysis of $S_2O_3I^-$ preventing to exceed the diffusion control limit with k_{-R4}. It clearly means that the fate of $S_2O_3I^-$ is to be converted rapidly into either $S_2O_3OH^-$ or HSO_3^-, but our measurements do not provide a solid basis to choose unambiguously between them. We are, however, in favor of step R5 because it coincides with Awtrey

and Connick's explanation[6] of the formation of sulfate in both the thiosulfate—iodine reaction in high iodine excess and at low iodide concentration, and with the fact that the rate coefficient of the direct reaction of thiosulfate with $S_2O_3I^-$ determined by Scheper and Margerum[9] is much higher than k_{R5}, resulting in only trace amounts of sulfate during a normal iodometric titration process.

Step R6 is also a rapid reaction that converts $S_2O_3OH^-$ into HSO_3^-. The individual rate coefficient of k_{R6} cannot be determined from the experiments presented here. Any value higher than 10^2 M^{-1} s^{-1} leads to the same final results. Therefore, we have set k_{R6} to an arbitrary but reasonable value of 10^5 M^{-1} s^{-1}.

Step R7 is the well-known very rapid oxidation of sulfite by iodine. The rate coefficient of this reaction was determined by Yiin and Margerum.[17] Therefore, we fixed the value of k_{R7} to 3.1×10^9 M^{-1} s^{-1}.

For the sake of completeness, the iodine hydrolysis was also considered.

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+ \qquad (10)$$
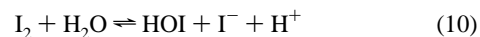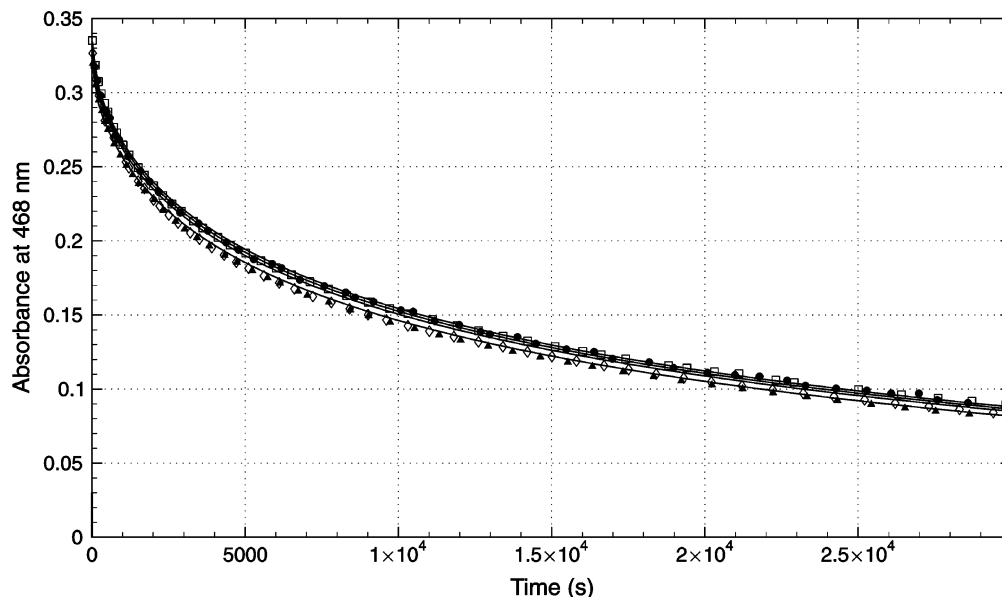
Figure 5. Measured (symbols) and calculated (solid lines) kinetic curves at the wavelength of 468 nm. $[I_2]_0 = 0.449$ mM, $[S_4O_6^{2-}]_0 = 0.1$ mM, $[I^-]_0 = 0$, pH = 4.55(●), 4.85(□), 5.25(▲), 5.55(◇).

This reaction was studied by several authors,[19,20] and all of the rate coefficients, including the hydroxide-driven hydrolysis of iodine, are well-known. Because no effect of this step on the fitted kinetic curves in the pH range studied here is realized, we did not include this process in the final model.

Table 2 summarizes the fitted and fixed rate coefficients used in the evaluation procedure. Figures 2−5 clearly demonstrate that the model is capable of providing a good description of the experimental data over wide concentration ranges of the reactants as well as that of the iodide ion. The average deviation between the measured and calculated data was found to be 0.0039, which is close to the experimentally achievable limit of the error of the spectrophotometer.

For the sake of completeness, it should also be mentioned that it is not necessary to suppose that the back reaction is fast to obtain meaningful results from a mathematical point of view. If the initial value of k_{-R2} is decreased to 10^3 M^{-1} s^{-1}, then the total correlation between parameters k_{-R2}, k_{R3}, and k_{R4} disappears, and the average deviation will decrease slightly to 0.0036 absorbance units with k_{R2}, k_{-R2}, k_{R3}, and k_{R4} as 6.57 M^{-1} s^{-1}, 144 M^{-1} s^{-1}, 9.15×10^{-4} s^{-1}, and 0.504 M^{-1} s^{-1}, respectively. The main difference between the two parameter sets is that $S_4O_6I^-$ accumulates during the reaction with the latter parameter set, resulting in $S_2O_3I^-$ and $S_2O_3OH^-$ as end products in high tetrathionate excess in a longer time scale. Accumulation of these species has already been postulated by Awtrey and Connick[10] to account for the unexpected iodide dependence of the apparent rate coefficients. Therefore, we have tried to seek, in the ultraviolet range, spectral evidence of an absorbing species other than iodine, triiodide, iodide, and tetrathionate produced during the reaction. Unfortunately, all of these efforts have failed. Therefore, we have concluded that, in agreement with Awtrey and Connick's result, the initiating equilibrium is established rapidly and shifted far to the left, but the dependence of the apparent rate coefficient (k_a) cannot be explained by accumulation of $S_2O_3I^-$ and $S_2O_3OH^-$.

Formal Kinetics. As one may easily notice, the steady-state approximation can be applied to HSO_3^-, $S_2O_3I^-$, $S_2O_3OH^-$, and $S_4O_6I^-$ without any restriction because all of them are only short-lived intermediates of the reaction. A straightforward derivation leads to the following formal rate equation

$$-\frac{1}{7}\frac{dT_{I_2}}{dt} = [S_4O_6^{2-}]T_{I_2}\frac{k_{R2}k_{R3} + k_{R2}k_{R4}[I^-]}{k_{R3} + (k_{-R2} + k_{R3}K + k_{R4})[I^-] +} $$
$$K(k_{-R2} + k_{R4})[I^-]^2 \qquad (11)$$

where K is the formation constant of triiodide ion and $T_{I_2} = [I_2] + [I_3^-]$. Taking into consideration that $k_{-R2} \gg k_{R4}$, $k_{-R2} \gg k_{R3}K$, eq 11 can be reduced to

$$-\frac{1}{7}\frac{dT_{I_2}}{dt} = [S_4O_6^{2-}]T_{I_2}\frac{k_{R2}k_{R3} + k_{R2}k_{R4}[I^-]}{k_{R3} + k_{-R2}[I^-] + Kk_{-R2}[I^-]^2} \qquad (12)$$

If $[I^-] \gg k_{R3}/k_{-R2} = 2.1 \times 10^{-5}$ M, then eq 12 can be simplified further to

$$-\frac{1}{7}\frac{dT_{I_2}}{dt} = k_{app}\frac{[S_4O_6^{2-}]T_{I_2}}{[I^-]} \qquad (13)$$

where

$$k_{app} = \frac{1 + \dfrac{k_{R4}}{k_{R3}}[I^-]}{\dfrac{k_{-R2}}{k_{R2}k_{R3}} + K\dfrac{k_{-R2}}{k_{R2}k_{R3}}[I^-]} \qquad (14)$$

This latter expression entirely coincides with Awtrey and Connick's result, and with certain restrictions eq 13 may be applied for estimating the rate coefficients of individual kinetic curves in both the presence and absence of the iodide ion. It, however, also indicates that the apparent rate coefficient obtained from eq 13 has to depend on the concentration of iodide because

$$\lim_{[I^-]\to 0} k_{app} = \frac{k_{R2}k_{R3}}{k_{-R2}} \approx 4.1 \times 10^{-5} \text{ s}^{-1} \qquad (15)$$

and

$$\lim_{[I^-]\to\infty} k_{app} = \frac{k_{R2}k_{R4}}{Kk_{-R2}} \approx 3.6 \times 10^{-5} \text{ s}^{-1} \qquad (16)$$

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Although the effect of iodide concentration on the apparent rate coefficient is not so pronounced in our experimental circumstances as compared to that found in Awtrey and Connick's work,[10] our kinetic model provides a reasonable explanation for the iodide dependence of the apparent rate coefficient obtained from eq 13.

Furthermore, eq 11 also enlightens two important consequences of the kinetic model. First, at the beginning of the reaction, without initial addition of the iodide ion the spontaneous hydrolysis of iodine (10^{-4} M) itself yields an approximate value of 10^{-6} M for the concentration of iodide, where the simplified rate equation is no longer valid. In this case, eq 11 can be simplified to

$$-\frac{1}{7}\frac{dT_{I_2}}{dt} = [S_4O_6^{2-}]T_{I_2}k_{R2} \tag{17}$$

It is clear that k_{R2} can be determined independently from the early stages of the reaction in the absence of the iodide ion. Second, eq 11 also strengthens the central role of step R4 because if k_{R4} is considered to be 0, then at high initial iodide concentration eq 11 could be simplified to

$$-\frac{1}{7}\frac{dT_{I_2}}{dt} = \frac{[S_4O_6^{2-}]T_{I_2}}{[I^-]}\frac{k_{R2}k_{R3}}{k_{-R2} + Kk_{-R2}[I^-]} \approx \frac{[S_4O_6^{2-}]T_{I_2}}{[I^-]^2}\frac{k_{R2}k_{R3}}{Kk_{-R2}} \tag{18}$$

Such an effective second-order inhibition by the iodide ion has never been observed either by Awtrey and Connick or by us.

Conclusions

In this paper, we have shown, in agreement with a previous study,[10] that the iodine−tetrathionate reaction proceeds via an intermediate proposed to be $S_4O_6I^-$. We have confirmed Awtrey and Connick's early result that this intermediate is equilibrated rapidly with the iodide ion and the equilibrium is shifted far to the left. It has also been demonstrated that the triiodide formation in itself is insufficient to describe the iodide inhibition of the reaction. A new, reasonable reaction has been suggested to account for the iodide dependence of the title reaction quantitatively. Our suggested kinetic model perfectly reflects the behavior of the system in both the absence and presence of iodide and provides an interpretation of the complexity of the kinetics and the mechanism of the tetrathionate−iodine reaction noted by Awtrey and Connick. On the basis of the proposed kinetic model, we have also provided a sound explanation of the dependence of the apparent rate coefficient on the iodide concentration obtained from eq 13 by an individual curve-fitting method. The most important consequence of our work is that there is no need to assume a species accumulated during the reaction, as was suggested as a possible interpretation in the early work,[10] to account for the unusual iodide dependence of the apparent rate coefficient.

It should also be mentioned that any simplified evaluation procedure, based solely on initial rate studies and on dependencies of the apparent rate coefficients determined individually for each kinetic curve, would be insufficient to obtain a reliable mechanism that is able to explain all of the most important characteristics of the system. Therefore, it is strongly recommended to use recently available evaluation procedures and computational techniques including the simultaneous curve-fitting method to elucidate the mechanism of an unknown chemical system.

Supporting Information Available: The measured and calculated absorbances of all of the kinetic curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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