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Complex Kinetics of a Landolt-Type Reaction: The Later Phase of the Thiosulfate–Iodate Reaction

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The thiosulfate–iodate reaction has been studied spectrophotometrically in slightly acidic medium at 25.0 ± 0.1 °C in acetate/acetic acid buffer by monitoring the absorbance at 468 nm at the isosbestic point of iodine–triiodide ion system. The formation of iodine after the Landolt time follows a rather complex kinetic behavior depending on the pH and on the concentration of the reactants as well. It is shown that the key intermediate of the reaction is I_2O_2 , its equilibrium formation from the well-known Dushman reaction along with their further reactions followed by subsequent reactions of HOI , HIO_2 , $S_2O_3OH^-$, and $S_2O_3I^-$ adequately accounts for all the experimentally measured characteristics of the kinetic curves. A 19-step kinetic model is proposed and discussed with 13 fitted and 7 fixed parameters in detail.

Introduction

The sulfite–iodate reaction has long been known as a classical type of clock reaction since Landolt's original discovery.¹ The qualitative picture of the reaction has also been well-accepted, iodate relatively slowly oxidizes sulfite into sulfate accompanied by the formation of iodide as a result of the reduction of iodate. Formation of iodide, however, opens up the route to the appearance of the Dushman reaction² in which the amount of iodine formed is quickly³ removed as long as sulfite is present in the reaction system. Once the reducing agent sulfite is completely used up, iodine starts to accumulate, indicating the end of the so-called Landolt time. The concentration dependence of the Landolt time has been studied intensively in the past^{4–6} but resulted in different relationships with regard to the concentration of the reactants. Recent studies,^{7,8} however, clearly showed that these deviations arose only from the different experimental conditions applied and a general complex formula exists for the concentration dependence of the Landolt time.

In general, it is also expected if sulfite is replaced with a different reducing agent that can react with iodate relatively slowly but rapidly reduces iodine, then the system in question behaves as a Landolt-type reaction as well. Eggert and Scharnow have already reported that among the possible simple inorganic oxyanions only thiosulfate fulfills this criterion.⁹ In the case of $Fe(CN)_6^{4-}$ and AsO_3^{3-} their oxidation by iodine may be slower than their reactions with iodate in certain experimental conditions; therefore, the Landolt effect (sudden appearance of the $I_2 + I^- \rightleftharpoons I_3^-$ equilibrium) may already be manifested in the presence of an appreciable fraction of the reducing agent.⁹ Though the thiosulfate and sulfite ions were classified in the same group of Landolt-type reactions the formation of iodine after the Landolt time has never been studied in detail. The fact that in the sulfite–iodate reaction only the Dushman reaction is responsible for the formation of iodine after the Landolt time but in the thiosulfate–iodate reaction the Dushman reaction is

perturbed by the noninert tetrathionate ion, may result in a completely different kinetic behavior.

The Landolt reaction has been brought into the focus of interest by searching new chemical oscillators in the mid-1980s. Often the original Landolt reaction perturbed by suitable components such as ferrocyanide, thiosulfate resulted in oscillations in a continuously fed stirred tank reactor (CSTR).^{10,11} Even the very rare large amplitude pH-oscillation phenomenon has also been found in the thiosulfate perturbation of the Landolt reaction in batch system.¹² The skeleton mechanism of these combined systems has been accepted^{13,14} and even a temperature oscillation could be explained in case of the iodate–sulfite–thiosulfate system.¹⁵ More recently, these systems are thoroughly studied to produce different spatiotemporal structures and may thus have potential applications in designing chemical waves, Turing structures, and even pH responsive gels with rhythmical motions.^{16–19} Therefore, to gain deeper insight into the intimate details of the Landolt reaction perturbed by thiosulfate we decided to investigate the later phase of thiosulfate–iodate reaction. Although the detailed kinetics and the mechanism of the thiosulfate–iodate reaction was already studied 80 years ago by Rieder,²⁰ recent studies have pointed out^{11,12,14} that the reaction cannot exclusively produce tetrathionate, sulfite has to be formed as well to explain adequately the batch pH oscillatory behavior.

Experimental Section

Materials and Buffers. All the chemicals (sodium thiosulfate, potassium iodate, potassium iodide, acetic acid, sodium acetate) were of the highest purity available commercially and used without further purification. The stock solutions were freshly prepared each day from double-distilled and twice ion-exchanged water. The concentration of the thiosulfate was determined prior to each run by standard iodometric titrations. The pH of the solutions was regulated between 3.34 and 4.24 by acetic acid/acetate buffer taking the pK_a of acetic acid as 4.55.²¹ The acetate concentration was always kept constant as 0.1 M, and the pH was adjusted by the necessary amount of acetic acid. The temperature of the reaction vessel was maintained at 25.0 ± 0.1 °C. The initial concentrations of the

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[‡] This paper is dedicated to the memory of Dénes Varga, who passed away after finishing the experimental work of this system.

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TABLE 1: Fitted and Fixed Rate Coefficients of the Proposed Kinetic Model^a

step	rate equation	parameter
(R1)	$k_{R1}[I_2][I^-]$	$5.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
(-R1)	$k_{-R1}[I_3^-]$	$8.5 \times 10^6 \text{ s}^{-1}$
(R2)	$k_{R2}[S_2O_3^{2-}][IO_3^-]$	$(2.84 \pm 0.17) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$
(R3)	$k_{R3}[S_2O_3^{2-}][HIO_2]$	$k_{R3}/k_{R10} = 6.65 \pm 1.20$
(R4)	$k_{R4}[S_2O_3^{2-}][HOI]$	$k_{R4}/k_{R9} = 8.76 \pm 0.48$
(R5)	$k_{R5}[S_2O_3^{2-}][HOI]$	$k_{R5}/k_{R9} = 2.55 \pm 0.16$
(R6)	$k_{R6}[IO_3^-][I^-][H^+]^2$	$K_{R6} = k_{R6}/k_{-R6} = 100 \text{ M}^{-3}$
(-R6)	$k_{-R6}[I_2O_2]$	
(R7)	$k_{R7}[S_2O_3^{2-}][I_2O_2]$	$K_{R6}k_{R7} = (5.74 \pm 0.06) \times 10^9 \text{ M}^{-4} \text{ s}^{-1}$
(R8)	$k_{R8}[I^-][I_2O_2]$	$K_{R6}k_{R8} = (4.26 \pm 0.02) \times 10^8 \text{ M}^{-4} \text{ s}^{-1}$
(R9)	$k_{R9}[I^-][HOI]$	$3.67 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
(R10)	$k_{R10}[S_2O_3^{2-}][I_2]$	$\leq 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
(R11)	$(k_{R11} + k'_{R11}[H^+])[S_2O_3^{2-}][S_2O_3OH^-]$	$k_{R11} = 50 \text{ M}^{-1} \text{ s}^{-1}$; $k'_{R11} = 2.5 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$
(R12)	$k_{R12}[S_2O_3OH^-][I_2]$	$(1.94 \pm 0.06) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$
(R13)	$k_{R13}[S_2O_3OH^-][IO_3^-][H^+]$	$71.8 \pm 1.2 \text{ M}^{-2} \text{ s}^{-1}$
(R14)	$k_{R14}[S_2O_3I^-][IO_3^-]$	$3.58 \pm 0.12 \text{ M}^{-1} \text{ s}^{-1}$
(R15)	$k_{R15}[S_2O_3I^-]^2[I^-]$	$7.96 \pm 0.56 \text{ M}^{-2} \text{ s}^{-1}$
(R16)	$k_{R16}[S_4O_6^{2-}][I_2]$	$(8.41 \pm 0.12) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$
(-R16)	$k_{-R16}[S_4O_6I^-][I^-]$	$K_{R16} = k_{R16}/k_{-R16} = 1.92 \times 10^{-7}$
(R17)	$k_{R17}[S_4O_6I^-]$	$k_{R17}/k_{-R16} = (4.9 \pm 0.1) \times 10^{-3} \text{ M}$
(R18)	$k_{R18}[HSO_3^-][I_2]$	$3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
(R19)	$k_{R19}[HSO_3^-][HIO_2]$	$k_{R19}/k_{R18} = 6.32 \pm 0.35$

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

reactants for all the 108 kinetic runs are collected in Table 1 of the Supporting Information.

Methods and Instrumentation. The reaction was followed by a Zeiss S10 diode array spectrophotometer in the visible range without using the deuterium lamp to prevent the photochemical decomposition of tetrathionate at a longer time scale.²² The reaction has been carried out in a standard quartz cuvette equipped with magnetic stirrer and Teflon cap having 1 cm optical path. The buffer components were delivered from a pipet first followed by the addition of thiosulfate and iodide (if necessary) solutions. The stirring rate was then controlled at 750 rpm to provide sufficiently fast (within 1 s) mixing of the reactants before injecting the iodate solution from a fast delivery pipet. The spectra of the reacting solution at the wavelength range of 400–700 nm was acquired up to 15 000–50 000 s.

Data Treatment. MRA studies have shown²³ that the only absorbing species in the visible range are iodine and triiodide ion. Therefore, the simultaneous evaluation of the kinetic curves was carried out at the isosbestic point of I_2 – I_3^- system at 468 nm by the program package ZiTa.²⁴ The molar absorbance of both species was found to be $750 \text{ M}^{-1} \text{ cm}^{-1}$ at this wavelength. Originally, each kinetic run contained more than 400 absorbance–time data pairs; therefore, it was necessary to reduce the number of time points (50–60) to avoid unnecessary time-consuming calculations. The essence of this method has already been described elsewhere.²⁵ To obtain the kinetic model and the rate coefficients, an absolute fitting procedure has been chosen to minimize the average deviation between the measured and calculated absorbance. Altogether almost 5800 experimental

points from the 108 kinetic series were used for the simultaneous evaluation. Our quantitative criterion for an acceptable fit was that the average deviation for the absolute fit approach 0.008 (in case of relative average deviation it corresponds to approximately 2.5%), which is close to the experimentally achievable limit of error taking the complexity of the kinetic curves into account (see later).

Results

Preliminary Observations. The most important characteristics of the kinetic curves can be summarized as follows:

- Figure 1 shows the effect of the initial concentration of thiosulfate on the length of the Landolt time as well as on formation of total amount of iodine ($[I_2] + [I_3^-]$) at the later phase of the reaction. First, the insert indicates that the induction period decreases with increasing thiosulfate concentration within the range studied. Second, as thiosulfate disappears from the reacting solution the concentration of iodine starts to increase. At low initial thiosulfate concentrations, however, the monotonous formation of the total amount of iodine goes through an inflection point. At higher thiosulfate concentrations the total amount of iodine reaches a maximum followed by a decrease in its concentration.

- Figure 2 indicates the effect of the iodate concentration on the formation of iodine. It is easily seen that the Landolt time significantly decreases by an increase of the initial iodate concentration. The shape of the absorbance–time curves also varies; at low iodate concentration the formation of the total amount of iodine shows a saturation-like kinetic curves, but at

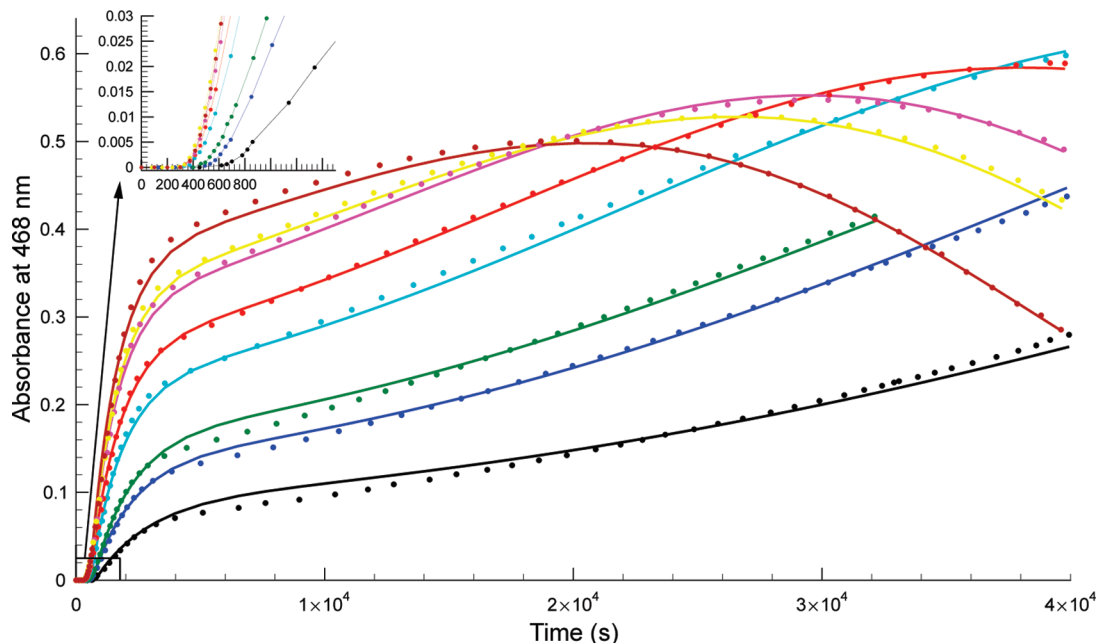


Figure 1. Measured (dots) and calculated (solid lines) absorbance–time curves at pH = 3.64 and $[\text{IO}_3^-]_0 = 0.004$ M in the absence of initially added iodide ion. $[\text{S}_2\text{O}_3^{2-}]_0/\text{mM} = 2.0$ (black), 3.0 (blue), 4.0 (green), 5.0 (cyan), 6.0 (red), 7.4 (magenta), 8.4 (yellow), and 10.0 (brown). The inset shows the initial phase of the reaction.

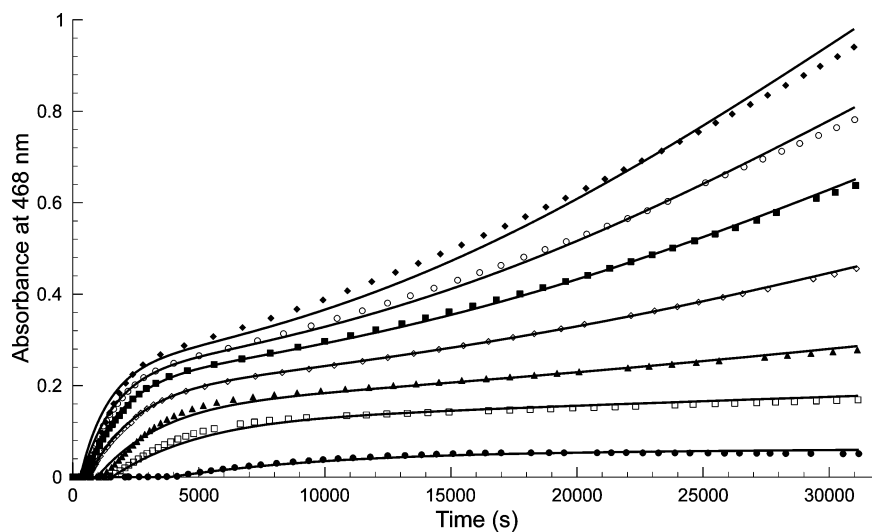


Figure 2. Measured (symbols) and calculated (solid lines) absorbance–time curves at pH = 3.94 and $[\text{S}_2\text{O}_3^{2-}]_0 = 0.0057$ M in the absence of initially added iodide ion. $[\text{IO}_3^-]_0/\text{mM} = 2.0$ (●), 3.0 (□), 4.0 (▲), 6.0 (◇), 8.0 (■), 10.0 (○), 12.0 (◆).

higher iodate concentration the increase of $[\text{I}_2] + [\text{I}_3^-]$ goes through an inflection point.

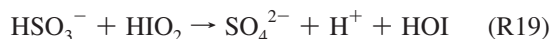
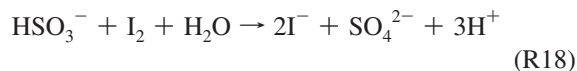
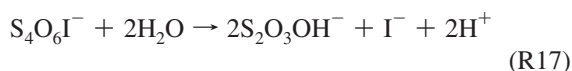
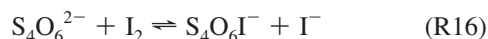
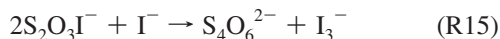
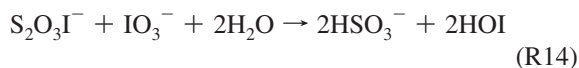
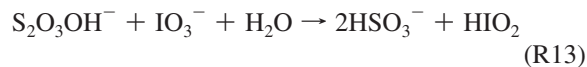
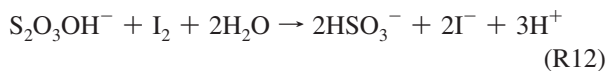
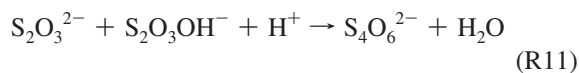
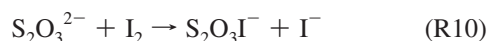
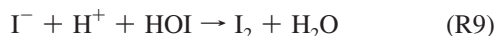
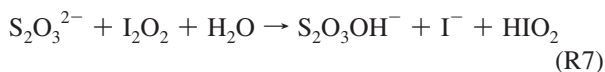
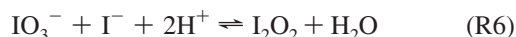
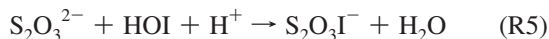
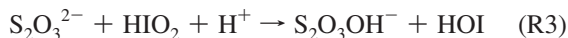
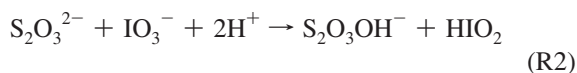
• Figure 3 depicts the pH dependence of the formation of the total amount of iodine. As seen, the Landolt time decreases with decreasing pH. At higher pHs the iodine formed after the Landolt time levels off at 2:1 thiosulfate–iodate initial ratio. With a decrease of pH the amount of iodine formed increases and the absorbance–time curves first go through an inflection point. A further decrease in pH changes the shape of the measured kinetic traces and results in a maximum of the concentration of total amount of iodine as a function of time.

• Figure 4 shows the effect of the initially added iodide ion on the Landolt time as well as on the shape of the kinetic traces. As easily seen, the Landolt time decreases and the amount of iodine formed significantly increases with increasing iodide concentration.

Proposed Kinetic Model. To build up the kinetic model, we have chosen the following set of species that most likely

participate in the reaction mechanism. This group consists of the reactants thiosulfate and iodate, the products sulfate, iodide, and tetrathionate, and finally the intermediates such as hydrogen sulfite, iodosic acid, hypoiodous acid, I_2O_2 , $\text{S}_2\text{O}_3\text{OH}^-$, $\text{S}_4\text{O}_6\text{I}^-$, and $\text{S}_2\text{O}_3\text{I}^-$ and the species H^+ , OH^- , and H_2O that are always present in an aqueous medium. After that, all the possible mono- and bimolecular steps of these species were considered along with their H^+ -catalyzed pathways. During the fitting procedure, the steps, the rate coefficients of which became insensitive on the average deviation, were omitted step by step. This method has been applied successfully in several cases of our previous work.^{25–28} After long but straightforward systematic reduction, the following model has emerged.





The rapid de- and reprotonation process E1 was taken into account with known equilibrium constant to follow the slight change in pH during the reaction. This acid dissociation equilibrium may be regarded as an auxiliary process necessary for the detailed calculation, but it is not a central part of the proposed model. Table 1 contains the fitted and fixed kinetic

parameters used in the simultaneous evaluation of the kinetic curves. The average deviation was found to be 0.008 absorbance unit (AU). The Supporting Information containing all the measured and calculated kinetic curves indicates a sound description of the measured curves by the proposed model.

Discussion

Step R1 is the rapid equilibrium formation of triiodide ion investigated by several authors.^{29,30} The rate coefficients of the forward and reverse reactions were set to $k_{\text{R1}} = 5.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-\text{R1}} = 8.5 \times 10^6 \text{ s}^{-1}$, respectively, to give $\log \beta_{\text{I}_3^-} = 2.83$, where $\beta_{\text{I}_3^-}$ is the formation constant of triiodide ion.²¹

Step R2 is a second-order rate-determining process responsible for the initiation of the reaction that may proceed via a simple oxygen transfer from the iodate molecule to the thiosulfate ion. The surprising result of our calculation is that this reaction turned out to be pH-independent despite the fact that the overall thiosulfate–iodate reaction strongly depends on pH, as found in earlier works.^{14,20} As we shall see later, our result is not contradictory with the previous ones, because step R2 is not the only rate-determining process of the kinetic model proposed. Namely, as the reaction proceeds, more and more iodate is reduced to iodide ion that results in an increase of the concentration of the steady-state intermediate I_2O_2 , which also converts thiosulfate eventually into sulfate and tetrathionate ions. The formation of I_2O_2 , however, depends on the square of $[\text{H}^+]$, meaning that the overall reaction strongly depends on pH as expected.

Step R3 is the fast oxidation of thiosulfate ion by iodosic acid formed in the initiation process. Evidently, this reaction must be much faster than step R2 because of the higher reactivity of thiosulfate toward iodosic acid. We found the rate coefficient of this reaction to be in total correlation with that of step R10. The reason for the correlation can be understood as follows. Since iodine formed via a rapid reaction (step R9) and one of the main source of hypoiodous acid is step R3 at the early phase of the reaction, iodine has to be removed quickly so as not to accumulate during the Landolt time. The ratio of k_{R3} and k_{R10} was found to be 6.65 ± 1.20 if k_{R10} is not higher than $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

Step R4 is a relatively fast formal oxygen transfer process to oxidize thiosulfate with hypoiodous acid. The individual rate coefficient of this reaction cannot be determined from our experiments. The calculation showed that there is a total correlation between the parameters k_{R4} , k_{R5} , and k_{R9} ; therefore, only the ratio of $k_{\text{R4}}/k_{\text{R9}}$ and $k_{\text{R5}}/k_{\text{R9}}$ could be calculated. Chemically it means that hypoiodous acid is a reactive intermediate in the present system having relatively low steady-state concentration. Since k_{R9} was determined independently³¹ as $3.67 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and our calculation showed that $k_{\text{R4}}/k_{\text{R9}}$ is 8.76 ± 0.48 , we could calculate a value of $(3.2 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for k_{R4} , indicating that this reaction is close to the diffusion controlled limit as expected by the fact that iodine also rapidly oxidizes thiosulfate.³²

Step R5 is a competitive process with step R4 that leads to the formation of $\text{S}_2\text{O}_3\text{I}^-$ instead of hypoiodous acid and $\text{S}_2\text{O}_3\text{OH}^-$. This process is a formal electrophilic I^+ transfer frequently occurring in different oxidation reactions of hypohalogenous acids.^{33,34} It may seem surprising that hypoiodous acid can react with thiosulfate via an oxygen transfer (step R4) and a I^+ transfer (step R5) pathway simultaneously as well, but this result is not a unique feature of the kinetic behavior of hypohalogenous acid. Fogelman et al. have already reported³³ that hypochlorous acid reacts with sulfite via parallel oxygen

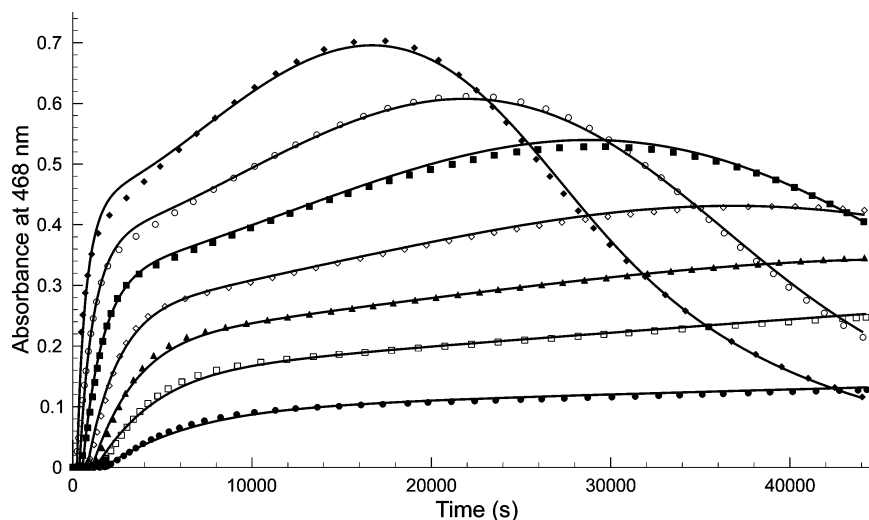


Figure 3. Measured (symbols) and calculated (solid lines) absorbance–time curves at $[\text{IO}_3^-]_0 = 0.004 \text{ M}$ and at $[\text{S}_2\text{O}_3^{2-}]_0 = 0.008 \text{ M}$ in the absence of initially added iodide ion. pH = 4.24 (●), 4.09 (□), 3.94 (▲), 3.79 (◇), 3.64 (■), 3.49 (○), 3.34 (◆).

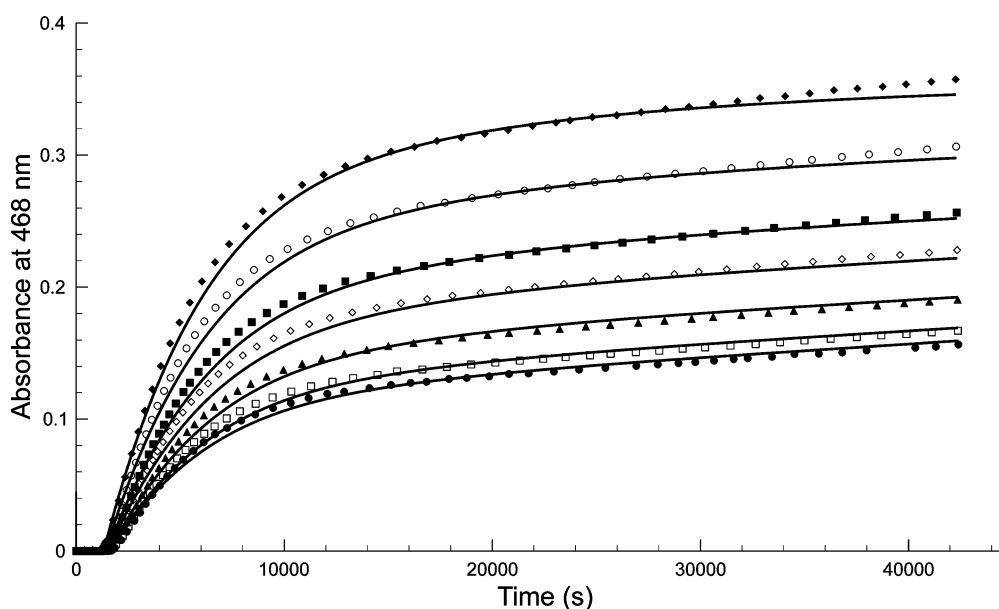


Figure 4. Measured (symbols) and calculated (solid lines) absorbance–time curves at $[\text{IO}_3^-]_0 = 0.004 \text{ M}$, $[\text{S}_2\text{O}_3^{2-}]_0 = 0.0077 \text{ M}$ and pH = 4.24 in the presence of initially added iodide ion. $[\text{I}^-]_0/\text{mM} = 0.2$ (●), 0.3 (□), 0.5 (▲), 0.7 (◇), 0.9 (■), 1.2 (○), 1.5 (◆).

transfer and Cl^+ transfer to produce sulfate and chloride eventually. On the basis of this analogy, one may expect that hypoiodous acid may behave in the same way in the title reaction. Our calculation indicated that $k_{\text{R5}}/k_{\text{R9}}$ is 2.55 ± 0.16 , which means that one can calculate $(9.4 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for k_{R5} .

Step R6 is the well-known equilibrium suggested by several researchers³⁵ to interpret many experimentally found aspects of the Dushman reaction. We found that neither the rate coefficient of the forward nor that of the reverse reaction could be determined independently from our measurements. This process is rapidly equilibrated and provides I_2O_2 as a steady-state intermediate. We set an arbitrary $K_{\text{R6}} = k_{\text{R6}}/k_{-\text{R6}} = 100 \text{ M}^{-3}$ value that is able to maintain the concentration of I_2O_2 in a sufficiently low level under our experimental conditions.

Step R7 is the other rate-determining step of the kinetic model and also responsible for the effect of pH on the Landolt time. Evidently, this route is opened up when the concentration of iodide reaches a certain level (at pH = 4.0 the rate of step R7 is equal to that of step R1 at $[\text{I}^-] \approx 0.0013 \text{ M}$) and gradually overtakes the governing role as the reaction proceeds. We can

only determine the value of $5.74 \times 10^9 \text{ M}^{-4} \text{ s}^{-1}$ for $K_{\text{R6}}k_{\text{R7}}$. It is also interesting to note that this is one of the parameters that could be determined the most precisely. The underlying chemistry seems to be clear, though at the early stages of the reaction the role of this route is negligible, the increase in the concentration of the product iodide ion increases the importance of this pathway during the reaction and gradually takes over the role of step R1. Chemically, it means that step R7 is responsible for the pH dependence of the Landolt time.

Step R8 is the other important reaction of the intermediate I_2O_2 that has a dual role in determining the kinetics of the reaction. Iodide ion competes with thiosulfate to react with I_2O_2 and therefore not only partly affects the length of the Landolt time but also has a significant contribution to the later phase of the reaction to produce iodine via hypoiodous acid. One may also notice that combining step R8 with steps R9 and R12 results in an autocatalytic production of iodine. This feature is only partly manifested in some experimental curves, where the maximum amount of iodine is reached via an absorbance–time curve having an inflection point. Our calculation showed that

only $k_{R6}k_{R8}$ can be determined from our experiments which was found to be $4.26 \times 10^8 \text{ M}^{-4} \text{ s}^{-1}$.

Step R9 is responsible for the formation of iodine. The rate coefficient of this reaction was established³¹ previously as $3.67 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; therefore, we used this value as a fixed parameter during the calculation procedure.

Step R10 is the initiating process of the well-known fast thiosulfate–iodine reaction.³² The absolute value of this rate coefficient cannot be determined from our experiments, but total correlation was found between k_{R3} and k_{R10} if the latter one is not higher than $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Actually, our calculations have provided a slight minimum in the standard deviation if k_{R10} is fixed at $10^6 \text{ M}^{-1} \text{ s}^{-1}$. It is interesting to note that the actual value of this rate coefficient is only slightly lower than that found by Scheper and Margerum for the rate determining step of thiosulfate–iodine reaction.³⁶ Since the decrease in the average deviation (less than 3%) cannot be decisive in determining the absolute value of k_{R10} , we inclined to report only the ratio of k_{R3} and k_{R10} .

Step R11 is also a fast reaction to produce tetrathionate ion from the intermediate $\text{S}_2\text{O}_3\text{OH}^-$. From our experiments we were unable to calculate the individual rate coefficient of this reaction. Other researchers^{37–39} have, however, found that this reaction has a pH-dependent term besides the pH-independent one, and even both rate coefficients were determined.³⁹ Therefore, we have fixed these values k_{R11} and k'_{R11} as $50 \text{ M}^{-1} \text{ s}^{-1}$ and $2.5 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$.

Step R12 is responsible for the slow removal of iodine by $\text{S}_2\text{O}_3\text{OH}^-$ at the later kinetic phase of the reaction. It also means that $\text{S}_2\text{O}_3\text{OH}^-$ has to be a relatively long-lived intermediate under the present experimental conditions. Elimination of this step from the final model would lead to a more than 50% increase in the final average deviation (0.012 absorbance unit) from which we concluded this step to be firmly established. Our investigations in other related systems like the tetrathionate–bromine²⁶ and the tetrathionate–hypochlorous acid²⁷ ones showed that the role of $\text{S}_2\text{O}_3\text{OH}^-$ and $\text{S}_2\text{O}_3\text{X}^-$, where X can be either chlorine or bromine, is commutable in the kinetic model suggested. We have also tried to seek evidence for this fact in the thiosulfate–iodate system with no success. It is therefore concluded that the long-lived intermediate in the thiosulfate–iodate system is $\text{S}_2\text{O}_3\text{OH}^-$.

Step R13 is the other route that removes the long-lived intermediate $\text{S}_2\text{O}_3\text{OH}^-$ by iodate. Our calculations indicated that the rate of this reaction also depends on pH. It follows from the experimental fact that significantly more iodine forms with decreasing pH in excess of iodate. It is easily understood by the help of this pH-dependent reaction since iodosic acid formed in this process will react with HSO_3^- to give HOI (see: step R19 later), which then produces iodine via step R9.

Step R14 has a dual role in the kinetic model because on the one hand it prevents the buildup of $\text{S}_2\text{O}_3\text{I}^-$ and on the other hand in iodate excess it provides hypoiodous acid that produces iodine by its reaction with iodide ion. The rate coefficient of this reaction was found to be $3.58 \pm 0.12 \text{ M}^{-1} \text{ s}^{-1}$.

Step R15 was already proposed by Awtrey and Connick in the thiosulfate–iodine reaction, although they suggested the following rather complicated rate law for this reaction:³²

$$r = k \frac{[\text{S}_2\text{O}_3\text{I}^-]^2 [\text{I}^-]^2}{[\text{I}_3^-]} \quad (1)$$

where k was found to be $5000 \text{ M}^{-2} \text{ min}^{-1}$. In the case of $[\text{I}_2] = 10^{-4} \text{ M}$ bearing in mind that the stability constant of triiodide ion is 660 M^{-1} , we could calculate $1200 \text{ M}^{-2} \text{ s}^{-1}$, which is in

reasonable agreement with our calculated $k_{R15} = 7960 \pm 560 \text{ M}^{-2} \text{ s}^{-1}$ value. The triiodide inhibition suggested by Awtrey and Connick, however, has not been found. It should also be noted that changing the $k_{R5}[\text{S}_2\text{O}_3\text{I}^-]^2[\text{I}^-]$ rate equation by the $k_{R15}[\text{S}_2\text{O}_3\text{I}^-][\text{I}^-]$ would lead to a slightly higher average deviation (0.0095 AU). However, we noticed systematic deviations between the experimental and the calculated kinetic curves especially at larger initial thiosulfate concentrations and lower pHs. We concluded that our results support the rate equation indicated in Table 1 for step R15 rather than any other one.

Step R16 is the well-known initiating equilibrium process of the tetrathionate–iodine reaction in which formal I^+ transfer occurs.^{28,40} Our calculations have provided for k_{R16} a value of $(8.41 \pm 0.12) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. Since we found total correlation between the parameters k_{-R16} and k_{R17} and previously we determined²⁸ this equilibrium constant to be 1.92×10^{-7} , we set k_{-R16} as $4.38 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and calculated k_{R17} (see later).

Step R17 is the hydrolysis of $\text{S}_4\text{O}_6\text{I}^-$ formed in step R16. Although Awtrey and Connick⁴⁰ suggested the following reaction for the hydrolysis of $\text{S}_4\text{O}_6\text{I}^-$



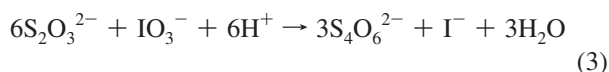
it was already pointed out in our previous work²⁸ that eq 2 can completely be substituted with step R17. The present experiments, however, rather confirm step R17 than eq 2 for the hydrolysis of $\text{S}_4\text{O}_6\text{I}^-$ since inclusion of the latter process would lead to an unacceptably high average deviation (0.0189 AU) in the present system.

Step R18 is the well-known fast reaction between hydrogen sulfite and iodine. This reaction was thoroughly studied by Yiin and Margerum³ and even the rate coefficient of this process was determined to be $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Therefore, we have fixed k_{R18} at this value.

Step R19 is also fast reaction between hydrogen sulfite and iodosic acid producing HOI. We found that k_{R19} is in total correlation with k_{R18} ; therefore, we could only calculate the k_{R19}/k_{R18} ratio. The underlying chemistry is clear; the short-lived intermediate HSO_3^- reacts quickly with iodine and iodosic acid to give the product iodide ion and HOI, respectively. As pointed out earlier, HOI has a decisive role in producing iodine but it has to be controlled as well by step R18. We found the k_{R19}/k_{R18} ratio to be 6.32 ± 0.35 , from which we could calculate $1.96 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for k_{R19} , indicating that this reaction is essentially diffusion controlled.

Finally, we shall point out how the seemingly complicated absorbance–time curves, which reflect the concentration of the total amount iodine formed via the reaction, can easily be explained by the kinetic model proposed. We shall see that iodide ion plays a crucial role to drive the reaction. As long as thiosulfate is not consumed, the concentration of iodide ion increases monotonously because all the iodine is removed by the well-known fast thiosulfate–iodine reaction. Once thiosulfate is completely removed from the reacting solution the concentration of iodine starts to build up as a result of steps R8 and R9, and simultaneously the concentration of iodide ion starts to decrease. These processes are responsible for the relatively fast increase of the total amount of iodine after the Landolt period. It is well-known that at higher iodide concentrations the tetrathionate–iodine reaction is strongly inhibited by iodide ions.^{28,40} The decrease in the iodide concentration therefore opens up this slow reaction that would decrease the concentration of iodine and simultaneously produce iodide ion, but as

long as enough iodate is present in the reaction mixture, it supplies the necessary amount of I_2O_2 via step R8 at a low steady-state concentration level from which iodine can still form at a much slower rate. During this stage of the reaction the main components, iodate and tetrathionate ions, are slowly removed. These changes, therefore, result in a much slower increase of the total amount of iodine compared to the period right after the end of the Landolt time. The shape of the absorbance–time curves at the final stage of the reaction depends on the concentration of tetrathionate and iodate. If tetrathionate is in excess, i.e., the initial thiosulfate–iodate concentration ratio is high, then iodate slowly disappears from the reacting mixture, preventing the formation of iodine via I_2O_2 . It means that tetrathionate eventually consumes all the iodine responsible for decrease of the absorbance at the final stage. It should be noted that in the case of the initial thiosulfate–iodate concentration ratio being larger than 6, no iodine is formed if one takes the following overall equation into account:



The opposite case, when the iodate is in excess over tetrathionate, means that all the reacted iodate molecules are transformed finally into iodine, resulting in leveling off the absorbance–time curves.

Conclusion

This paper elucidates the kinetics and mechanism of the later phase of the thiosulfate–iodate reaction that shows unexpectedly complex kinetic behavior after the Landolt period, where iodine starts to form in appropriate concentration ranges of the reactants. The complexity of the measured kinetic curves clearly suggests that no simplified evaluation (individual exponential curve fitting, initial rate studies, isolation method, etc.) ever exists to be able to lead to a proposal of a reliable kinetic model of such systems. As we already pointed out in our previous work,⁴¹ although it evidently takes significantly more time, the choice of the simultaneous evaluation of the kinetic curves is more preferable than the simplified evaluation techniques even in the case of relatively simple chemical systems. In the case of a complicated system, like the thiosulfate–iodate reaction, however, the simultaneous evaluation of the kinetic curves is the only way to unravel its kinetics and mechanism.

An important remark should, however, be emphasized. As seen, the proposed kinetic model, almost perfectly describes the measured kinetic curves at a relatively wide concentration range of the reactants but in some cases it is not able to predict properly the length of the Landolt period. (See some kinetic curves in the Supporting Information, e.g., Figures S3A, S5B, and S5C.) This inaccuracy emerges from the fact that at large initial thiosulfate concentrations the measured absorbance signal is too small compared to all the other cases (evidently, with a huge excess of thiosulfate no iodine forms at all). It means that further experiments are required to explore the thiosulfate–iodate reaction at higher thiosulfate concentrations but they cannot be simply done by following the evolution of iodine concentration.

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

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