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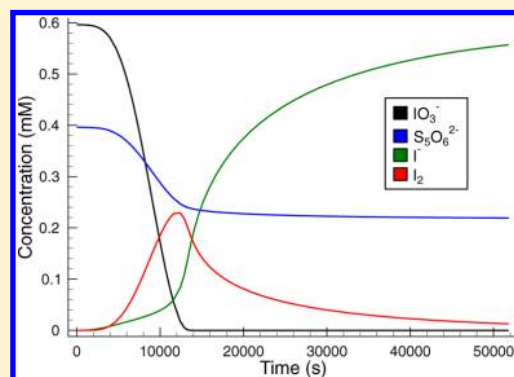
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A Possible Candidate to Be Classified as an Autocatalysis-Driven Clock Reaction: Kinetics of the Pentathionate–Iodate Reaction

Li Xu and Attila K. Horváth*

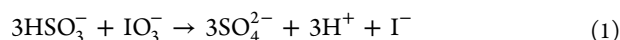
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ABSTRACT: The pentathionate–iodate reaction has been investigated by spectrophotometrically monitoring the formation of the total amount of iodine at 468 nm in the presence of phosphoric acid/dihydrogen phosphate buffer. We noticed that iodine forms only after a fairly long time lag, and the inverse of time necessary to produce a certain amount of iodine is linearly proportional to the initial concentration of iodate ion and the square of the hydrogen ion concentration, while depending complexly on the concentration of substrate pentathionate. This reaction can therefore be treated as a clock reaction but differs from the original Landolt reaction in the sense that substrate pentathionate and the clock species iodine coexist for a relatively long time—due to their relatively slow direct reaction—depending on the experimental circumstances. Furthermore, we also provided experimental evidence that iodide ion acts as an autocatalyst of the system. A 14-step kinetic model is proposed in which the mechanisms of the pentathionate–iodine, bisulfite–iodate, and the well-known Dushman reactions are combined. A thorough analysis revealed that the direct pentathionate–iodate reaction plays a role only to produce iodide ions via a finite sequence of reactions, and once its concentration reaches a certain level, the reaction is almost exclusively governed by the pentathionate–iodine and the Dushman reactions. As expected, a strong catalytic effect of the buffer composition is also found that can readily be explained by its well-known catalytic influence on the original Dushman reaction.

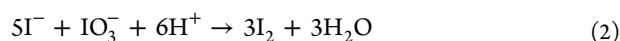


INTRODUCTION

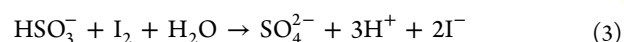
The sulfite/bisulfite–iodate reaction or even better known as Landolt reaction is probably one of the most familiar chemical reaction for any chemists all around the world and has been thoroughly investigated since Landolt's original discovery.^{1,2} It has been confirmed to be autocatalytic with respect to both hydrogen and iodide ions. It behaves as a simple clock reaction as a result of the sudden appearance of I₂ accompanied by consumption of substrate sulfite after a well-defined time lag under batch conditions at suitable concentration ranges of the reactants.^{3–5} In a continuously stirred tank reaction (CSTR), it exhibits bistability between a flow state branch (F) and a thermodynamic state branch (T) producing a hysteresis loop.^{4–6} Additionally, in one-side-fed spatial reaction (OSFR), oscillations^{4–6} and sustained wave patterns^{4,5,7,8} have been observed. The qualitative picture of the reaction has long been accepted:^{9,10} the reaction starts with a slow oxidation of hydrogen sulfite by iodate yielding an iodide ion



followed by the well-known Dushman reaction¹¹



but no color change appears unless the reactant hydrogen sulfite is entirely consumed due to the fast oxidation of hydrogen sulfite by iodine:



Concentration dependence of the Landolt time^{9–12} has been studied for several decades, but the results showed perceptible discrepancies in the relationships regarding the concentration of reactants. Recently the investigations,^{13,14} however, provided a clear explanation of how these differences can be explained by the different experimental conditions. Moreover, a general complex formula also exists for the concentration dependence of the Landolt time at buffered conditions.¹⁴

A special kinetic feature of this system provides a possibility that perturbation of the original Landolt reaction by suitable components such as ferrocyanide,^{15–19} thiourea,^{20,21} or thiosulfate,^{22,23} sustained oscillations or complex oscillations in pH, temperature oscillation, and an emergence of spatiotemporal phenomena can readily be observed. These systems are often called mixed Landolt reactions. As an example, the iodate–sulfite–thiosulfate (IST) reaction is autocatalytic with respect to hydrogen and iodide ions and shows complex pH oscillations,^{22–24} temperature oscillations²⁵ in closed and/or CSTR system and presents pH- and iodine waves in a reaction–diffusion system.²⁶ Skeleton mechanism of the reaction has been proposed and used to describe the phenomena mentioned above.^{22–25,27} More recently, Liu²⁸ et

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al. found different spatiotemporal structures like iodine patterns, pH patterns, cellular fronts and Turing structures and proposed a mechanism with positive and negative feedback processes for explaining the pattern formation. Not surprisingly, the topics dealing with Landolt or Landolt-type reactions have still remained in the focus of interests since its original discovery.

Survey of the literature has showed that for the IST system, no detailed overall dynamics model has been obtained except for a revised simple model²⁷ by which the pH oscillations in the batch and CSTR system can be explained. However, it is also mentioned that the region of the batch oscillation in the revised model is somewhat shifted in the concentration space when comparing the simulations with the experiments. This difference suggests that the intermediates of the individual reactions might also play a significant role, meaning that the simplified model should be extended. Consequently, investigation of the kinetics of the subsystems of the iodate–sulfite–thiosulfate reaction may provide additional mechanistic information to revise the kinetic model of the composite system. The mechanism of the IST system should evidently be much more complex than the original Landolt reaction. A major subsystem would be the iodate–thiosulfate²⁹ reaction in which the other subsystems including the thiosulfate–iodine reaction,^{30,31} tetrathionate–iodine reaction,^{32,33} and tetrathionate–iodate reaction³⁴ may also have a significant contribution to the kinetic feature mentioned above. Therefore, the investigation of iodate–thiosulfate seems to be critically important for a deeper insight into the intimate details of the IST system. The kinetics and mechanism of the iodate–thiosulfate was studied by Rieder,²⁹ who supposed an exclusive formation of tetrathionate during the course of reaction. More recent studies^{24,28,35} have, however, pointed out that the reaction cannot exclusively produce tetrathionate, and sulfite has to be formed as well to adequately explain the batch pH oscillatory behavior and the pattern formations. A 19-step kinetic model was proposed³⁵ that almost perfectly described the measured kinetic curves at a relatively wide concentration range of the reactants, in which the iodine–thiosulfate, tetrathionate–iodine, and iodine–hydrogen sulfite reactions³⁶ were involved. The only problem with this model is the lack of properly predicting the length of Landolt period at large initial thiosulfate concentrations. This means that further experiments are required to explore additional processes that may take place at higher thiosulfate concentrations. Recent investigations on the kinetics of the oxidation of thiosulfate by different oxidizing agents like hydrogen peroxide–thiosulfate,³⁷ chlorite,³⁸ and hypochlorous acid³⁹ have clearly revealed that pentathionate forms in detectable amounts during the course of these reactions and may therefore contribute to the exotic kinetic behavior via its further reactions.

The aim of this paper is to unravel the kinetics and mechanism of the pentathionate–iodate reaction as well as to characterize it as a possible candidate of the Landolt-type reaction.

MATERIALS AND INSTRUMENTATION

Materials and Buffers. Potassium pentathionate was prepared as described previously,⁴⁰ and its purity was found to be better than 97.0%. The stock solution was checked prior to each experiment, and once the purity of the solid sample was proven to be decreased due to the formation of elementary sulfur and other sulfur species, it was discarded, and a new

potassium pentathionate sample was prepared. Potassium iodate (Reanal), phosphoric acid, sodium dihydrogen phosphate, and sodium perchlorate were of the highest purity commercially available and were used without further purification. Twice ion-exchanged and double-distilled water was used to prepare all stock solutions. Phosphoric/dihydrogen phosphate buffer was used to maintain the pH of solutions between 1.3 and 2.2 by taking the pK_a of phosphoric acid as 1.80.⁴¹ The initial concentration of dihydrogen phosphate, $[H_2PO_4^-]$, was always kept constant at 0.1 M, and the desired pH was adjusted by the necessary amount of phosphoric acid. The ionic strength was adjusted to be 0.5 M by adding the necessary amount of sodium perchlorate. The temperature of the reaction vessel was maintained at 25.0 ± 0.1 °C. Initial concentrations of pentathionate and iodate ions were varied in the ranges of 0.1–6.0 mM and 0.25–4.0 mM, respectively. In this experimental setup, the reaction was investigated at 159 different experimental conditions, and several experiments were also repeated in different cases. They convinced us about good reproducibility of the kinetic measurements.

Methods and Instrumentation. The reaction was followed by a Zeiss S600 diode array spectrophotometer in the visible range without using the deuterium lamp of spectrophotometer. The reaction was carried out in a standard quartz cuvette equipped with a magnetic stirrer and a Teflon cap having 1 cm optical path. The buffer components and sodium perchlorate followed by pentathionate solution were delivered into the cuvette by a pipet. The stirring rate was controlled at 750 rpm to provide sufficiently fast mixing of the reactants before injecting iodate solution from a fast delivery pipet. In the case of studying the effect of iodide, the buffer components, sodium perchlorate, pentathionate, and iodide were delivered into the cuvette followed by injection of iodate. The spectrum of the reaction solutions at the wavelength range of 400–800 nm was acquired up to approximately 10 000–190 000 s.

DATA TREATMENT

In the visible range, only iodine and triiodide were found to have an absorption, therefore the isosbestic point of the iodine–triiodide system ($\lambda = 468$ nm) was selected for the parameter estimation by the ChemMech/ZiTa program package developed to fit basically unlimited experimental series.⁴² Molar absorbances of both species at this wavelength were taken into consideration as $\epsilon_{I_2} = \epsilon_{I_3^-} = 750 \text{ M}^{-1} \text{ cm}^{-1}$. Originally, each kinetic run contained more than 200 absorbance–time data pairs, therefore it was necessary to reduce the number of time points (40–80) to avoid unnecessary time-consuming calculations. The essence of this method has already been described elsewhere.⁴³ Altogether, almost 11 000 experimental points from the 159 kinetic series were used for the simultaneous evaluation. Our quantitative criterion for an acceptable fit was that the average deviation for the relative fit approached 4.0%, which is close to the experimentally achievable limit of error.

RESULTS

Preliminary Observation. Typical experimental data are illustrated in Figure 1, indicating that iodine forms only after a well-defined time lag. In addition to that the absorbance increase at 800 nm suggests that a light-scattering species must form during the course of reaction because none of the possible

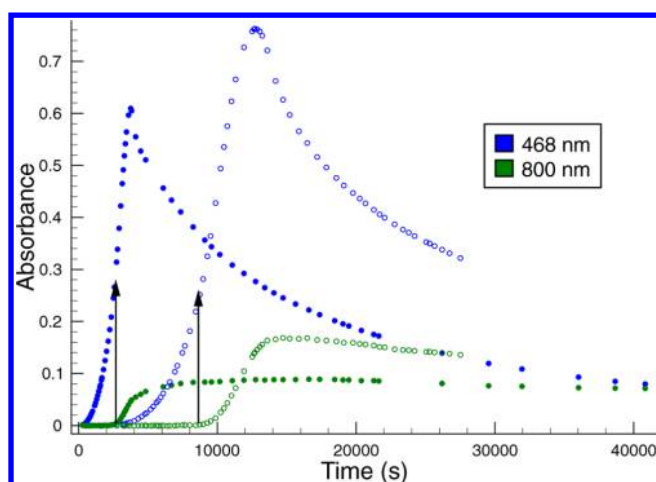


Figure 1. Measured absorbance–time series at two different wavelengths. Conditions are as follows: $[\text{S}_5\text{O}_6^{2-}]_0 = 1.0 \text{ mM}$; $[\text{IO}_3^-]_0 = 1.6 \text{ mM}$; $\text{pH} = 1.8$ (empty symbols); $[\text{S}_5\text{O}_6^{2-}]_0 = 1.4 \text{ mM}$; $[\text{IO}_3^-]_0 = 1.5 \text{ mM}$; $\text{pH} = 1.4$ (solid symbols). Arrows indicate the place of truncation.

end-products (any sulfur species, iodine, triiodide) have detectable absorbance at this wavelength.

Moreover, after the reaction is completed, a detectable amount of colloidal sulfur precipitation can be collected from the cuvette. Since a light-scattering species disturbs the quantitative determination of concentration from the measured absorbance at the wavelength range in question, we concluded that for quantitative purposes we should truncate all the absorbance–time curves after the appearance of a detectable amount of colloidal sulfur. Such an example (the place of truncation) is also shown in Figure 1. This figure also strengthens the fact that in pentathionate excess, the total amount of iodine goes through a maximum and finally slowly disappears from the solution. It indirectly proves that the appearance of iodine after a well-defined time-lag is not the consequence of the complete consumption of pentathionate. Later we shall also see that pentathionate and iodine coexist for a relatively long period of time due to the slow pentathionate–iodine reaction, especially when the concentration of iodide ion becomes non-negligible. Consequently, in this sense it means that the iodate–pentathionate system cannot be treated as a true Landolt-type clock reaction. In those reactions (for example, sulfite–iodate, sulfite–bromate, thiosulfate–iodate), the appearance of iodine or bromine is the consequence of the complete removal of substrate due to the fact that the substrate (sulfite or thiosulfate) instantaneously reacts with iodine or bromine. Furthermore, an important observation is yet to be highlighted. As shown in Figure 1, the appearance of iodine has a characteristic sigmoidal shape that may either refer to an autocatalytic feature or simply to a delayed consecutive reaction scheme. Figure 2 indicates a series of experiments where the initial concentration of iodide was varied, while the rest of the conditions were kept constant. As seen, the time necessary to build up the concentration of iodine is significantly shortened by an initial addition of iodide. Consequently, we concluded that the iodide ion is the real autocatalyst of the reaction. Combining the observed clock behavior with this experimental fact, we propose that this reaction is better to be classified as an autocatalysis-driven clock reaction (see Discussion later).

To further enlighten our results, it is also important to analyze the dependence of the time lag necessary for the

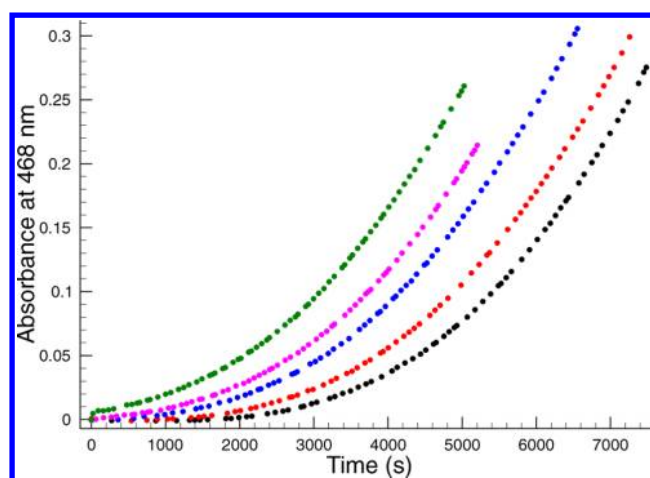


Figure 2. Measured absorbance–time series at 468 nm. Conditions are as follows: $[\text{S}_5\text{O}_6^{2-}]_0 = 0.6 \text{ mM}$; $[\text{IO}_3^-]_0 = 1.7 \text{ mM}$; $\text{pH} = 1.8$; $\text{I} = 0.5 \text{ M}$. $[\text{I}^-]_0/\mu\text{M} = 0.0$ (black); 1.07 (red); 5.33 (blue); 10.0 (magenta); 25.0 (green).

appearance of iodine. For an easy characterization, we define t_i as the time necessary to reach the absorbance 0.01 absorbance unit at 468 nm, which corresponds to $[\text{I}_2] = 1.33 \times 10^{-5} \text{ M}$, and analyzed the concentration dependence of t_i . The main advantage of this definition is that it can exactly be determined experimentally, and no disturbing side reaction (precipitation of sulfur) can be taken into consideration during the analysis.

Concentration Dependence of t_i . Figure 3 shows the dependencies of t_i on the concentration of pentathionate while

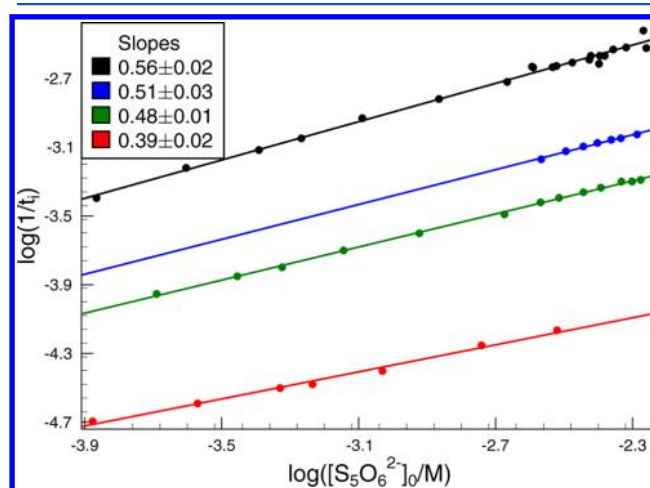


Figure 3. Dependence of t_i on the concentration of pentathionate. Conditions are as follows: $[\text{IO}_3^-]_0 = 1.5 \text{ mM}$; $\text{pH} = 1.43$ (black), 1.69 (blue), 1.82 (green), 2.24 (red).

keeping the rest of the conditions constant. One can easily realize that pH clearly affects the influence of the initial pentathionate concentration on the reciprocal of t_i . The log–log plot suggests that the formal kinetic order of pentathionate increases with decreasing pH . Since this value is significantly lower than unity within the concentration range, it refers to a complex overall effect on the formation of iodine. A plausible explanation of this phenomenon is that in the beginning stage of the reaction, iodate slowly oxidizes pentathionate into sulfate while it is reduced to an iodide ion. The iodide ion reacts with the iodate ion in the well-known Dushman reaction to produce

iodine.¹¹ Then the pentathionate ion slowly reduces iodine⁴⁰ to reform an iodide ion ready to open up a new cycle. This reduction, however, becomes slower as the reaction proceeds, because the iodide ion formed inhibits the pentathionate–iodine reaction.⁴⁰ As a result, once the concentration of iodide ions reaches a certain value, the reaction is mainly governed by the sequence of Dushman reaction and the pH-independent pentathionate–iodine reaction, making the initiative pentathionate–iodate reaction unessential. Consequently, at higher pHs, the initiative pentathionate–iodate reaction becomes less and less important in controlling the concentration of iodide ion, therefore t_i gradually becomes less dependent on the initial concentration of pentathionate. (It can be understood from the decreasing kinetic order of pentathionate as a function of pH.)

Figure 4 indicates the effect of initial iodate concentration on t_i . It is clear that the formal kinetic order of iodate can be

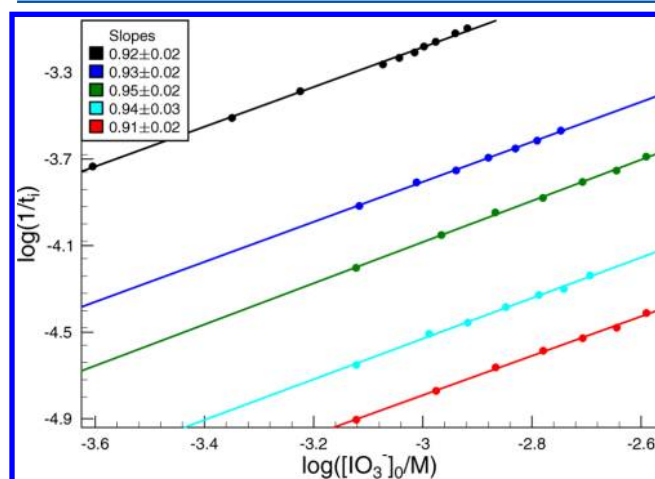


Figure 4. Dependence of t_i on the concentration of iodate. Conditions are as follows: $[S_5O_6^{2-}]_0 = 0.38$ mM and pH = 1.43 (black); $[S_5O_6^{2-}]_0 = 1.0$ mM and pH = 1.82 (blue); $[S_5O_6^{2-}]_0 = 0.26$ mM and pH = 1.82 (green); $[S_5O_6^{2-}]_0 = 1.0$ mM and pH = 2.24 (cyan); $[S_5O_6^{2-}]_0 = 0.25$ mM and pH = 2.24 (red).

treated as unity. As a natural continuation of our earlier point of view, this experimental fact can easily be understood because the Dushman reaction is first order with respect to iodate concentration. So if the formal kinetic order of iodate in the starting pentathionate–iodate reaction is also unity, then the overall effect should also give a first-order dependence.

Further elucidating the concentration dependence of t_i , Figure 5 explains that the formal kinetic order of the hydrogen ion is definitely 2. It further supports our idea that the Dushman reaction plays a central role governing the pentathionate–iodate reaction. Later it is shown that the rates of neither the starting nor any additional reactions depend on $[H^+]^2$.

Effect of Buffer Concentration and the Ionic Strength.

It is well-known that the rate of the Dushman reaction is strongly affected by the ionic strength, the nature of the buffer components, and even the concentration of the buffer components as well.⁴⁴ Moreover, phosphates can efficiently catalyze the iodate–iodide reaction.⁴⁵ This clearly means if our assumption, that the Dushman reaction plays a decisive role in determining the kinetics of the title reaction, is valid, then both the absolute concentration of buffer components at constant ionic strength and pH as well as changing the ionic strength at constant buffer composition and pH should have a significant

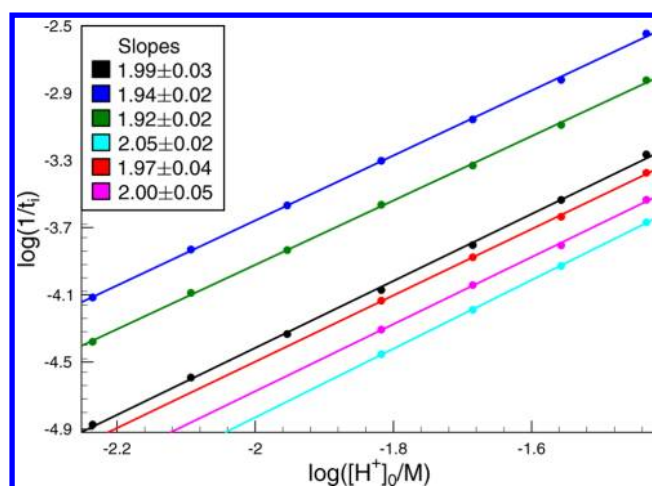


Figure 5. Dependence of t_i on the concentration of hydrogen ions. Conditions are as follows: $[IO_3^-]_0 = 0.75$ mM, $[S_5O_6^{2-}]_0 = 0.5$ mM (black); $[IO_3^-]_0 = 1.5$ mM, $[S_5O_6^{2-}]_0 = 6.0$ mM (blue); $[IO_3^-]_0 = 1.5$ mM, $[S_5O_6^{2-}]_0 = 1.5$ mM (green); $[IO_3^-]_0 = 0.25$ mM, $[S_5O_6^{2-}]_0 = 0.38$ mM (cyan); $[IO_3^-]_0 = 0.6$ mM, $[S_5O_6^{2-}]_0 = 0.38$ mM (red); $[IO_3^-]_0 = 0.35$ mM, $[S_5O_6^{2-}]_0 = 0.38$ mM (magenta).

effect on the kinetic runs. Figures 6 and 7 show the effect of the buffer components and that of the ionic strength, respectively.

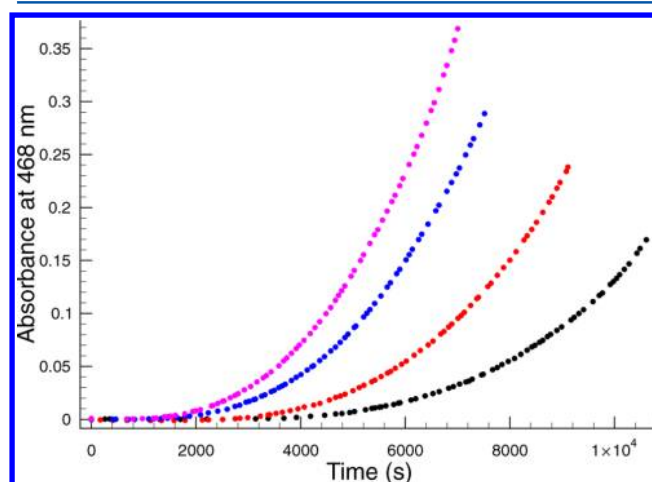


Figure 6. Effect of the concentration of buffer components on the formation of iodine. Conditions are as follows: $[IO_3^-]_0 = 1.7$ mM, $[S_5O_6^{2-}]_0 = 0.6$ mM, pH = 1.8, I = 0.5 M adjusted by the necessary amount of sodium perchlorate. $TPO_4^{3-}/M = 0.1$ (black), 0.35 (red), 0.65 (blue), 0.95 (magenta).

It is clear, as expected, that both of them have a significant accelerating effect on the formation of iodine. These observations therefore further support our general idea on the mechanism of the pentathionate–iodate reaction.

Proposed Kinetics Model. To establish the kinetic model of the title reaction for quantitatively describing the measured absorbance–time curves, it is clear that the kinetic model of the pentathionate–iodine reaction⁴⁰ and that of Dushman reaction^{11,13,14,44} should certainly be included. Taking into consideration that HSO_5^- , $S_2O_3OH^-$, $S_2O_3I^-$, $S_3O_3OH^-$, $S_3O_3I^-$, I_2O_2 , HIO_2 , and HOI are well-known intermediates of the above-mentioned reactions, we then considered all the conceivable mono and bimolecular reactions of these species including the reactants as well. As a start, the rate equation of all

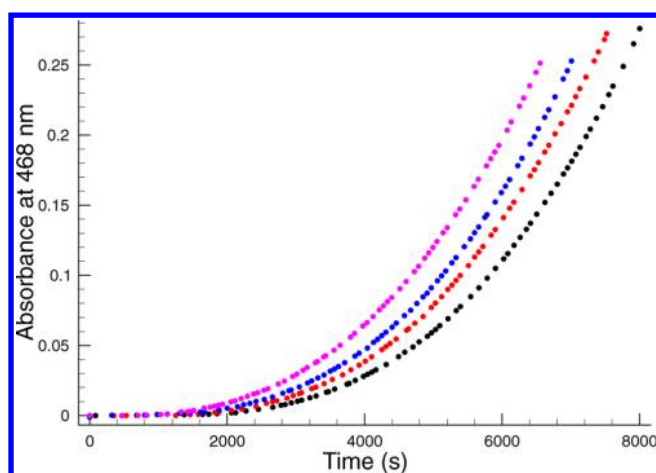
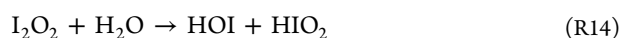
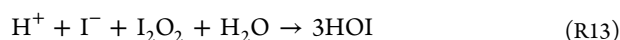
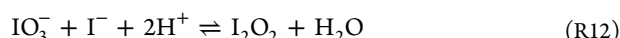
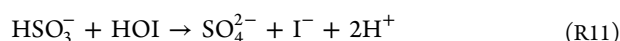
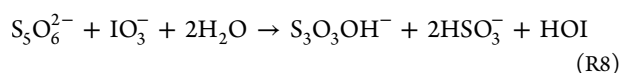
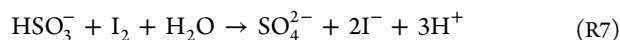
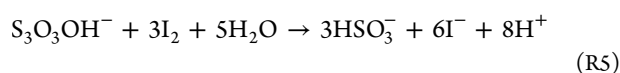
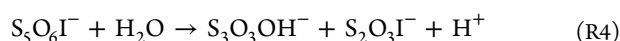
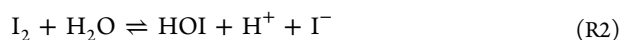


Figure 7. Effect of ionic strength on the formation of iodine. Conditions are as follows: $[\text{IO}_3^-]_0 = 1.7 \text{ mM}$, $[\text{S}_2\text{O}_6^{2-}]_0 = 0.6 \text{ mM}$, $\text{pH} = 1.8$, $T_{\text{PO}_4^{3-}} = 0.65 \text{ M}$. $I = 0.334 \text{ M}$ (black), 0.5 M (red), 0.7 M (blue), 1.0 M (magenta) adjusted by sodium perchlorate.

these reactions is supposed to have three terms: the first one is independent of $[\text{H}^+]$, the second and third terms are proportional to $[\text{H}^+]$ and $[\text{H}^+]^2$, respectively. Systematically eliminating those reactions that did not have any effect on the quality of fit, we arrived at the following kinetic model:



Rate coefficients determined by nonlinear simultaneous parameter estimation are illustrated in Table 1.

The average deviation was found to be 3.7% by a relative fitting procedure. Altogether, only four fitted parameters were used, and the rest of the parameters was either fixed or directly taken from previous reports. Figures 8–10 demonstrate the quality of the fit for representative examples and also support

Table 1. Fitted and Fixed Rate Coefficients of the Proposed Kinetic Model^a

step	rate equation	parameter value
R1	$k_{\text{R1}}[\text{I}_3^-]$	$8.5 \times 10^6 \text{ s}^{-1}$
	$k_{-\text{R1}}[\text{I}_2][\text{I}^-]$	$5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
R2	$k_{\text{R2}}[\text{I}_2]$	0.0552 s^{-1}
	$k_{-\text{R2}}[\text{HOI}][\text{I}^-][\text{H}^+]$	$1.023 \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$
R2'	$k_{\text{R2}'}[\text{I}_2][\text{H}^+]^{-1}$	$1.98 \times 10^{-3} \text{ Ms}^{-1}$
	$k_{-\text{R2}'}[\text{HOI}][\text{I}^-]$	$3.67 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
R3	$k_{\text{R3}}[\text{S}_2\text{O}_6^{2-}][\text{I}_2]$	$10 \text{ M}^{-1} \text{ s}^{-1}$
	$k_{-\text{R3}}[\text{S}_2\text{O}_6\text{I}^-][\text{I}^-]$	$10^6 \text{ M}^{-1} \text{ s}^{-1}$
R4	$k_{\text{R4}}[\text{S}_2\text{O}_6\text{I}^-]$	$1.63 \pm 0.07 \text{ s}^{-1}$
R5	$k_{\text{R5}}[\text{S}_3\text{O}_3\text{OH}^-][\text{I}_2]$	$10^4 \text{ M}^{-1} \text{ s}^{-1}$
R6	$k_{\text{R6}}[\text{S}_2\text{O}_3\text{I}^-][\text{I}_2]$	$10^4 \text{ M}^{-1} \text{ s}^{-1}$
R7	$k_{\text{R7}}[\text{HSO}_3^-][\text{I}_2]$	$3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
R8	$k_{\text{R8}}[\text{S}_2\text{O}_6^{2-}][\text{IO}_3^-][\text{H}^+]$	$(2.05 \pm 0.18) \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$
R9	$k_{\text{R9}}[\text{HSO}_3^-][\text{IO}_3^-][\text{H}^+]$	$8800 \text{ M}^{-2} \text{ s}^{-1}$
R9'	$k_{\text{R9}'}[\text{HSO}_3^-][\text{IO}_3^-][\text{H}^+]^2$	$10^8 \text{ M}^{-3} \text{ s}^{-1}$
R10	$k_{\text{R10}}[\text{HIO}_2][\text{I}^-][\text{H}^+]$	$10^9 \text{ M}^{-2} \text{ s}^{-1}$
R11	$k_{\text{R11}}[\text{HSO}_3^-][\text{HOI}]$	$10^9 \text{ M}^{-1} \text{ s}^{-1}$
R12	$k_{\text{R12}}[\text{IO}_3^-][\text{I}^-][\text{H}^+]^2$	$10^7 \text{ M}^{-3} \text{ s}^{-1}$
	$k_{-\text{R12}}[\text{I}_2\text{O}_2]$	10^6 s^{-1}
R13	$k_{\text{R13}}[\text{I}_2\text{O}_2][\text{I}^-]$	$(1.72 \pm 0.12) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
R14	$k_{\text{R14}}[\text{I}_2\text{O}_2][\text{H}^+]$	$5770 \pm 380 \text{ M}^{-1} \text{ s}^{-1}$

^aNo error indicates that the given parameter is fixed during the calculation process.

the fact that the proposed kinetic model is working properly under our experimental conditions.

DISCUSSION

As indicated, Step E1 is only an auxiliary process, necessary to take the slight pH change into account during the course of reaction. The ratio of rate coefficients of the rapid forward and reverse reaction was adjusted to give the pK_1 of phosphoric acid to be 1.80.⁴¹

Step R1 is the well-known rapid equilibrium formation of triiodide ion studied by several research groups independently.^{46,47} The rate coefficients of the forward and backward reactions were directly taken as $8.5 \times 10^6 \text{ s}^{-1}$ and $5.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively, to give the formation constant of triiodide as 2.83.⁴¹

Step R2 is the iodine hydrolysis studied thoroughly in detail by Eigen,⁴⁸ Palmer,⁴⁹ and Lengyel et al.⁵⁰ We directly adopted and fixed the rate coefficients determined by the most recent study.⁵⁰

Steps R3–R6 were directly adopted from our previous study.⁴⁰ We have already pointed out there that R3 is a rapidly established equilibrium shifted far to the left, and steps R5 and R6 are rapid processes; the absolute values of these rate coefficients cannot be determined from our experiments. Therefore, we have set the rate coefficients of k_{R3} , $k_{-\text{R3}}$, k_{R5} , and k_{R6} as $10 \text{ M}^{-1} \text{ s}^{-1}$, $10^6 \text{ M}^{-1} \text{ s}^{-1}$, $10^4 \text{ M}^{-1} \text{ s}^{-1}$, and $10^4 \text{ M}^{-1} \text{ s}^{-1}$, respectively. As a start, we fixed k_{R4} to be 3.29 s^{-1} as determined in our previous work,⁴⁰ but it turned out, as expected, that this parameter can also be determined from the present work. The reason can easily be understood as follows: although at first glance this reaction may also be treated as a Landolt-type clock reaction, the coexistence of the substrate pentathionate ion and iodine (the species determining the clock behavior) indicates that this reaction should rather belong to a different type of clock reaction. The fact that the time scale of

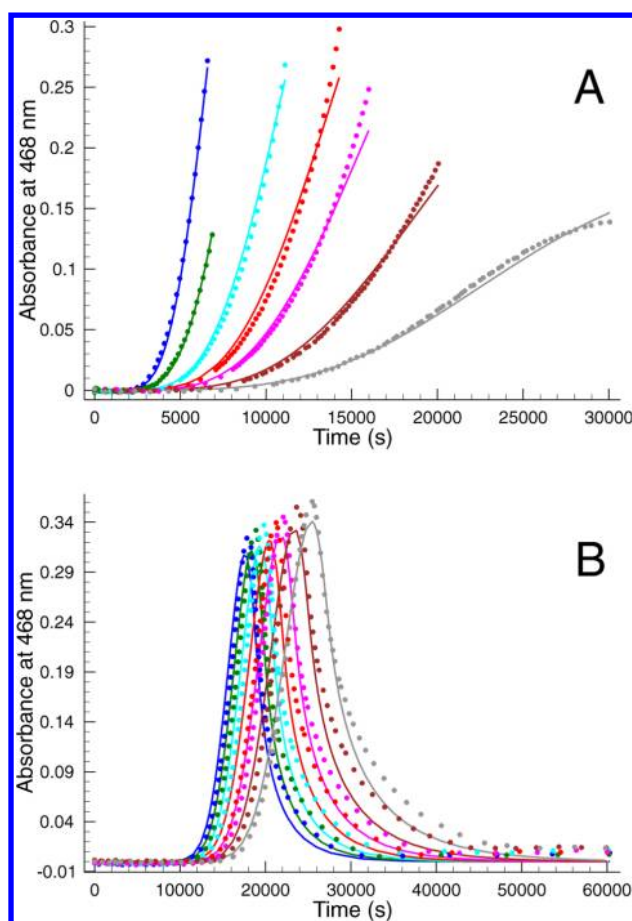


Figure 8. Experimental (dots) and fitted (solid lines) absorbance–time curves at 468 nm with respect to changing the concentration of pentathionate. Conditions are as follows: (A) $[IO_3^-]_0 = 1.5$ mM; pH = 1.7; $[S_5O_6^{2-}]_0$ /mM = 1.9 (blue); 1.2 (green); 0.72 (cyan); 0.48 (red); 0.35 (magenta); 0.21 (brown); 0.12 (gray). (B) $[IO_3^-]_0 = 1.5$ mM; pH = 2.2; $[S_5O_6^{2-}]_0$ /mM = 6.0 (blue); 5.5 (green); 5.0 (cyan); 4.5 (red); 4.0 (magenta); 3.5 (brown); 3.0 (gray).

the title reaction coincides with that of the pentathionate–iodine reaction, however, provides an opportunity for us to determine k_{R4} from these studies as well. We found k_{R4} to be 1.63 ± 0.07 , which is in reasonable agreement with the value obtained previously.⁴⁰

Step R7 is the well-known fast reaction between HSO_3^- and iodine studied thoroughly by Yiin and Margerum.³⁶ We therefore fixed k_{R7} during the whole calculation process to be 3.1×10^9 M⁻¹ s⁻¹, as previously determined.³⁶

Step R8 is the initiation of the title reaction that essentially breaks up the sulfur chain of pentathionate. As a result, iodate is reduced to hypoiodous acid, which is further reduced to iodide by bisulfite (see Step R11 later). Eventually, this sequence of reaction generates iodide ion, the key species of the system. We found that the rate of the initiating reaction should be linearly proportional to $[H^+]$. It would suggest an apparent contradiction to our experimental findings that $1/t_i$ is proportional to the square of H^+ . However, this finding can easily be reconciled by the fact that once the concentration of iodide ions reaches a certain value, the reaction is not governed anymore by step R8. From that point, as shown previously, the overall effect of the pentathionate–iodine and the Dushman reactions determines the conversion of the title reaction. Because the rate of the Dushman reaction is proportional to the square of $[H^+]$, the

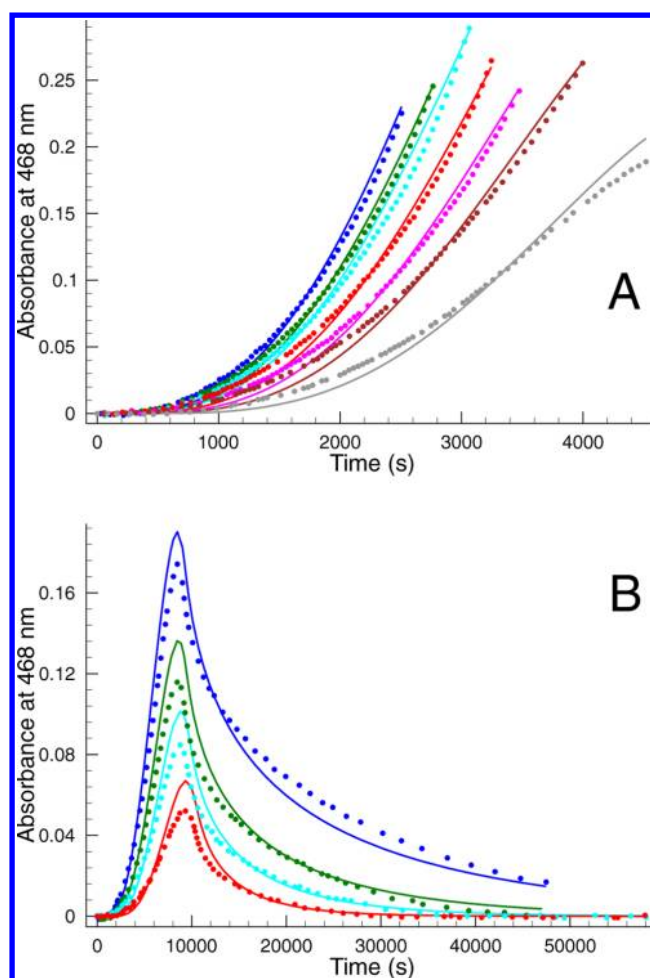


Figure 9. Experimental (dots) and fitted (solid lines) absorbance–time curves at 468 nm with respect to changing the concentration of iodate. Conditions are as follows: (A) $[S_5O_6^{2-}]_0 = 1.0$ mM; pH = 1.3; $[IO_3^-]_0$ /mM = 2.0 (blue); 1.8 (green); 1.6 (cyan); 1.4 (red); 1.2 (magenta); 1.0 (brown); 0.75 (gray). (B) $[S_5O_6^{2-}]_0 = 0.38$ mM; pH = 1.4; $[S_5O_6^{2-}]_0$ /mM = 0.6 (blue); 0.45 (green); 0.35 (cyan); 0.25 (red).

overall effect is that $1/t_i$ also becomes proportional to $[H^+]^2$. We have also tried to assign different $[H^+]$ -dependencies to the initiating reaction with no success. If the rate of step R8 was considered to be pH-independent or to be dependent on $[H^+]^2$, the average deviation was found to be 9.9% and 14.4%, respectively, from which we concluded that the rate of Step R8 has to depend on $[H^+]$.

Step R9 is the initial step of the Landolt reaction generating the intermediate iodous acid. The rate coefficients k_{R9} and k'_{R9} were directly adopted from a previous work and fixed during the calculation process.²⁴

Step R10 is the relatively rapid comproportionation of iodous acid and iodide ion to form hypoiodous acid. The rate coefficient of this process was fixed at $k_{R10} = 10^9$ M⁻² s⁻¹ as proposed by Lengyel and his co-workers.⁵¹

Step R11 is the fast oxidation of bisulfite by hypoiodous acid via a formal oxygen transfer process. The rate coefficient of this reaction cannot be determined directly from our present experiments. Considering that both iodine and hypoiodous acid are very reactive oxidants of S(IV) species, we have chosen k_{R11} to be 10^9 M⁻¹ s⁻¹, close to that of Step R7.

Step R12 is the well-accepted initiating equilibrium of the Dushman reaction,^{11,44} where I_2O_2 is considered to be a steady-

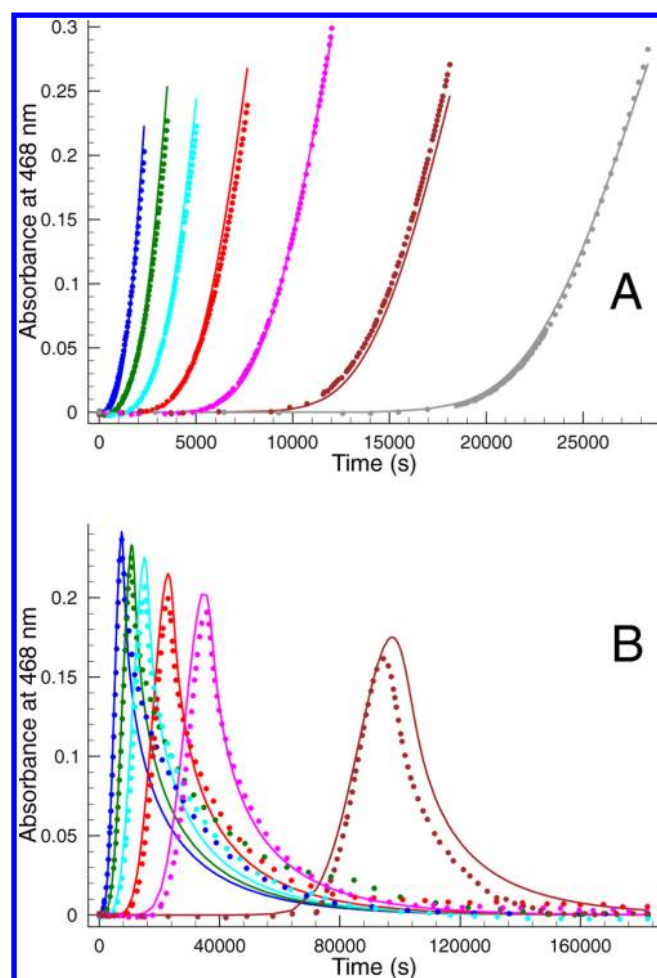


Figure 10. Experimental (dots) and fitted (solid lines) absorbance–time curves at 468 nm with respect to changing pH. Conditions are as follows: (A) $[S_5O_6^{2-}]_0 = 1.5$ mM; $[IO_3^-]_0 = 1.5$; pH = 1.3 (blue); 1.45 (green); 1.6 (cyan); 1.75 (red); 1.9 (magenta); 2.0 (brown); 2.2 (gray). (B) $[S_5O_6^{2-}]_0 = 0.5$ mM; $[IO_3^-]_0 = 0.75$ mM; pH = 1.3 (blue); 1.45 (green); 1.6 (cyan); 1.75 (red); 1.9 (magenta); 2.2 (brown).

state intermediate originally proposed by Bray to explain the complex rate equation of the Dushman reaction.⁵² Later, experimental evidence of the formation of $H_2I_2O_3$ was also reported in huge excess of iodate at highly acidic conditions,⁵³ but I_2O_2 and $H_2I_2O_3$ are kinetically indistinguishable species. So far, this equilibrium constant has not been determined, therefore to provide I_2O_2 as a low concentration steady-state intermediate and to establish the equilibrium rapidly under our time scale, we set k_{R12} and k_{-R12} to be 10^7 M⁻³ s⁻¹ and 10^6 s⁻¹, respectively.

Steps R13 and R14 are the main driving force of the Dushman reaction in the absence and presence of iodide ion, respectively. It is generally thought that buffer assistance occurs via further reactions of the intermediate I_2O_2 .⁴⁴ Part of our experiments provided an opportunity to show the effect of buffer component ($H_2PO_4^-$) concentration on the values of k_{R13} and k_{R14} . The results are shown in Figure 11. As expected, a strong influence is obtained that clearly supports the general idea of the buffer-assisted pathway of reactions of I_2O_2 . From our point of view, this is the first direct experimental evidence that such an effect can uniquely be attributed to a certain part of reaction sequences involved in an overall reaction mechanism obtained from a global simultaneous fit of series of experiments.

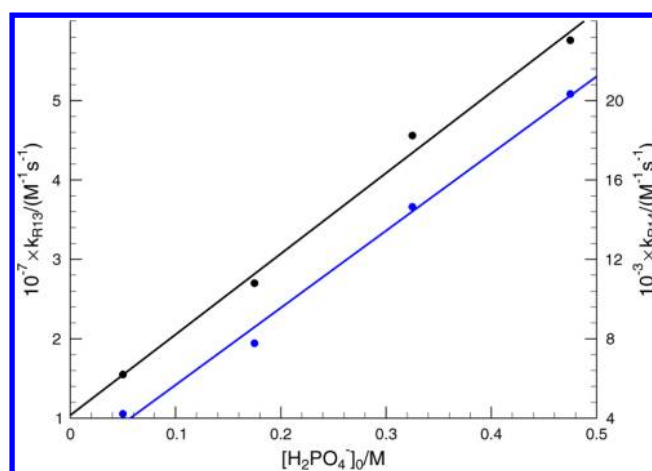


Figure 11. Plot of k_{R13} and k_{R14} against the initial concentration of $[H_2PO_4^-]_0$ at $I = 0.5$ M and pH = 1.80. $[S_5O_6^{2-}]_0 = 0.6$ mM and $[IO_3^-]_0 = 1.7$ mM.

As can also be seen from Figure 11, the practical linear dependence of k_{R13} and k_{R14} on $[H_2PO_4^-]_0$ offers a convenient tool to check the reliability of these rate coefficients obtained from the majority of the experiments at $[H_2PO_4^-]_0 = 0.1$ M. At this condition, Figure 11 provides $k_{R13} = 2.05 \times 10^7$ M⁻¹ s⁻¹ and $k_{R14} = 5670$ M⁻¹ s⁻¹, meaning that both values are in a very good agreement with the corresponding values indicated in Table 1. Furthermore, it provides a possibility to compare the rate coefficient of the overall Dushman reaction with $K_{12}k_{R13} = 2.05 \times 10^8$ M⁻⁴ s⁻¹, which is approximately an order of magnitude lower than that found in the presence of acetic acid/acetate buffer,¹³ but is in a very good agreement with the value (3.2×10^8 M⁻⁴ s⁻¹) obtained at acetate buffer-free conditions.⁴⁴

A word is in order here as well regarding the explanation of the autocatalytic effect of iodide ion. As can be seen, the sequence of steps R8 and R11 produces iodide ions in a slow process at the beginning stage of the reaction, resulting in its accumulation. Once its concentration reaches a certain level, it ignites the overall Dushman reaction (see Steps R12–R14) that produces iodine. However, at this stage, the concentration of pentathionate is still high enough to completely reduce iodine into iodide ions essentially within no time resulting in a further, but accelerated accumulation of the autocatalyst. This stage lasts until the concentration of pentathionate ion becomes low enough not to remove iodine rapidly anymore. As a result, it rings the bell for the clock behavior. Of course this stage is further enhanced by the fact that increasing iodide ion concentration inhibits the pentathionate–iodine reaction.⁴⁰ Moreover, it means that, although iodine has already appeared in the solution, pentathionate ion also exists in a detectable amount. Furthermore, even in relative excess of the substrate, iodine persists for a fairly long time, but finally, depending on the excess of substrate, iodine disappears from the solution. A selected example is indicated in Figure 12. In that sense, this reaction differs from the original Landolt clock-reaction because, in that case, iodine cannot appear unless bisulfite is exhausted. Moreover, the original Landolt reaction does not exhibit clock behavior if the substrate is in stoichiometric excess, but it is still autocatalytic with respect to both iodide and hydrogen ions under that condition.⁵⁴ In other words, it means that the so-called Landolt-time (the time point of the appearance of iodine) and the time of the complete consumption of the substrate (bisulfite) necessarily coincides

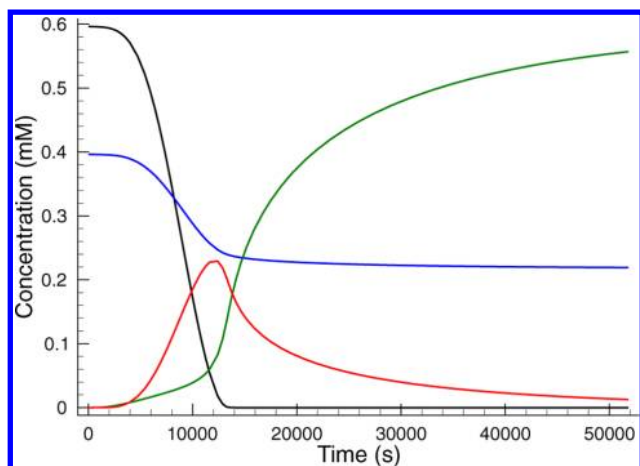


Figure 12. Simulated concentration–time curves in excess of pentathionate. Conditions are as follows: pH = 1.4; $[S_5O_6^{2-}]_0 = 0.4$ mM; $[IO_3^-]_0 = 0.6$ mM. The red curve belongs to iodine, while the green one to iodide ion.

in the case of the Landolt reaction. In addition to that, certain stoichiometric constraints must be held to observe the appearance of iodine. Opposite to this, in the case of the pentathionate–iodate reaction, the time point when iodine appears in the solution and the time point of the complete consumption of substrate are distinctly different. However, it is also true that the reaction is autocatalytic with respect to iodide ion, meaning that the title reaction should somehow be connected to the original Landolt reaction. In addition to the iodide autocatalysis, strong proton autocatalysis is also expected to appear in the title reaction in the case of unbuffered conditions, but this feature is completely suppressed in our case when using buffered solutions. Furthermore, even in stoichiometric excess of the substrate, the clock species (iodine) appears. It raises an important question of whether the title reaction can be classified as a clock reaction or not. It is out of the question that the main core of the present reaction and that of the Landolt reaction are the same. It is also clear that our system also displays clock-behavior, i.e., the clock species appears after a well-defined and reproducible time lag. Common sense therefore suggests that it should be designated as a clock reaction. However, the main difference, namely, the substrate coexists with the clock species for a long period of time, supports the concept that this reaction should rather be classified in a different category of clock reaction. Therefore, for the Landolt reaction, we suggest the substrate-depletive clock reaction category, while for the pentathionate–iodate system, we suggest the autocatalysis-driven clock reaction category. A manuscript to summarize this general concept is currently being prepared.

Finally, we should also mention again that the proposed model has to be extended because it is not able to explain the formation of colloidal sulfur. This, however, is outside the scope of this study, because the appearance of colloidal sulfur prevents the quantitative determination of any species by UV–vis spectroscopy. As mentioned previously, it was enlightened that those parts of the kinetic curves were truncated, meaning that there is not enough quantitative experimental information to propose a firmly based route leading to the formation of colloidal sulfur.

CONCLUSION

In this paper we have elucidated the kinetics and mechanism of the pentathionate–iodate reaction. Furthermore, we have clearly shown that the title reaction resembles the classical Landolt reaction in several aspects such as iodine clock behavior, core of mechanism, etc. There are, however, notably significant differences between these systems: (a) the time point when iodine appears in the solution may significantly be different from the time point when substrate pentathionate is consumed, whereas these time points are the same in the case of the Landolt reaction, (b) the feature of the appearance and the lack of appearance of the clock species in excess of substrate. To take the similarities and also the differences into account, we suggest a distinct category within the generally used term of “clock reactions”, where the pentathionate–iodate reaction may rather belong: the category of autocatalysis-driven clock reactions. Meanwhile, the hydrogen-sulfite–iodate reaction is better to be assigned to the category of substrate-depletive clock reactions.

Finally, we would like to mention that further facts that provide precise clarification of the definition of the term “clock reaction” as well as reclassification of these systems is eagerly expected. Even nowadays, more than 130 years after the original discovery of clock behavior, an induction time is unintentionally used to identify a reaction to be a “clock reaction”, a “Landolt-type reaction”, and “autocatalytic” in a growing number of publications in leading scientific journals.^{55–58} This fact has just recently been noticed by Lente et al., who made a clear distinction between the different types of reactions exhibiting an induction period.⁵⁹ As a result, their main point is that the appearance of an induction period does not necessarily mean “clock” behavior. Our example clearly shows that some, but not all, autocatalytic reactions may be classified as autocatalysis-driven clock reactions. Thorough survey of the literature revealed that a couple of different systems exists, remarkably resembling our present system such as the thiocyanate–iodate,⁶⁰ aminoiminomethanesulfonic acid–iodate,⁶¹ 2-aminoethanethiolsulfuric acid–iodate,⁶² and dimethylaminoiminomethanesulfonic acid–iodate⁶³ reactions. Realizing the major difference between their clock behaviors compared to that of the original Landolt reaction has, however, remained unnoticed so far.

We hope that our suggestion here may pave the way to clarify the meaning of the generally used term “clock reaction”. It strongly supports the general rule as well that it is better to doublecheck any sophisticated designation to a reaction being investigated by considering and understanding its mechanistic details.

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Notes

The authors declare no competing financial interest.

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