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Oxygen−Sulfur Species Distribution and Kinetic Analysis in the Hydrogen Peroxide−Thiosulfate System

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We have carried out species determination and kinetic analysis in the hydrogen peroxide−thiosulfate reaction by means of capillary electrophoresis and high performance liquid chromatography. In addition to thiosulfate, dithionate, trithionate, and tetrathionate, other polythionates such as pentathionate and hexathionate were detected during the oxidation process. The polythionates found are sensitive to the pH, with the average length of the sulfur chain decreasing with increasing pH. By varying the pH and the concentrations of the reactants, we find that the reaction is first order with respect to each of the reactants with rate constant $k = 0.025\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. With $HOS_2O_3^-$, HSO_3^-/SO_3^{2-}, $S_3O_6^{2-}$, $S_4O_6^{2-}$, and $S_5O_6^{2-}$ as key intermediates that are eventually oxidized to sulfate, a proposed 14-step kinetic model simulates the reaction process, including the evolution of the thiosulfate and tetrathionate concentrations at various pHs.

Introduction

The well-known oxidation of thiosulfate ion by hydrogen peroxide exhibits interesting nonlinear dynamical phenomena, such as thermokinetic oscillations with large amplitude temperature variations under quasiadiabatic conditions,[1] and oscillations as well as multistationary states when the reaction is catalyzed by cupric ions (HPTCu reaction) in an isothermal continuously stirred tank reactor (CSTR).[2] Abel[3] studied the HPTCu reaction in a closed system a century ago and found that Cu^{2+} significantly enhances the reaction rate. Hopf and infinite period bifurcations have been identified in the pH-regulated $H_2O_2-S_2O_3^{2-}-Cu^{2+}-NaOH$ system in a semibatch reactor.[4,5] When sulfite is introduced into the catalyst-free system in a CSTR, it exhibits two types of limit cycle pH oscillations with different frequencies, complex periodic behavior and chaos.[6] Furthermore, temperature compensation has been found in this system; that is, there exists a temperature range in which the period of oscillation is almost unaffected by temperature.[7,8] Spatiotemporal behavior, for example, a transition from propagating fronts to target patterns, has been seen in the $H_2O_2-S_2O_3^{2-}-SO_3^{2-}$ reaction.[9] This system displays oscillatory dynamics ranging from simple and mixed-mode oscillations to multistability and chaos.[10] Small perturbation by one of the reactants can produce a transient oscillatory response, which implies that this reaction is also excitable.[11]

Schiller has shown that the $H_2O_2-S_2O_3^{2-}$ reaction kinetics are first order with respect to each of the reactants at pH 7−9, and the formation of the intermediate $HOS_2O_3^-$ is the rate-determining step.[12] Voslař et al.[13] studied the oxidation of tetrathionate by hydrogen peroxide in a weakly alkaline medium by the method of initial reaction rates, and found that the rate-determining step was first order with respect to tetrathionate, hydrogen peroxide, and OH^- ions. Thiosulfate, sulfite, and trithionate were detected as intermediates. These authors also concluded that there was no distinct catalytic effect of Cu^{2+}, in contrast to earlier suggestions.

A mixture of $S_4O_6^{2-}$ and SO_4^{2-}, the composition of which depends on the pH, is the major product of the $H_2O_2-S_2O_3^{2-}$ reaction (see reactions E1 and E2 below), with low pH favoring $S_4O_6^{2-}$, while high pH favors SO_4^{2-}.[12]

$$H_2O_2 + 2S_2O_3^{2-} + 2H^+ \rightarrow S_4O_6^{2-} + 2H_2O \qquad \text{(E1)}$$

$$4H_2O_2 + S_2O_3^{2-} \rightarrow 2SO_4^{2-} + 3H_2O + 2H^+ \qquad \text{(E2)}$$

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Sulfite/bisulfite, another long-lived intermediate in addition to tetrathionate, arises from the oxidation of $HOS_2O_3^-$ by H_2O_2.[14] Yokosuka et al.[15] suggested that trithionate was formed as well as tetrathionate when pH > 4, but this was not confirmed by thin layer chromatography analysis.[16] The key intermediates, tetrathionate and sulfite, can react not only with the oxidant, but also with each other, making the mechanism particularly complicated.[17−20]

On the basis of a simple four-step reaction scheme proposed by Schiller,[12] a detailed mechanistic model was first presented for the Cu^{2+}-catalyzed reaction by Kurin-Csörgei et al.,[14] in which formation of the intermediate $HOS_2O_3^-$ and attack on that species by the reactants play key roles to give oscillatory behavior. Analogous to $S_2O_3Cl^-$ and $S_2O_3I^-$,[21,22] which were suggested as intermediates in halogen-sulfur redox reactions, and supported by molecular orbital calculations,[23] $HOS_2O_3^-$ has been postulated several times in the literature.[12,14] Building upon kinetics studies of the $H_2O_2{-}S_4O_6^{2-}$ system[13] by the method of initial reaction rates, Voslař et al.[13] developed a 10-step model based on the Kurin-Csörgei model and tetrathionate sulfitolysis which could be treated as subsystem of the $H_2O_2{-}S_2O_3^{2-}$ system. Under the conditions employed, the hydrolysis of tetrathionate,[20,24−27] and thus the formation of trithionate and pentathionate, must also be taken into account.[20] The above studies leave open a number of questions relevant to the mechanism, for example, how the distribution of polythionates formed in the reaction varies with pH.[10,11,13] The earlier model and parameters,[6,11−14] which yield mixed-mode oscillation regimes[10] and bifurcation diagrams[11] by optimizing the values of the adjustable parameters, do not successfully reproduce the time series for the periodically pulsed system.[11] The reaction mechanism involves at least three independent autocatalytic loops,[6] but only the oxidation of bisulfite by peroxide seems to be experimentally justified. Thus a more comprehensive analysis seems warranted.[28]

In the oxidation of sulfur (-II) species, such as sulfide, to sulfate, it is difficult to distinguish the UV-absorbing species to monitor the time course of each. In the oxidation of thiosulfate by hypochlorite[29] and of tetrathionate by bromine[30] in weakly acidic media, it was assumed that polythionates such as pentathionate and hexathionate are formed based on spectroscopic data. The fitting procedure, however, provided a significantly different molar absorbance for pentathionate than measured by other workers.[31,32] Application of new experimental techniques to directly obtain more experimental information is clearly needed.[33−35]

To determine the relevant species, classical titration methods are quite time-consuming and difficult to employ in the presence of multiple similar species, while overlapping absorption bands hinder the application of spectroscopic methods. Fast separation technologies offer the promise of being able to monitor species simultaneously to obtain more direct and detailed information about the reaction kinetics. Fortunately, high performance liquid chromatography (HPLC) and capillary electrophoresis (CE), which have advantages in directness, speed, and precision compared to traditional methods, are increasingly being used in studies of the redox reactions of sulfur species.[19,33−40] Successful application of these separation techniques requires that (i) the reaction to be monitored be slow compared to the separation process; (ii), the pH and other conditions used in the separation process not alter the reaction mechanism or affect the rate of the reaction of interest, that is, the reaction should occur within the HPLC column or capillary in the same manner as in solution; and (iii) concentrations of relevant species in the reaction solution are measurable within the linear range of detection.

In the present work, we monitor the $H_2O_2{-}S_2O_3^{2-}$ reaction at several pHs and oxidant to reductant ratios, tracing the various sulfur species during the reaction process to establish the relationship between the reaction rate and the reaction conditions.

Experimental Section

Materials and Solutions. Commercially available reagents of the highest purity were used without further purification. All solutions were prepared with Milli-Q water with a conductivity of 18.2 MΩ·cm. Hydrogen peroxide (30% solution) was purchased from Sigma-Aldrich. Stock solutions were prepared by dilution to a concentration of 0.4 M and stored in the dark in brown bottles. The stock concentration was checked at least every 3 days by $KMnO_4$ titration. Thiosulfate stock solution (0.01 M) was standardized by iodometric titration once a week after preparation. Dithionate was prepared by oxidation of sulfite with manganese dioxide in strong acidic solution.[41] Trithionate as the potassium salt was used as a standard and was prepared according to the method given in ref 13. Its purity[42,43] was found to be 98.5%. Potassium tetrathionate, $K_2S_4O_6$, was purchased from Fluka with purity better than

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99.0%. Sodium sulfite and sodium sulfate stock solutions were prepared by dissolving appropriate amounts. Mobile phase and running buffer solutions for the HPLC and CE separations, respectively, were dilute solutions of acetate, phosphate, or carbonate with additives to improve selectivity and resolution. The pH buffer solutions for the oxidation reaction were prepared starting with 0.05 M acetate, phosphate, or carbonate and adjusted to the desired pH with the corresponding acid or sodium hydroxide solution. The ionic strength of each reaction solution was then adjusted to $I \approx 0.2$ M by adding an appropriate amount of sodium perchlorate.

Instrumentation and Methods. The HPLC separation experiments were conducted on a Dionex Summit System equipped with a variable wavelength detector (VWD). A C18 silicon column was used; the mobile phase was composed of 0.015 M phosphate buffer solution containing 7.0 mM tetrapropylammonium hydroxide (TPAOH), as ion-pair agent, and acetonitrile.[44] The separation performance was optimized to a ratio of 88:12 ($v_{\mathrm{water}}/v_{\mathrm{acetonitrile}}$). The ratio of the mobile phase was changed in a small range to achieve the desired separation performance. The pH of the mobile phase was adjusted to be the same as that of the reaction solution.

The electrophoresis experiments were carried out on a P/ACE MDQ Capillary Electrophoresis System (Beckman Coulter Inc., Fullerton, CA, U.S.A.) equipped with a DAD detector. A fused silica capillary of 75 μm i.d. and 57 cm total length (50 cm to the detector) was used. Samples were injected using an autosampler in the hydrodynamic mode by overpressure (0.5 psi.) for 5 s. 32 Karat Software (Beckman Coulter Inc.) was used for data acquisition and analysis. Data were taken at 214 nm for most of the separations, with shorter wavelengths, for example, 195 nm, used for trithionate and sulfite. In weakly acidic conditions, the running buffers were composed of 5 mM KH_2PO_4 and 5 mM $(NH_4)_2SO_4$ and adjusted to the desired pH with appropriate acid and/or base. In neutral and basic conditions, as the electroosmotic flow (EOF) increases with the pH, a modifier, hexadimethrine bromide (HDB)[45] was introduced to the running buffer solution to reverse the direction of EOF to decrease the migration time.

Here, we reproduce and optimize the separation conditions for the relevant sulfur species by HPLC and CE to monitor the $H_2O_2-S_2O_3^{2-}$ reaction in the pH range 3.0−11.0. At pH < 3.0, elemental sulfur forms in significant amounts because of the hydrolysis of thiosulfate.[46]

Reactions were initiated by introducing appropriate quantities of reactants into the pH buffer solutions. A portion of the solution in the reactor was withdrawn at regular intervals with a syringe and injected into the HPLC system or, with an autosampler, into the CE system for the analyses. All experiments, including the reaction and separation processes, were conducted at 25 °C. The reaction solutions were saturated with nitrogen during the reaction. The mobile phase (for HPLC) and running buffer (for CE) were degassed before the separation experiments. However, it was found in separate experiments that the dissolved oxygen from air influences neither the component determination nor the kinetics of the solution reaction significantly. Samples were filtered through a 0.45 μm membrane filter before injection.

Data Treatment. Chromatographic data at 214 and 230 nm were used for most of the kinetic measurements. Only experimental data with concentrations higher than 5% of the initial thiosulfate value were used for evaluation of the kinetics of the hydrogen peroxide-thiosulfate reaction. A typical HPLC run under our optimal conditions took 15 min, compared with 6 min for a CE run. At comparable concentration ratios of oxidant to reductant, such as 1:1 or 5:1, the reactions were slow enough to afford detailed information about the species in the reaction mixture. At least 8 data points from HPLC and 20 data points from CE (see below) were collected in a typical reaction. Stabilities of intermediates, especially polythionates, could be evaluated as a function of pH from the data obtained. At higher oxidant to reductant ratios, fewer data points could be obtained by HPLC, for example, we could only get 3 points under the condition $[H_2O_2]_0 = 30.0$ mM, $[S_2O_3^{2-}]_0 = 1.0$ mM and pH 5.0. Therefore, most of the reaction rate studies under pseudo-first order conditions with excess hydrogen peroxide were carried out by CE, with data from HPLC providing some additional information on the intermediates, especially polythionates.

Simulations of our proposed mechanism were carried out with the Berkeley Madonna software.[34,35] The ordinary differential equations used in the simulations are given in the Supporting Information. The Stiff Method was used, with tolerance set to 1.0×10^{-5}.

Results

Component Separation. The long-lived sulfur species that are likely to exist in the reaction system include sulfide, polysulfide, thiosulfate, dithionate, trithionate, tetrathionate, pentathionate, hexathionate, sulfite, and sulfate. Although there is no universally applicable chromatographic or electrophoretic strategy that allows separation of all these species in a single run, many reports describe the detection of one or more of these compounds in a variety of systems.[19,36−40,44]

As mentioned above, it is important that the separation conditions used not alter the reaction mechanism nor significantly affect the rate of the reaction. Some species, such as thiosulfate, dithionate, trithionate, and tetrathionate were identified by comparing their migration time to that of a standard. Others, like pentathionate and hexathionate were identified by comparing their HPLC retention factors with those found in the literature.[39] Typical profiles of components separated by CE and HPLC are shown in Figure 1. Thiosulfate and its oxidation products were baseline separated in a relatively short time, and their calibration curves for quantitative detection were also determined, so these methods are suitable for kinetics studies by repeated extraction and analysis of samples over the course of the reaction. The results clearly indicate that in acidic solution higher polythionates are formed in addition to tetrathionate and that these species are stable even in excess hydrogen peroxide.

As seen in Figure 2, the detectable polythionates vary with the pH. The mean number of sulfur atoms contained in the polythionates, *n*, decreases with pH. pH is the key factor for the stability of polythionates according to our experiments with a range of reactant ratios, ($[H_2O_2]_0/[S_2O_3^{2-}]_0$), from 5 to 35. Dithionate was stable at all pHs, with a constant concentration throughout the reaction, which agrees with previous reports,[41,47] but higher polythionates were only detected in specific pH ranges. Surprisingly, though trithionate seems more stable than tetrathionate in non-basic solution, it was only detected when pH > 6.0, which may be due to its particular formation path. Under strongly basic conditions, sulfate replaces tetrathionate as the main product in the system. Pentathionate and hexathionate could be detected under acidic conditions, in agreement with results on similar

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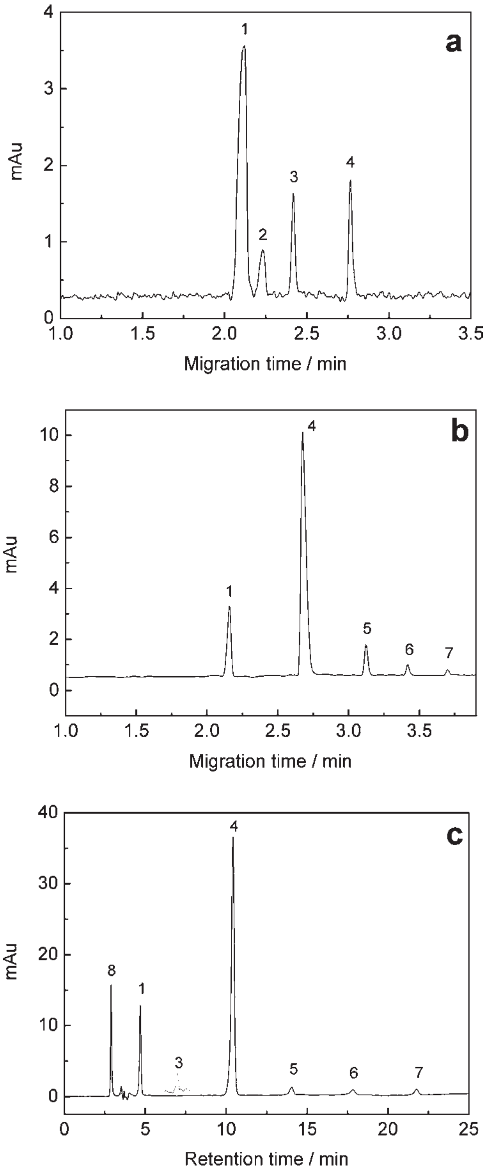

Figure 1. Typical electropherograms and chromatogram of the species in the $H_2O_2-S_2O_3^{2-}$ reaction system. Electropherograms: $[H_2O_2]_0 = 0.020$ M and $[S_2O_3^{2-}]_0 = 0.001$ M; (a) pH 7.0, reaction time = 30 min, absorption wavelength = 195 nm; (b) pH 2.0, reaction time = 25 min, absorption wavelength = 214 nm. Chromatogram: $[H_2O_2]_0 = 0.010$ M and $[S_2O_3^{2-}]_0 =$ 0.001 M; (c) pH 2.0, reaction time = 35 min, absorption wavelength = 230 nm. Peaks: 1, $S_2O_3^{2-}$; 2, $S_2O_6^{2-}$; 3, $S_3O_6^{2-}$; 4, $S_4O_6^{2-}$; 5, $S_5O_6^{2-}$; 6, $S_6O_6^{2-}$; 7, $S_7O_6^{2-}$; 8, H_2O_2.

reaction systems.[29,30] Heptathionate was detected only in strongly acidic medium, that is, pH < 2.0. In separate experiments, heptathionate was also found in the hydrolysis of thiosulfate at low pH.

Reaction Kinetics. The general form of the rate equation for reaction between H_2O_2 and $S_2O_3^{2-}$ can be expressed as follows:

$$-\mathrm{d}[S_2O_3^{2-}]/\mathrm{d}t = k[H_2O_2]^{\alpha}[S_2O_3^{2-}]^{\beta}$$

When H_2O_2 is in large excess, we have $[H_2O_2] \approx [H_2O_2]_0$, and the rate equation can be written as:

$$-\mathrm{d}[S_2O_3^{2-}]/\mathrm{d}t = k_{\mathrm{obs}}[S_2O_3^{2-}]^{\beta}$$

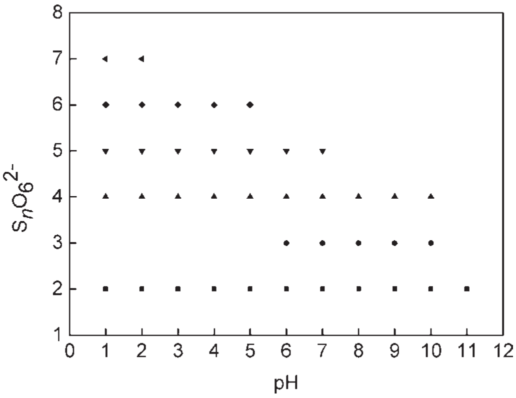

Figure 2. pH dependence of *n* (number of sulfur atoms in polythionates) in the $H_2O_2-S_2O_3^{2-}$ reaction system. Detectable sulfur species with HPLC and CE at various reaction pHs are $S_2O_6^{2-}$ (squares), $S_3O_6^{2-}$ (circles), $S_4O_6^{2-}$ (up pointing triangles), $S_5O_6^{2-}$ (down pointing triangles), $S_6O_6^{2-}$ (diamonds) and $S_7O_6^{2-}$ (left pointing triangles).

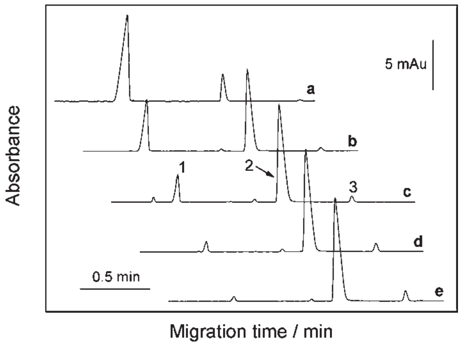

Figure 3. Time-courses of species in the $H_2O_2-S_2O_3^{2-}$ reaction system. Separation buffer: 5 mM $(NH_4)_2SO_4$ and 5 mM KH_2PO_4. $[H_2O_2]_0 =$ 0.014 M, $[S_2O_3^{2-}]_0 = 0.001$ M; pH 5.0; 25 °C. Reaction time, t = 3 min (a), 19 min (b), 35 min (c), 50 min (d), and 65 min (e). Peaks: 1, $S_2O_3^{2-}$; 2, $S_4O_6^{2-}$; 3, $S_5O_6^{2-}$.

where

$$k_{\mathrm{obs}} = k[H_2O_2]^{\alpha}$$

Figure 3 shows a typical set of CE separation runs under such conditions. The peak areas are proportional to the various species concentrations at the time of injection. Figure 4 (a) presents typical profiles at pH 5.0, which show that the rate of thiosulfate oxidation increases significantly with the initial concentration of hydrogen peroxide. We obtained linear plots of $\ln([S_2O_3^{2-}]_0/[S_2O_3^{2-}]_t)$ versus reaction time (Figure 4 (b)), indicating that the reaction is first order with respect to $S_2O_3^{2-}$, that is, $\beta = 1$.

The pseudo-first order rate constants, k_{obs}, calculated from the slopes of the straight lines obtained in Figure 4(b), are shown versus $[H_2O_2]_0$ in Figure 5. The linear relationship allows us to calculate the reaction order with respect to H_2O_2 as well as the rate constant.

Under acidic conditions, the major oxidation product is tetrathionate, together with some other polythionates. These species are stable. The pH dependence of the reaction rate under these circumstances is negligible. However, in basic solution, polythionates start to decompose[17,18,20,24–27] and oxidize to regenerate thiosulfate, which can reinitiate the $H_2O_2-S_2O_3^{2-}$ reaction. The stoichiometry and kinetics are obviously different under these conditions. Nevertheless, the

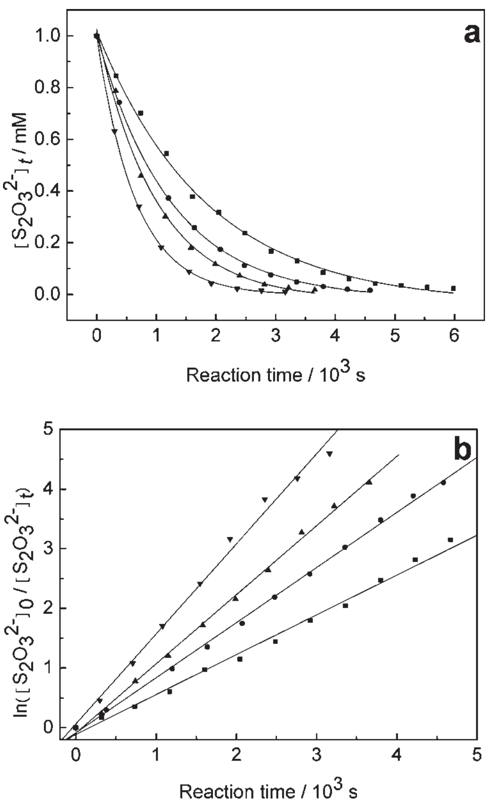

Figure 4. Kinetic curves of the hydrogen peroxide-thiosulfate reaction with different initial concentration ratios (a) and, (b) plot of ln ($[S_2O_3^{2-}]_0/[S_2O_3^{2-}]_t$) vs reaction time. $[S_2O_3^{2-}]_0$ = 0.001 M; $[H_2O_2]_0$ = 0.010M(squares), 0.015 M(circles), 0.020 M(up pointing triangles) and 0.025 M(down pointing triangles); pH 5.0; 25 °C.

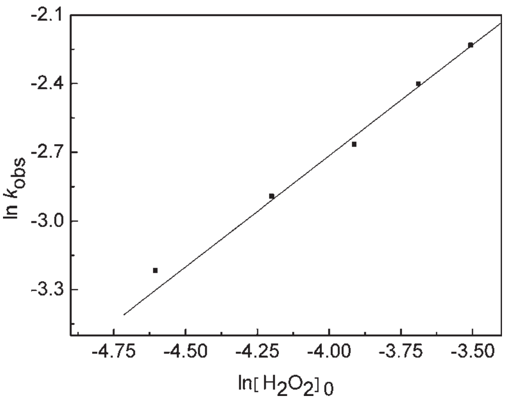

Figure 5. Dependence of the pseudo-first order rate constant k_{obs} on the initial hydrogen peroxide concentration. $[S_2O_3^{2-}]_0$ = 0.001 M, pH 5.0, T = 25 °C.

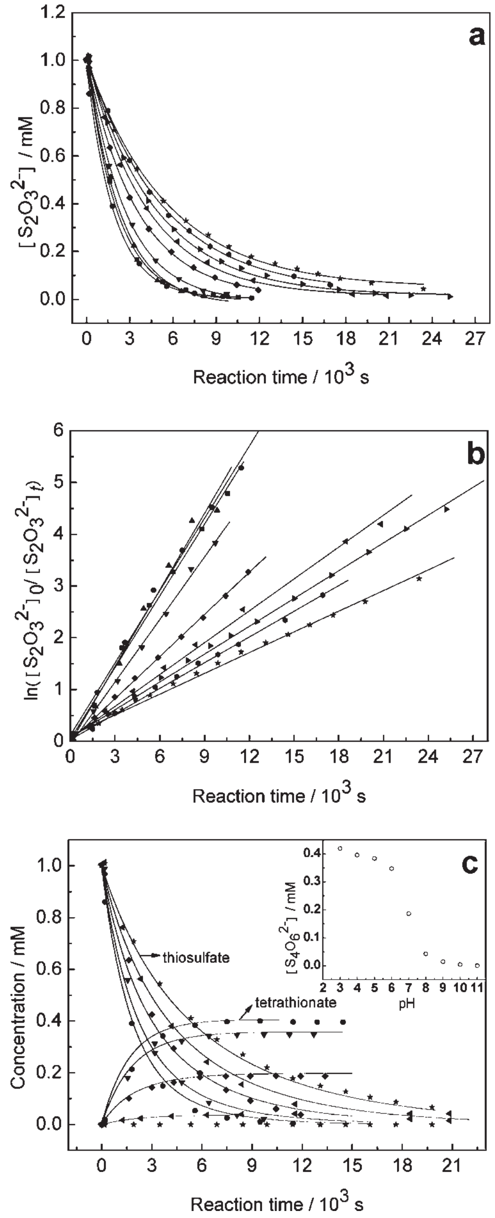

Figure 6. Kinetic curves for the hydrogen peroxide-thiosulfate reaction at various pHs. (a) Measured (symbols) and first-order fitted kinetic curves (lines), $[S_2O_3^{2-}]$ vs time; (b) linearity relationship of ln ($[S_2O_3^{2-}]_0/[S_2O_3^{2-}]_t$) vs time and (c) calculated kinetic curves (lines) of thiosulfate (decreasing) and tetrathionate (increasing) with measured data (symbols). $[H_2O_2]_0$ = 0.010M, $[S_2O_3^{2-}]_0$ = 0.001 M; pH 3.0 (squares), 4.0 (circles), 5.0 (up pointing triangles), 6.0 (down pointing triangles), 7.0 (diamonds), 8.0 (left pointing triangles), 9.0 (right pointing triangles), 10.0 (hexagons) and 11.0 (five pointed stars); 25 °C. Inset shows the final concentration of tetrathionate (open circles).

rate law is still first order in thiosulfate, with slightly larger pseudo-first order rate constants (slopes in Figure 6 (b)) in acidic than in basic conditions, a phenomenon we discuss below. Table 1 lists the calculated rate constants and reaction order for H_2O_2 at each pH investigated. On increasing the pH, we observe a decrease in k and a small increase in α. We conclude that the reaction is first order with respect to each of the reactants. Earlier simulations[6,11−14] employ rate constants between 0.019 M^{-1} s^{-1} and 0.023 M^{-1} s^{-1}, which are consistent with our results, particularly in the basic pH range.

As mentioned above, the formation of tetrathionate decreases with increasing pH. At pH 10.5−11.0, we can no longer detect tetrahionate in the reaction solution. Figure 6 (c) illustrates the kinetic curves of thiosulfate and tetrathionate at various pHs. More than 70% of the thiosulfate is transformed to tetrathionate at pH < 6.0, but for pH > 8.0, this falls to less than 10%. Interestingly, pH 7.0 is the watershed for the formation of tetrathionate: the inset in Figure 6 (c) shows the final concentration of tetrathionate when the residual thiosulfate is less than 5% of its initial concentration. We conclude that the reaction pathway depends critically on the pH.

Mechanistic Model. The model R1−R14 that we propose here builds upon models developed by Kurin-Csörgei et al.,[14]

Table 1. Reaction Order with Respect to Hydrogen Peroxide, α, and Rate Constant k Calculated from Experimental Results under Pseudo-First Order Reaction Conditions

pH	α	k/M^{-1} s^{-1}
3.0	0.90	0.048
4.0	0.93	0.045
5.0	0.97	0.040
6.0	0.96	0.036
7.0	1.05	0.027
8.0	0.98	0.025
9.0	1.09	0.022
10.0	1.02	0.019
11.0	1.12	0.016

Voslař et al.,[13] and Varga et al.[20] for the $H_2O_2-S_2O_3^{2-}$, $H_2O_2-S_4O_6^{2-}$ and $S_4O_6^{2-}$ decomposition reactions, respectively, with some modification of selected reactions and parameters.

$$H_2O_2 + S_2O_3^{2-} \rightarrow HOS_2O_3^{-} + OH^{-} \qquad (R1)$$

$$H_2O_2 + HOS_2O_3^{-} \rightarrow 2HSO_3^{-} + H^{+} \qquad (R2)$$

$$HOS_2O_3^{-} + S_2O_3^{2-} + H^{+} \rightarrow S_4O_6^{2-} + H_2O \qquad (R3)$$

$$2HOS_2O_3^{-} + H_2O \rightarrow S_2O_3^{2-} + 2SO_3^{2-} + 4H^{+} \qquad (R4)$$

$$S_4O_6^{2-} + OH^{-} \rightarrow S_2O_3^{2-} + HOS_2O_3^{-} \qquad (R5)$$

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-} \qquad (R6)$$

$$S_4O_6^{2-} + S_2O_3^{2-} \leftrightarrow S_5O_6^{2-} + SO_3^{2-} \qquad (R7)$$

$$S_4O_6^{2-} + HOS_2O_3^{-} \rightarrow S_5O_6^{2-} + SO_4^{2-} + H^{+} \qquad (R8)$$

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^{+} \qquad (R9)$$

$$S_5O_6^{2-} + 3OH^{-} \rightarrow 2.5S_2O_3^{2-} + 1.5H_2O \qquad (R10)$$

$$HSO_3^{-} + H_2O_2 \rightarrow SO_4^{2-} + H_2O + H^{+} \qquad (R11)$$

$$SO_3^{2-} + H_2O_2 \rightarrow SO_4^{2-} + H_2O \qquad (R12)$$

$$HSO_3^{-} \leftrightarrow H^{+} + SO_3^{2-} \qquad (R13)$$

$$H_2O_2 \leftrightarrow HO_2^{-} + H^{+} \qquad (R14)$$

Reaction rates and rate constants for the mechanism R1−R14 are given in Table 2. $HOS_2O_3^-$ is included as a key intermediate because of its crucial role in the thiosulfate/tetrathionate-hydrogen peroxide and tetrathionate-chlorite reactions.[6,11−14] We detected trithionate and pentathionate, and these species are also known to participate in rearrangement reactions of tetrathionate.[20] Though hexathionate and heptathionate were also detected, they exist only under strongly acidic conditions (pH $<$ 5.0 and 2.0, respectively) in trace amounts, so their contributions to the mechanism can safely be ignored. Sulfite/bisulfite arises as an intermediate in the ultimate oxidation of thiosulfate to sulfate in neutral and basic conditions and also as an oxidation product of tetrathionate by hydrogen peroxide.[13]

Discussion

Step R1 is the initiating and rate-determining step in the oxidation of thiosulfate by hydrogen peroxide. Initial formation of a peroxide-thiosulfate pair is followed by a shift in electron density away from the peroxide oxygen nearer the sulfur of the thiosulfate ion toward the other peroxide oxygen. Then thiosulfate displaces a hydroxyl ion from the hydrogen peroxide to form the $HOS_2O_3^-$ intermediate. This intermediate has been postulated in several systems to support kinetic observations,[6,11−14] but it has never been identified experimentally. In acetic acid-acetate buffer or dilute acid, the rate constant was suggested to be about 0.025 M^{-1} s^{-1} at room temperature,[48] a bit higher than the 0.019 M^{-1} s^{-1} obtained in the $H_2O_2-S_2O_3^{2-}-CN^-$ system.[12] The pseudo-first order rate constants k_{obs} of thiosulfate consumption are smaller at higher pHs (Figure 6 (b)). Under acidic conditions, reactions R3 and R7 accelerate the consumption of thiosulfate, resulting in a higher k_{obs}. Under basic conditions, thiosulfate-generating reactions R5, R6, and R10 are promoted by OH^-, slowing the net consumption of thiosulfate. Low initial hydrogen peroxide concentrations make this effect more apparent, because reaction R1 is then relatively slow. The rate constant $k_1 = k$ and the reaction order (α) with respect to hydrogen peroxide, decreasing and increasing with pH (see Table 1), respectively, were obtained from the slope (α) and intercept (ln k) by plotting ln k_{obs} versus ln $[H_2O_2]_0$ as in Figure 5. We choose $k_1 = 0.025$ M^{-1} s^{-1} in the model to correspond to neutral or slightly basic conditions, where the value of k_1 is roughly the average over the entire pH range and the kinetics are first order with respect to hydrogen peroxide.

Step R2 and R3 describe the competition of the reactants for the $HOS_2O_3^-$ intermediate. The outcome of these interactions determines the ratio of products, HSO_3^- and $S_4O_6^{2-}$, which depends on the pH. At pH $<$ 5.0, Abel reported that thiosulfate was oxidized almost quantitatively by hydrogen peroxide to form tetrathionate.[49] Accordingly, R3 is the dominant pathway under acidic conditions. Schiller proposed mixed products of sulfate and tetrathionate, corresponding to a combination of R2 and R3, for neutral and alkaline systems.[12] In the models reported previously, the rate law for R2 involved only H_2O_2 and $HOS_2O_3^-$. We explored the effects of including a hydroxide acceleration term in the rate law for R2. However, our simulations showed that the pH dependence of R2 has much less influence on the course of the reaction than that of R3. When this term is left out of the model, our calculations give good agreement with the experimental results by using the reported rate constant of 50 M^{-1} s^{-1} for R2[13] and a pH-dependent rate for R3. Under acidic conditions, the reaction kinetics is essentially first order

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Table 2. Reaction Rates and Rate Constants for the Mechanism R1−R14

step	rate equations	rate constants at 25 °C	ref.
R1	$v_1 = k_1[H_2O_2][S_2O_3^{2-}]$	$k_1 = 0.025\ M^{-1}\ s^{-1}$	this work
R2	$v_2 = k_2\ [H_2O_2][HOS_2O_3^{-}]$	$k_2 = 50.0\ M^{-1}\ s^{-1}$	13
R3	$v_3 = k_3\ [H^+]/([H^+] + 1.0 \times 10^{-6})\ [HOS_2O_3^{-}][S_2O_3^{2-}]$	$k_3 = 4.0 \times 10^3\ M^{-1}\ s^{-1}$	this work
R4	$v_4 = k_4\ [HOS_2O_3^{-}]^2$	$k_4 = 10^4\ M^{-1}\ s^{-1}$	this work
R5	$v_5 = k_5\ [S_4O_6^{2-}][OH^-]$	$k_5 = 0.02\ M^{-1}\ s^{-1}$	20, 26
R6	$v_6 = k_6[S_4O_6^{2-}][SO_3^{2-}]$	$k_6 = 0.55\ M^{-1}\ s^{-1}$	20
R7	$v_7 = k_7[S_4O_6^{2-}][S_2O_3^{2-}] - k_{-7}[S_5O_6^{2-}][SO_3^{2-}]$	$k_7 = 1 \times 10^{-4}\ M^{-1}\ s^{-1}$, $k_{-7} = 1000\ M^{-1}\ s^{-1}$	20
R8	$v_8 = k_8[S_4O_6^{2-}][HOS_2O_3^{2-}]$	$k_8 = 58\ M^{-1}\ s^{-1}$	20
R9	$v_9 = k_9[S_3O_6^{2-}]$	$k_9 = 6.0 \times 10^{-7}\ s^{-1}$	53, 54
R10	$v_{10} = k_{10}\ [S_5O_6^{2-}][OH^-]$	$k_{10} = 1000\ M^{-1}\ s^{-1}$	20
R11	$v_{11} = (k_{11} + k_{11}'\ [H^+])\ [H_2O_2][HSO_3^{-}]$	$k_{11} = 7.0\ M^{-1}\ s^{-1}$, $k_{11}' = 1.48 \times 10^7\ M^{-2}s^{-1}$	56
R12	$v_{12} = k_{12}[H_2O_2][SO_3^{2-}]$	$k_{12} = 0.20\ M^{-1}\ s^{-1}$	58
R13	$v_{13} = k_{13}[HSO_3^{-}] - k_{-13}[H^+][SO_3^{2-}]$	$k_{13} = 3.0 \times 10^3\ s^{-1}$, $k_{-13} = 5.0 \times 10^{10}\ M^{-1}\ s^{-1}$	28
R14	$v_{14} = k_{14}[H_2O_2] - k_{-14}[H^+][HO_2^{-}]$	$k_{14} = 0.025\ s^{-1}$, $k_{-14} = 1.0 \times 10^{10}\ M^{-1}\ s^{-1}$	28

in thiosulfate, with almost no dependence on pH. In basic solution, however, $[H^+]$ significantly affects the rate, especially the formation of tetrathionate. A pH-dependent rate expression for R3, $k_3' = 4000[H^+]/([H^+] + 1.0 \times 10^{-6})$, nicely captures this aspect of the experimental results. The ratio (k_3'/k_2) decreases with pH, consistent with the results reported by Schiller,[12] Kurin-Csörgei[14] (at acidic conditions), and Voslař[13] (at alkaline conditions).

Step R4 is the decomposition of $HOS_2O_3^-$ to produce thiosulfate and sulfite. Varga and Horváth[20] report that this reaction is not elementary, and probably proceeds via formation of an intermediate disulfite, $S_2O_5^{2-}$, via steps like E3 and E4,

$$2HOS_2O_3^- \rightarrow S_2O_3^{2-} + S_2O_5^{2-} + 2H^+ \qquad (E3)$$

$$S_2O_5^{2-} + H_2O \rightarrow 2SO_3^{2-} + 2H^+ \qquad (E4)$$

which are similar to suggestions made by Voslař et al[13] for the initial process of tetrathionate oxidation by hydrogen peroxide. Their calculations support this reaction, which produces thiosulfate and sulfite under neutral and basic conditions. Its rate law, which we adopt, is second order with respect to $HOS_2O_3^-$ and independent of pH. To better fit the observed slower depletion of thiosulfate and growth of tetrathionate, and hence the lower amounts of tetrathionate ultimately formed, at higher pH, we employ a smaller rate constant, $10^4\ M^{-1}\ s^{-1}$, instead of the reported value[20] of $10^7\ M^{-1}\ s^{-1}$.

Step R5 is the alkaline decomposition of tetrathionate via scission of the central S−S bond, resulting in nucleophilic displacement of thiosulfate by hydroxide ion to yield thiosulfate and the intermediate $HOS_2O_3^-$. Rolia et al.,[25] Varga et al.,[20] and Zhang et al.[26] have independently estimated the rate constant k_5 at different ionic strengths. Their results were $0.0051\ M^{-1}\ s^{-1}$, $0.044\ M^{-1}\ s^{-1}$, and $0.38\ M^{-1}\ s^{-1}$, respectively. Breuer and Jeffrey[27] report that the decomposition of tetrathionate is affected by concentration, ionic strength and even the identity of the buffer electrolyte. Our fitting procedure yielded a value of $0.02\ M^{-1}\ s^{-1}$ for k_5 at our ionic strength of ≈0.2 M. This reaction has been suggested as a possible initial step in the decomposition of tetrathionate in alkaline solution and in the oxidation of tetrathionate by hydrogen peroxide.[13,25] In our experiments, tetrathionate was quite stable in acidic solution, even in the presence of excess hydrogen peroxide, but the amount of tetrathionate found decreased sharply in alkaline solution (Figure 6 (c)). Obviously, pH is a key determinant of the reaction kinetics because it affects not only the pathways for the hydrogen peroxide-thiosulfate reaction R2 and R3 but also the further reactions of several intermediates. We note that R5 is essentially the reverse of R3, with R3 favored under acidic conditions and R5 in basic conditions.

Step R6 is the well-known sulfitolysis of tetrathionate, which produces thiosulfate and trithionate.[17−19,50,51] This step is the only source of trithionate in the proposed model. This reaction has been successfully applied in the analysis of polythionates[17,18] and was later modified[50] for analyzing microamounts of polythionates. Varga and Horváth[20] propose a value of $k_6 = 0.547 \pm 0.005\ M^{-1}\ s^{-1}$, which agrees well with that determined by Foerster and Centner.[51] Contrary to earlier assumptions, Motellier and Descostes[19] conclude that this reaction only occurs under neutral and basic conditions, in agreement with our experimental observation that trithionate only forms at pH > 6.0. We adopt a rate constant of $0.55\ M^{-1}\ s^{-1}$ for this step.

Step R7 is the reversible rearrangement of tetrathionate, assisted by thiosulfate, to yield pentathionate and sulfite. Fava and Bresadola[24] determined a value of $3.9 \times 10^{-3}\ M^{-1}\ s^{-1}$ for the rate constant of the forward reaction, but failed to determine the reverse rate constant at 50 °C and ionic strength $I = 0.94$ M in neutral solution. Foss[52] obtained $k_7 = 1.3 \times 10^{-3}\ M^{-1}\ s^{-1}$ for the forward reaction at 25 °C and ionic strength $I = 1.15$ M. Again, because of the salt effect on the kinetics, Varga and Horváth[20] give a value of $1.94 \pm 0.08 \times 10^{-4}\ M^{-1}\ s^{-1}$ for k_7 in their calculation, which is approximately an order of magnitude lower than the value determined by Foss. Since no experimental value of k_{-7} was available, and pentathionate did not accumulate in detectable amounts in their measurements, they introduced $1220 \pm 40\ M^{-1}\ s^{-1}$ as the rate constant for the backward process. In our experiments, however, a considerable amount of pentathionate was detected under acidic conditions. We choose values of $1.0 \times 10^{-4}\ M^{-1}\ s^{-1}$ and $1000\ M^{-1}\ s^{-1}$ for the forward and backward reaction constants, respectively, which gives a pentathionate concentration of 10^{-5} M to 10^{-6} M in the simulations, consistent with our experimental results. We believe that this is the main reaction that consumes tetrathionate under acidic conditions.

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Step R8 is the attack on tetrathionate by the intermediate $HOS_2O_3^-$ to lengthen the sulfur chain and produce pentathionate. In the decomposition of tetrathionate, the formation of pentathionate increases with increasing initial tetrathionate concentration.[20] Obviously, this step is another pathway besides R7 for increasing the amount of pentathionate. In our experiments, pentathionates accumulate in acidic medium along with tetrathionate. In our simulations, we adopt the rate equation and rate constant proposed by Varga and Horváth.[20]

Step R9 is the first order decomposition of trithionate to yield thiosulfate and sulfate.[25,53,54] Rolia and Chakrabarti[25] obtained rate constants for the decomposition of trithionate in the range 10^{-5} to 10^{-4} s^{-1} at relatively high temperature (70−100 °C). From these values and the activation energies reported by Naito et al.[53] and Hofman-Bang,[54] we obtain pseudo-first order rate constants of 6.1×10^{-7} s^{-1} and 7.7×10^{-7} s^{-1}, respectively. We choose 6.0×10^{-7} s^{-1} as the rate constant in the model at our relatively low temperature. The small value of k_9 might suggest that this reaction can safely be deleted from the proposed model. Under the conditions of our experiments (pH < 11.0), trithionate is apparently stable enough to resist further oxidation and decomposition, similar to the behavior of tetrathionate in acidic solution. At high pH, that is, > 11.0, no trithionate was detected, presumably because the pH-dependent R3 is too slow in strongly alkaline solution to generate enough tetrathionate for the trithionate-producing sulfitolysis R6.

Step R10 is the alkaline decomposition of pentathionate. In neutral and weakly alkaline (pH < 9.0) solution, pentathionate is relatively stable to degradation, but at higher pH, it is no longer stable and decomposes to thiosulfate.[55] In our experiments, pentathionate was only detected at pH ≤ 7.0, presumably because of the low concentration of pentathionate formed and its hydrolysis under basic conditions. This step is not elementary. From the mechanism proposed by Varga and Horváth,[13] pentathionate is attacked by hydroxide ion at the γ-sulfur atom, yielding thiosulfate and $HOS_3O_3^-$, which undergoes further hydrolysis to form other intermediates, $S(OH)_2$ and $HS(OH)$, which can lead to the formation of elemental sulfur. In our experiments, faint yellow traces of elemental sulfur were observed at the bottom of our vials, especially under acidic conditions. Here, we treat this step as first order with respect to pentathionate and hydroxide, and adopt a rate constant of 1.0×10^3 M^{-1} s^{-1}.

Steps R11 and R12 are the oxidation of the HSO_3^-/SO_3^{2-} couple by hydrogen peroxide.[56] These reactions constitute the direct route to sulfate. R11 is the autocatalytic reaction in $[H^+]$ that drives pH oscillations in the $H_2O_2-S_2O_3^{2-}-SO_3^{2-}-H^+$ system.[6]

Steps R13 and R14 are the acid−base equilibria for HSO_3^-/SO_3^{2-} and H_2O_2/HO_2^-, respectively. Our system is pH-sensitive, so both of these acid−base equilibria should be incorporated in a full description. Although in our experiments the pH was kept constant by using buffers, we include these acid−base equilibria in the mechanism to make it applicable to further studies of the dynamical behavior of this system when the pH is allowed to vary.

The proposed model works well over a large range of reactant concentrations and pH, as seen in the simulation results presented in Figure 6(c), where we compare the experimental and simulated time-courses of thiosulfate and tetrathionate at several pHs.

Our model does not include the symmetric cleavage of tetrathionate by hydrogen peroxide to yield two molecules of the intermediate $HOS_2O_3^-$,[6,14] since this step is inconsistent with the stability of tetrathionate under acidic conditions in the presence of hydrogen peroxide. We instead postulate that the initial step of tetrathionate consumption is its reaction with hydroxide peroxide to give thiosulfate and peroxothiosulfate (see R5), which is more consistent with our experimental results. On the basis of these considerations, we attempted to incorporate a composite initial step in which tetrathionate is oxidized by hydrogen peroxide with third-order kinetics.[13] One may combine this step with the reversible reaction of tetrathionate and hydroxide R3 and R5, the oxidation of the intermediate $HOS_2O_3^-$ R2 and of sulfite by hydrogen peroxide R11, and the equilibrium between sulfite and bisulfite R13 to make a quasi-steady-state approximation for $HOS_2O_3^-$. Voslař et al.[13] show, however, that the above scheme contradicts their empirical rate law obtained by the method of initial reaction rates. Although they propose a plausible scheme, in which disulfite ($S_2O_5^{2-}$) is the core species,[13] there is no experimental evidence for the existence of this compound.[20] We detected a very small amount of dithionate ($S_2O_6^{2-}$) at several pHs and oxidant concentrations, which supports earlier stoichiometric measurements,[57−59] since dithionate should form via a radical pathway. From this point of view, dithionite ($S_2O_4^{2-}$) seems likely to form via decomposition of $HOS_2O_3^-$. These $S_2O_x^{2-}$ species could not be detected by our methods because of their weak UV absorptions and the limitations of our separation methods. Furthermore, they cannot persist for long times because of oxidation reactions with hydrogen peroxide. Accordingly, we suggest that the most likely processes for the formation of $S_2O_4^{2-}$ and its further oxidation are E5 and E6.

$$HOS_2O_3^- + OH^- \rightarrow S_2O_4^{2-} + H_2O \qquad (E5)$$

$$S_2O_4^{2-} + H_2O_2 \rightarrow 2HSO_3^- \qquad (E6)$$

Conclusion

We have conducted analytical and kinetics studies of the $H_2O_2-S_2O_3^{2-}$ reaction with the pH and oxidant to reductant ratio as control parameters by means of electrophoretic and chromatographic detection. The stabilities of the oxygen−sulfur species with respect to pH were investigated, and we find that the mean number of sulfur atoms contained in the polythionates decreases with increasing pH. The concentration of tetrathionate varies significantly with pH, and a switch in the dominant mechanism appears to occur around pH 6.0−7.0. Tetrathionate formation R3, which competes with $HOS_2O_3^-$ oxidation R2 and degradation R5 and R6, becomes less important at higher pH and initial concentration of hydrogen peroxide. This observation may be helpful in understanding the pH oscillatory dynamics in the unbuffered flow system at nearly neutral conditions. We have proposed a 14-step mechanistic model based on our experimental observations and previous models. This work may have applications not only to improving our understanding

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of the complex dynamics in this system but also to industrial processes such as lixiviation of noble metals.[26,27]

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Supporting Information Available: Ordinary differential equations used in simulations of the proposed mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.