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Oscillatory Reactions Involving Hydrogen Peroxide and Thiosulfate—Kinetics of the Oxidation of Tetrathionate by Hydrogen Peroxide

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The reaction between tetrathionate and hydrogen peroxide forms an important part of several pH oscillators based on the oxidation of thiosulfate. The kinetics of this reaction were examined in a batch reactor by measurement of the initial pH values in the range from 8 to 10.5. Experimental data were evaluated by the method of initial reaction rates combined with the assumption of instantaneously equilibrated acid–base reactions. The rate-determining step was found to be of the first order with respect to tetrathionate, hydrogen peroxide, and OH^- ions with the value of rate constant $k = (1.50 \pm 0.03) \times 10^2$ $(M^2\ s)^{-1}$ at 25 °C. In the alkaline solution, no distinct catalytic effect of Cu^{2+} was observed in contrast to earlier assumptions. The waveform of measured pH over the course of the reaction indicates that thiosulfate is probably an intermediate because characteristics of the curves are very similar to those for the oxidation of thiosulfate. We also measured the time evolution of concentrations of major components by the attenuated total internal reflectance infrared spectroscopy to further elucidate the underlying reaction mechanism. These measurements confirm the suspected role of thiosulfate as an intermediate in the studied reaction and provide valuable detailed information on the time evolution of thiosulfate, sulfite, sulfate, tetrathionate, and trithionate. These experimental observations are included in a simple mechanism that accurately simulates the reaction course in an alkaline solution. The results provide considerable new insights into the nature of autocatalysis in the hydrogen peroxide–thiosulfate–Cu^{2+} reaction and suggest that a new role for Cu^{2+} in the oscillatory dynamics observed in a flow-through reactor needs to be found.

Introduction

Research in open chemical systems with nonlinear oscillatory dynamics often requires cooperation among various branches of chemistry, from inorganic and analytical chemistry to physical chemistry and biochemistry.[1−3] A particularly wide group of reactions providing stable oscillatory behavior mostly associated with multiple steady states and excitability involves pH oscillators.[3,4] The experimentally well-founded reaction of thiosulfate with hydrogen peroxide catalyzed by cupric ions[5] (HPTCu) in an isothermal flow-through stirred tank reactor was among the first experimentally studied pH oscillators. Because of relatively easy experimentation and rich and diverse dynamics, it is a convenient model system for practical laboratory research in chemical nonlinear dynamics. An inherent part of this research is comparing experiments with proposed mathematical models and their mechanistic interpretation, which helps to understand more deeply the observed nonlinear phenomena and, more generally, the kinetics of aqueous sulfur chemistry.

The reaction mechanism of the HPTCu oscillator published by Kurin-Csörgei et al.[6] assumes three relatively stable intermediates over the course of the oxidation of thiosulfate

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by hydrogen peroxide; two of them are well-known species—sulfite and tetrathionate. According to a detailed study conducted by Rábai and Hanazaki,[7] this reaction mechanism involves at least three independent autocatalytic loops. The first one is based on the net production of OH^- ions during the primary reaction of thiosulfate with hydrogen peroxide catalyzed by cupric ions, which is assumed to be speeded up by an increase in pH. The second and third autocatalytic loops[7] involve a secondary oxidation of tetrathionate and sulfite, respectively. Despite the lack of experimentally observed oscillations in the absence of Cu^{2+} in an isothermal system,[5,7] Rábai and Hanazaki[7] found oscillations in the (simplified) HPTCu model[6] even when the effect of Cu^{2+} is left out of the mechanism. Two oscillatory modes were identified: high-amplitude, low-frequency oscillations are made possible by the second autocatalytic loop, while the third loop provides low-amplitude, high-frequency oscillations. A combination of both suboscillators, then, may generate the complex mixed-mode dynamics observed in the model.[6,7] Interestingly, mixed-mode oscillations were also observed in the experiments.[5]

Moreover, the HPTCu mechanism[6] does not take into account the experiments by Yokosuka et al.,[8] who report sulfate, thiosulfate, and trithionate as products of the tetrathionate oxidation by hydrogen peroxide. According to the HPTCu model, the only possible product is sulfate with the overall stoichiometry

$$S_4O_6^{2-} + 7H_2O_2 \rightarrow 4SO_4^{2-} + 6H^+ + 4H_2O \qquad (1)$$

The first step of this overall stoichiometry assumed in the HPTCu model[6] is

$$S_4O_6^{2-} + H_2O_2 \xrightarrow[OH^-]{} 2HOS_2O_3^- \qquad (2)$$

where the kinetics are of the first order with respect to tetrathionate, hydrogen peroxide, and hydroxide ions. The hypothesized peroxothiosulfate intermediate $HOS_2O_3^-$ is an analogue to certain previously studied compounds, where the HO group is replaced by iodine[9] or chlorine.[10] According to molecular orbital calculations,[11] $HOS_2O_3^-$ represents a slightly more stable isomer of the well-known dithionous acid anion $HS_2O_4^-$, and therefore, its occurrence in the HPTCu reaction seems likely. The subsequent reaction of thiosulfate with peroxothiosulfate

$$S_2O_3^{2-} + HOS_2O_3^- \rightarrow S_4O_6^{2-} + OH^- \qquad (3)$$

provides for a positive feedback. Thus, a combination of processes 2 and 3 generates the second autocatalytic loop included in the HPTCu model.[6] However, such autocatalysis does not take into account the previously published experimental observations.[8]

Another discrepancy in the model[6] can be found between the assumed first (Cu^{2+}-catalyzed) autocatalytic loop and experimental evidence against such an assumption.[12,13] Thus far, only the third above-mentioned autocatalytic loop in the HPTCu model—the well-known oxidation of bisulfite by peroxide[14]—seems experimentally warranted.

Accordingly, we have done a series of kinetic measurements of tetrathionate oxidation by hydrogen peroxide in an alkaline solution with the aim of determining the reaction rate dependence on the concentration of components involved and verifying a possible secondary catalytic effect of cupric ions in the HPTCu system mentioned by Orbán and Epstein.[5] Kinetics were examined in a batch reactor by using a pH meter in the range from 8 to 10.5. Experimental data were evaluated by a procedure described in the appendix, which combines the method of initial reaction rates and the assumption of instantaneously equilibrated acid—base reactions. To determine ambiguous reaction stoichiometry, we have also used infrared spectroscopy modified for measurements of aqueous solutions (Fourier transform infrared spectroscopy with an attenuated total reflection accessory, FT-IR/ATR). This technique was previously introduced as an accurate, noninvasive analytical method for the quantitation of mixtures of sulfur—oxygen anions.[15,16] Our results provide valuable and rather detailed information on the kinetics of the studied reaction and on the time evolution of thiosulfate, sulfite, sulfate, tetrathionate, and trithionate. It seems that the role of the tetrathionate oxidation stressed in ref 7 is not realistic in the model and new mechanistic features are needed for a thorough understanding of the dynamical phenomena experimentally observed in the HPT-Cu system.[5]

Experimental Section

Material. Commercially available chemicals of a guaranteed analytical purity—H_2O_2 (30% solution), $Na_2S_2O_3 \cdot 5H_2O$, $CuSO_4 \cdot 5H_2O$, Na_2SO_4, Na_2SO_3, NaOH, and $KMnO_4$ (Penta) and $K_2S_4O_6$ ($\geq$99.0%, Fluka)—were used without further purification. The purity of $K_2S_4O_6$ was checked by using both FT-IR and Raman spectroscopy. The measured spectra match the data presented in refs 17 and 18. No bands corresponding to other compounds (impurities) were detected. Demineralized water was exclusively used for the preparation of the solutions. A prepared stock solution of H_2O_2 ($c \cong 0.5$ M) was stored in the dark at 4 °C and checked by titration using a standard solution of $KMnO_4$ at least every 48 h. Under these conditions, the changes in concentration of the stock H_2O_2 solution were smaller than the relative deviation of repeated titrations ($\sigma \cong 0.2\%$).

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Potassium trithionate used as a standard was prepared according to a recipe given in refs 19 and 20: 84.5 mL of a 30% solution of hydrogen peroxide was added dropwise within a period of 6 h to a saturated, ice-cooled, stirred solution of 92.5 g of $Na_2S_2O_3{\cdot}5H_2O$. Because the reaction is exothermic, the temperature varied between 4 and 10 °C. The reading of the pH meter for the first 50 mL of added peroxide solution was in the range 10−11; later, the mixture gradually became neutral. Sulfate in the mixture was then precipitated by adding 55 g of $BaCl_2{\cdot}2H_2O$ dissolved in 140 mL of water and was filtered out as $BaSO_4$. Trithionate in the form of potassium salt was isolated from the continually stirred filtrate by crystallization initiated by adding an ethanol solution of potassium acetate (90 g of acetate + 500 mL of alcohol). Fine, purely white crystals of the product were, upon washing with 50 mL of water and 50 mL of ethanol, dried under ambient temperature to a constant mass (about 35 g). The product was checked using FT-IR and FT-Raman spectroscopy. The data obtained agree with the previously published results.[17,18]

Measurements in the Batch Reactor. Kinetic measurements were done in a closed jacketed glass reactor of 20 mL internal volume at 25.0 ± 0.5 °C under vigorous stirring by a magnetic stirrer. The reaction was, in most cases, initiated by adding a fresh solution of tetrathionate to a mixture of demineralized water and solutions of H_2O_2 and NaOH with known concentrations and given volume ratios. Initial concentrations of the species were chosen to correspond to typical conditions in the entire system of the HPTCu reaction[5] as well as to conditions relevant for the use of our method and are specified in the Results section.

The pH variation during the reaction was measured by a combined ROSS pH electrode (model 8156) connected to an ORION 525 A pH meter and a PC. Data were collected by the program LabVIEW 5.0.1 (National Instruments). A three-point calibration of the pH meter was done daily with the use of standard buffers (Sigma-Aldrich pH = 4.00, 7.00, and 10.00). Initial changes of pH were calculated from the measured time courses of pH (sampling frequency was 30−60 min^{-1}) as a first derivative of a regression polynomial of the second order at time $t \to 0$. The values of $\mathrm{dpH}/\mathrm{d}t|_{t=0}$ thus obtained were used to calculate the initial reaction rates v_0, on the basis of an assumption of rapid equilibration of acid−base reactions (see Appendix). By plotting the calculated v_0 against the initial concentrations of the reactants, the kinetic order of the reaction is obtained. The method described in the appendix is a modified version of a general formulation found in ref 21 and has been successfully applied to the bromate−sulfite−ferrocyanide pH-oscillatory reaction, which involves five acid−base equilibrium reactions.[3,21]

Infrared Spectroscopy. In selected cases, the instantaneous concentration of sulfur−oxygen species present in the samples taken from the reaction mixture during the reaction was measured, because pH evolution does not offer exhaustive information on the composition of the reaction mixture and a corresponding unknown reaction stoichiometry. The multicomponent analysis of FT-IR/ATR spectra of mixtures of sulfur−oxygen anions[16] was used. Infrared spectra were collected using a Nexus FT-IR spectrometer (Thermo Nicolet, U. S. A.) equipped with a MIRacle single-bounce horizontal ATR accessory. The liquid samples were placed on a ZnSe crystal. Afterward, four scans were accumulated per spectrum at 4 cm^{-1} resolution. The spectral data acquisition time was approximately 4 s. The system allows for collecting such spectra every 6 s. At least four repetitive measurements were performed for every sample of standards. Water and acetone were used to clean the surface of the ZnSe crystal. The programs OMNIC 6.0, 7.0, and 7.1 (Thermo Nicolet, U. S. A.) were used to process the spectral data (subtraction of the water spectrum and automatic baseline correction). The quantitative analysis was performed using TQ Analyst 7.0 (Thermo Nicolet, U. S. A.). The analysis was based on a partial-least-squares method.[15] The principal component spectra, pure component spectra, and the values of predicted residual error sum of squares[15] were used as calibration diagnostic tools to optimize the developed quantitative method based on more than 140 calibration and 50 validation spectra of carefully prepared calibration mixtures.

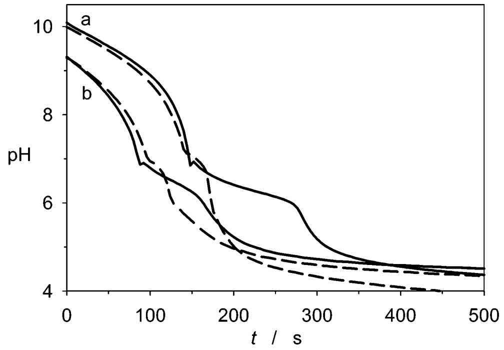

Figure 1. Comparison of characteristic waveforms of kinetic curves measured with (dashed line) and without (full line) added Cu^{2+}. Initial concentrations: (a) $[S_4O_6^{2-}]_0 = 1.0 \times 10^{-2}$ M, $[H_2O_2]_0 = 0.175$ M, $[Cu^{2+}]_0 = 1.0 \times 10^{-4}$ M; (b) $[S_4O_6^{2-}]_0 = 1.25 \times 10^{-2}$ M, $[H_2O_2]_0 = 0.125$ M, $[Cu^{2+}]_0 = 5.0 \times 10^{-5}$ M.The initial pH was adjusted by adding a solution of 1 M NaOH.

A macro (OMNIC Macros/Basic 7.0, Thermo Nicolet, U. S. A.) was created to perform a semiautomatic data collection and an automatic data save during continuous kinetic measurements. The results of continuous measurements were compared with data obtained from samples repeatedly taken from the reaction mixture during a second control experiment to indicate possible systematic errors in the long-running kinetic measurements due to the absence of stirring and thermoregulation of the reaction mixture on the ATR crystal.

Results

Typical kinetic curves occurring during the oxidation of tetrathionate by hydrogen peroxide in an alkaline solution are displayed in Figure 1. Two sets of experiments at different initial concentrations (a and b) are shown here, each represented by two curves−one with added cupric ions (dashed) and the other without. The characteristic waveform of the curves measured without Cu^{2+} ions indicates two different stages of the reaction, the first one in the alkaline region and the second one near and below pH ≈ 7. The latter is similar to kinetic curves obtained for the oxidation of thiosulfate by hydrogen peroxide.[5] This observation corresponds well to thiosulfate playing the role of an intermediate in tetrathionate oxidation by hydrogen peroxide.[8]

Measurement without Added Cupric Ions. The method of initial reaction rates modified for the case of measuring pH during the reaction (see the appendix) was used with the aim of determining the order of reaction with respect to tetrathionate and hydrogen peroxide and of determining the

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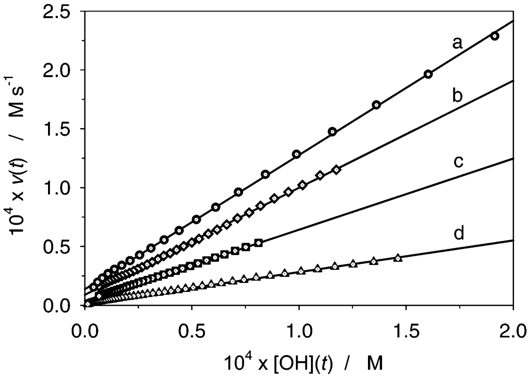

Figure 2. Evolution of the instantaneous reaction rate dependent on the actual concentration of OH^- (points) and the linear trends (lines). Initial concentration: $[Cu^{2+}]_0 = 0$ M; (a) $[S_4O_6^{2-}]_0 = 1.5 \times 10^{-2}$ M, $[H_2O_2]_0 = 0.13$ M; (b) $[S_4O_6^{2-}]_0 = 1.0 \times 10^{-2}$ M, $[H_2O_2]_0 = 0.175$ M; (c) $[S_4O_6^{2-}]_0 = 8.0 \times 10^{-3}$ M, $[H_2O_2]_0 = 0.15$ M; (d) $[S_4O_6^{2-}]_0 = 1.0 \times 10^{-2}$ M, $[H_2O_2]_0 = 4.36 \times 10^{-2}$ M.

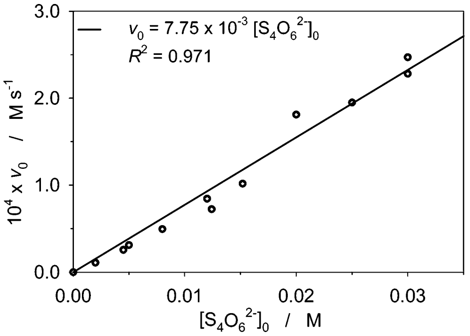

Figure 3. Linear dependence (regression line) of the initial reaction rate on the initial tetrathionate concentration ($[NaOH]_0 \cong 3 \times 10^{-3}$ M, $[H_2O_2]_0 = 0.15$ M, and $[Cu^{2+}]_0 = 0$ M).

reaction rate dependence on pH. An advantage of this approach is, among others, that we can obtain a good estimate of the dependence of the reaction rate v on pH from a single experiment, thus circumventing the usual procedure of the method of initial rates. Namely, if we avoid measurements at extreme values of pH and in the range of the buffering effect of acid−base equilibria (i.e., pH $\notin$ p$K_c \pm 1$), the change in the concentrations of the reactants or products leading to a change in pH by one or even more units can be neglected with respect to the initial concentrations of the reactants. Then, the reaction rate v depends only on pH, and it is, therefore, sufficient to plot the actual reaction rate $v(t)$ calculated from the measured time course of pH at various times (cf. eq A18 in the appendix at an actual time instead of an initial time) against the actual pH(t) or, equivalently, against the concentration of hydroxide ions $[OH^-](t)$, as shown in Figure 2. The linear trend expressed as regression lines is preserved in a sufficiently wide range of pH to clearly indicate first-order kinetics with respect to OH^-. In addition, the slopes increase with the product of initial reactant concentrations, and a statistically significant intercept, which the plots display, is related to stoichiometry to be discussed later.

Figure 3 indicates first-order dependence of the measured initial reaction rate on the initial tetrathionate concentration at $pH_0 \in [9.87; 9.95]$ and 0.15 M hydrogen peroxide. We also tried to fit the data to a second-order polynomial. The coefficient in the quadratic term as well as that in the constant term are statistically insignificant (at the significance level $\alpha = 0.05$). Likewise, Figure 4 shows linear trends of the initial reaction rate when the concentration of hydrogen peroxide was varied. Obtained regression lines do not have a significant intercept, suggesting that a nonoxidative decomposition of tetrathionate by hydroxide[22] does not interfere with our experiments. Slopes calculated for three different concentrations of tetrathionate correspond well to the linear trend inferred from Figure 3.

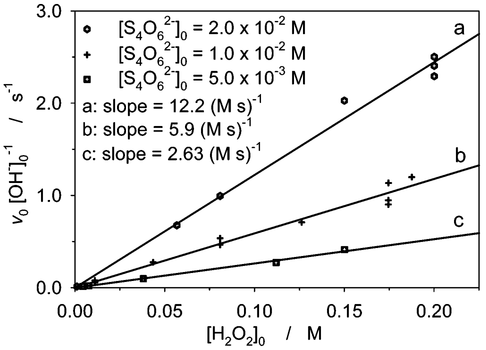

Figure 4. Dependences of the initial reaction rate relative to the concentration of OH^- ions on the concentration of hydrogen peroxide (points) and the corresponding regression lines for three different tetrathionate concentrations ($[Cu^{2+}]_0 = 0$ M).

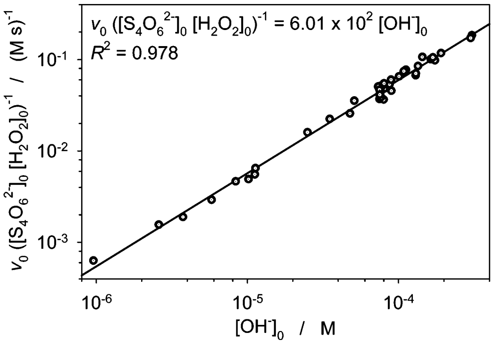

Figure 5. Measured initial reaction rate relative to the concentration of tetrathionate and hydrogen peroxide plotted against the initial concentration of hydroxide ions (points) and the corresponding regression line ($[Cu^{2+}]_0 = 0$ M).

Finally, when the initial rates obtained from the entire set of 41 measured kinetic curves are divided by the corresponding concentrations of tetrathionate and hydrogen peroxide, the results can be plotted together against the initial concentration of OH^- ions, see Figure 5. The figure reconfirms the first order with respect to $[OH^-]_0$ (compare to Figure 2 obtained from the reaction rate versus time dependence) and also reconfirms the first order with respect to tetrathionate and hydrogen peroxide. The regression line does not have a statistically significant intercept (significance level $\alpha = 0.05$), and its slope is $a = (6.01 \pm 0.09) \times 10^2$ $(M^2\ s)^{-1}$. The calculated standard deviation as well as the coefficient of determination implies an excellent fit of the data to the empirical relation

$$v_0 = a[H_2O_2]_0[S_4O_6^{2-}]_0[OH^-]_0 \qquad (4)$$

The parameter a, representing a product of the stoichiometric and the kinetic rate coefficients, was evaluated within

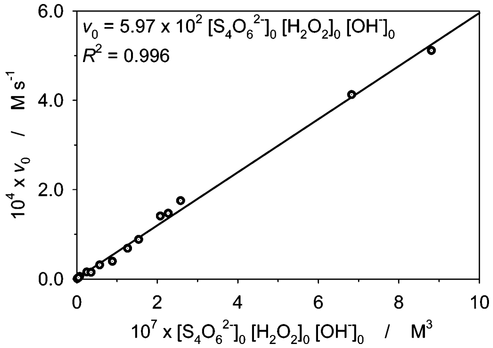

Figure 6. Linear dependence (regression line) of the initial reaction rate on the product of initial concentrations of tetrathionate, hydrogen peroxide, and hydroxide ions, $[Cu^{2+}]_0 \in [5; 10] \times 10^{-5}$ M.

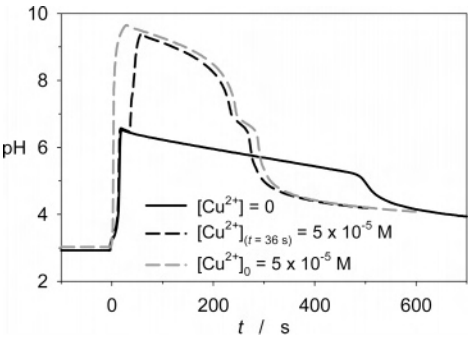

Figure 7. Characteristic waveform of kinetic curves corresponding to the oxidation of thiosulfate by hydrogen peroxide without cupric ions (full line) and with cupric ions added at two different times: dashed gray line at $t = 0$ s and dashed black line at $t = 36$ s. Initial conditions: $[S_2O_3^{2-}]_0 = 1.0 \times 10^{-2}$ M, $[H_2O_2]_0 = 0.20$ M, and $[HCl]_0 = 1.0 \times 10^{-3}$ M.

the concentration ranges $[S_4O_6^{2-}]_0 = 0-3 \times 10^{-2}$ M and $[H_2O_2]_0 = 0-0.20$ M and $pH_0 = 8-10.5$.

Effect of Cupric Ions. Fourteen measurements of kinetics with added $CuSO_4$ were done and evaluated in a similar fashion as the experiments without cupric ions. The concentration of Cu^{2+} in the reaction mixture was varied in the range 5.0×10^{-5} to 1.0×10^{-4} M (the ranges of other reactants were $[S_4O_6^{2-}]_0 = (5-20) \times 10^{-3}$ M and $[H_2O_2]_0 = (5.7-20) \times 10^{-2}$ M and $pH_0 = 8.1-10.7$). No effect on the initial rate in the alkaline solution was found. Following the form of eq 4, the plot of initial rates at various concentrations of Cu^{2+} against the product of initial concentrations of all three reactants is shown in Figure 6. It can be well fitted to a regression line with the slope $a^* = (5.97 \pm 0.09) \times 10^2\ (M^2\ s)^{-1}$, a value virtually identical with that from Figure 5. Thus, it is apparent that cupric ions in the alkaline solution affect neither the reaction order nor the rate constant.

Reaction Stoichiometry. A preliminary identification of products and intermediates can be made by comparing the kinetic curves for the oxidation of tetrathionate by hydrogen peroxide in Figure 1 with those obtained for the oxidation of thiosulfate by hydrogen peroxide. Results for the latter case are shown in Figure 7 where the well-known[12,13] catalytic effect of Cu^{2+} is displayed as a large-amplitude peak. By focusing on the course of the reactions without the presence of Cu^{2+}, we find certain similarities in the waveforms of the kinetic curves (full lines in Figures 1 and 7) in the pH range near pH ≈ 7. This observation suggests that thiosulfate could be one of the intermediates of the tetrathionate oxidation, in agreement with ref 8.

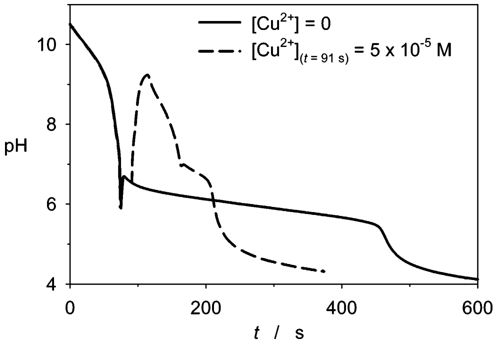

Figure 8. Dependence of pH on time during the oxidation of tetrathionate by hydrogen peroxide. The rapid increase of pH at $t = 91$ s as a response to the addition of $[Cu^{2+}] = 5.0 \times 10^{-2}$ M indicates the presence of thiosulfate as an intermediate. Initial conditions: $[S_4O_6^{2-}]_0 = 2.0 \times 10^{-2}$ M, $[H_2O_2]_0 = 0.20$ M, and $[NaOH]_0 \cong 1.5 \times 10^{-2}$ M.

This hypothesis could be examined by making use of the catalytic effect of cupric ions on the reaction of thiosulfate and hydrogen peroxide, which is known to provide tetrathionate and hydroxide ions.[12,13] As seen in Figure 7, this effect manifests itself whether the Cu^{2+} ions are added at $t = 0$ when the solution is acidic or at $t = 36$ s when the pH rises to a nearly neutral level and just starts to slowly decline. We have carried out a similar experiment with the oxidation of tetrathionate, see Figure 8. If we add Cu^{2+} ions shortly after the slowing down of the initially fast decrease of pH at $t = 91$ s, a quite similar effect to that in Figure 7 is observed. Thus, we conclude that thiosulfate indeed seems to be present in the reaction mixture.

Infrared Spectroscopy Measurements. To test our preliminary qualitative results, we decided to verify the appearance of thiosulfate and trithionate[8] in the reaction mixture using infrared spectroscopy modified for measurements of aqueous solutions (FT-IR/ATR).[15,16] Initially, we checked that the spectra of pure components (SO_4^{2-}, SO_3^{2-}, HSO_3^-, and $S_2O_3^{2-}$)—after subtracting water—coincided with the published ones.[15] However, the intensity of HSO_3^- bands is weak, and considering the sensitivity of the method and the expected concentration range of this intermediate in solutions containing hydrogen peroxide, HSO_3^- was not included in the calibration model. Parts a and b of Figure 9 show the measured four-scan FT-IR/ATR reference spectra (after subtracting water) of the solutions of 3.0×10^{-2} M potassium tetrathionate and 3.0×10^{-2} M potassium trithionate, respectively, which we could not find in the literature. Figure 9c shows the Raman and FT-IR/ATR spectra of the prepared solid potassium trithionate used as a standard instead of the commercially unavailable trithionate. They are fully consistent with the previously published results.[17,18]

We also examined whether the FT-IR/ATR spectra of the pure components are dependent on the alkalinity of the solutions. No significant differences have been observed

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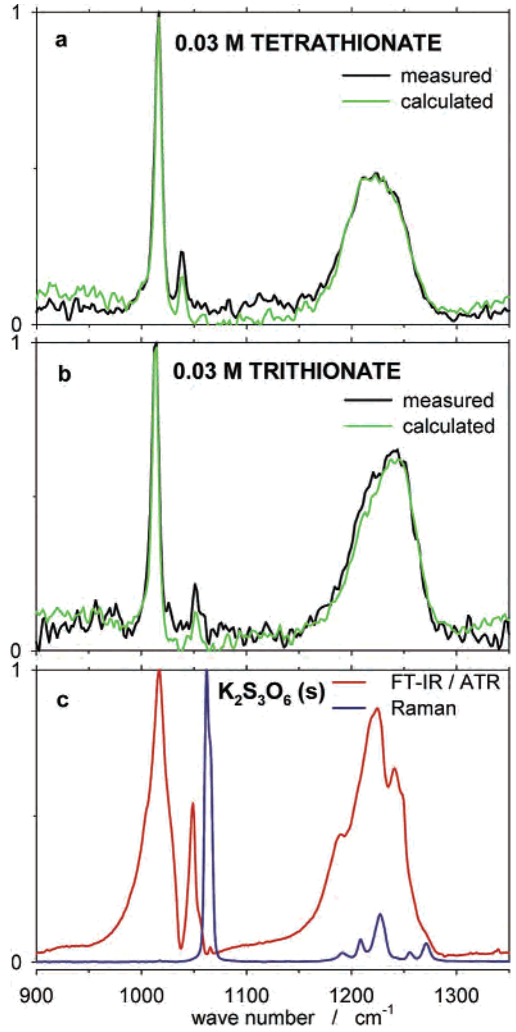

Figure 9. FT-IR/ATR spectra of potassium tetrathionate (a) and potassium trithionate (b) in water solutions compared with those calculated from the calibration model; (c) FT-IR/ATR and Raman spectra of the prepared solid potassium trithionate.

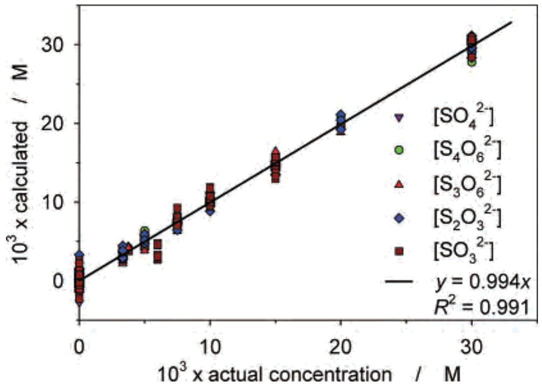

Figure 10. Calibration line of the sulfur-oxycompounds water solutions and their mixtures measured by FT-IR/ATR.

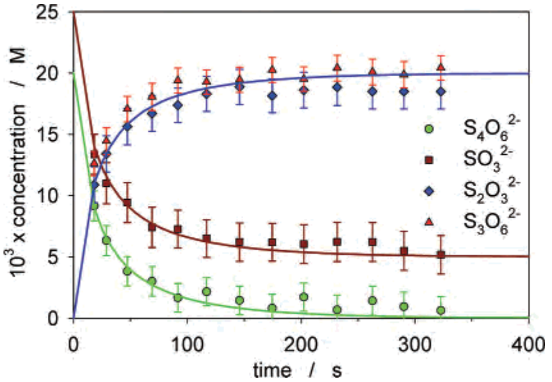

Figure 11. Concentrations of reactants and products during reaction 5 measured by FT-IR/ATR (points) and calculated from the model[23] (lines). Initial conditions: $[SO_3^{2-}]_0 = 2.5 \times 10^{-2}$ M, $[S_4O_6^{2-}]_0 = 2.0 \times 10^{-2}$ M, pH ≈ 9.5.

among the pure component spectra within the pH range from 5 to 10. Certain spectral changes are visible only for more concentrated tetrathionate solutions if the pH is near 11.

The calibration line shown in Figure 10 has been obtained by evaluating the spectra of water and 50 standard solutions of sulfite, sulfate, thiosulfate, tetrathionate, trithionate, and their stable mixtures within the range 0 to 3×10^{-2} M in the wavenumber range 850−1350 cm^{-1}. The quality of the calibration line can be assessed by calculating and comparing the coefficient of determination for each of the components separately: sulfite ($R^2 = 0.971$), sulfate ($R^2 = 0.993$), thiosulfate ($R^2 = 0.995$), tetrathionate ($R^2 = 0.996$), and trithionate ($R^2 = 0.994$). No detectable absorption band of 0.5 M hydrogen peroxide was observed in the specified spectral region. The calculated pure component spectra of both polythionates based on our calibration model are presented in Figure 9a and b together with the measured ones. The waveform of the calculated pure component spectra of other components also coincides with the experimental data. Considering the resolution of our experimental setup (4 cm^{-1}) and a limited number of coadded scans per spectrum, the detection limit is about 3×10^{-3} M for all evaluated components.

Following ref 23, we tested the analytical method by using the decomposition of tetrathionate by sulfite, which takes place in a moderately alkaline mixture according to

$$S_4O_6^{2-} + SO_3^{2-} \xrightarrow{k_r} S_3O_6^{2-} + S_2O_3^{2-} \qquad (5)$$

The time evolution of concentration for each measured component (the sulfate concentration does not exceed the detection limit) during the sulfitolysis of 2.0×10^{-2} M tetrathionate is shown in Figure 11 including uncertainties calculated from the calibration model. Motellier and Descostes[23] show that the reaction rate is directly proportional to the product of the reactant concentrations.

On the basis of this rate law, we found the values of the rate constant from four measurements by nonlinear regression of the experimental data. In agreement with earlier results,[23] our results show a striking dependence on the sum of initial concentrations of the reactants, which can be well described by the relation (written in the logarithmic form for convenience)

$$\log k_r = \log k_0 + 2z_S z_{TT}\left(\frac{A\sqrt{I}}{1+\sqrt{I}} - 0.1I\right) \qquad (6)$$

where I is the ionic strength in mol dm^{-3}, $A = 0.509$ at 25 °C, and $z_S = z_{TT} = -2$ are the electrostatic charges of both

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[23] Motellier, S.; Descostes, M. *J. Chromatogr., A* **2001**, *907*, 329−335.

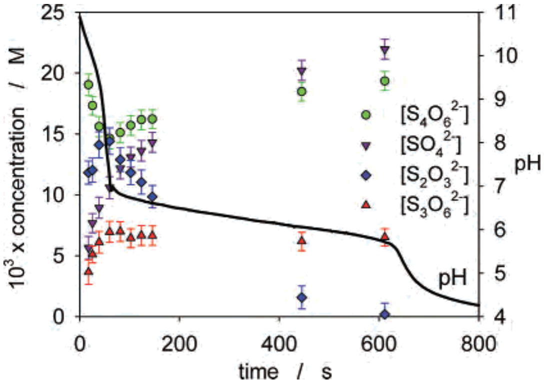

Figure 12. Time evolution of the measured pH and concentrations of sulfur-oxycompounds during the oxidation of tetrathionate by hydrogen peroxide in an alkaline solution. Initial conditions: $[S_4O_6^{2-}]_0 = 3.0 \times 10^{-2}$ M, $[H_2O_2]_0 = 0.169$ M, and $[NaOH]_0 \cong 3.8 \times 10^{-2}$ M.

reactants. For the limit value k_0, we obtain $k_0 = (2.7 \pm 0.2) \times 10^{-1}$ (M s)$^{-1}$ with the coefficient of determination $R^2 = 0.982$ within the range of ionic strength $I = 0.01-0.135$ M. Relation 6 can be derived by assuming equilibrium between an activated complex and both reactants,[24] where the activity coefficients are expressed from the Davies relation.[25]

Finally, to further support experimental evidence based on measurements of pH, we carried out experiments aimed at examining the presence of thiosulfate and trithionate in the reaction mixture during the tetrathionate oxidation. Figure 12 shows the time evolution of sulfur−oxycompounds concentrations and corresponding uncertainties along with pH values measured during the reaction of tetrathionate with hydrogen peroxide at ~25 °C in a batch. The highest concentrations of tetrathionate and hydroxide within the considered range were used. Under these conditions, thiosulfate is preferentially produced in the first stage of the reaction and sulfite does not appear in significant amounts. It is also apparent that trithionate is produced in the alkaline solution as a secondary product, while sulfate remains the main product.

Kinetic Model and Numerical Simulations. All of our experiments focused on the stoichiometry of tetrathionate oxidation by hydrogen peroxide in the alkaline solution clearly point to thiosulfate as an intermediate, in accordance with ref 8. The measured time evolution of several reacting species in the first minute in Figure 12 suggests that $[S_2O_3^{2-}] = [S_4O_6^{2-}]_0 - [S_4O_6^{2-}] \cong [SO_4^{2-}] + [S_3O_6^{2-}]$ with an error not exceeding the displayed uncertainties of the measurements. Therefore, the oxidation of tetrathionate by hydrogen peroxide in the alkaline solution may be described by the following overall reactions

$$S_4O_6^{2-} + 2H_2O_2 + 4OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + SO_3^{2-} + 4H_2O \quad (R1)$$

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-} \quad (R2)$$

The secondary oxidation of the intermediates—sulfite and thiosulfate—can apparently be neglected during the first phase of the reaction in the alkaline solution. These processes, however, entirely dominate in the neutral and weakly acidic solution, where tetrathionate is no longer oxidized by hydrogen peroxide, see Figures 5 and 12. Here, the observed moderate increase of tetrathionate concentration is a consequence of the successive oxidation of thiosulfate. If we are to model these experimental findings within the entire range of pH, we have to add to reactions R1 and R2 studied in this work a mechanistic description of the oxidation of sulfite[14,26] and thiosulfate.[27,28]

At pH < 5, oxidation of thiosulfate by hydrogen peroxide provides tetrathionate almost quantitatively.[27] In the neutral and alkaline range, Schiller[28] proposed sulfate and tetrathionate as mixed products, the formation of sulfate being preferred by higher pH and an excess of hydrogen peroxide. Schiller assumes the formation of the $HOS_2O_3^-$ intermediate and its further interaction with both reactants. This scheme has been used in the uncatalyzed part of the HPTCu[6] model:

$$S_2O_3^{2-} + H_2O_2 \rightarrow HOS_2O_3^- + OH^- \quad (R3)$$

$$H_2O_2 + HOS_2O_3^- \rightarrow 2HSO_3^- + H^+ \quad (R4)$$

$$H^+ + S_2O_3^{2-} + HOS_2O_3^- \rightarrow S_4O_6^{2-} + H_2O \quad (R5)$$

$$H_2O_2 + SO_3^{2-} \rightarrow SO_4^{2-} + H_2O \quad (R6)$$

$$H_2O_2 + HSO_3^- \rightarrow SO_4^{2-} + H_2O + H^+ \quad (R7)$$

$$H_2O \rightleftarrows H^+ + OH^- \quad (R8)$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-} \quad (R9)$$

$$H_2O_2 \rightleftarrows H^+ + HO_2^- \quad (R10)$$

Reactions R1−R10 then form a simple model that should describe our experimental results. The reaction rates corresponding to this model are shown in Table 1.

The rate constant $k_1 = 1.5 \times 10^2$ (M^2 s)$^{-1}$ corresponds to the slope obtained empirically from eq 4 divided by 4, which is the stoichiometric coefficient of hydroxide ions in R1. Parameters k_5/k_4 and $k_5{}^*/k_4$ were obtained from relative values of the rate constants of steps R5 and R4 published by Schiller.[28] Their ratio is proportional to the concentration of H^+ with a constant term $k_5/k_4 \cong 0.2$. The slope then increases with the ratio $[H_2O_2]_0/[S_2O_3^{2-}]_0$ up to a limit value $k_5{}^*/k_4 \approx 5 \times 10^7$ M^{-1}. In our experiments, hydrogen peroxide is always in large excess over thiosulfate, which appears only as an intermediate. Therefore, we use directly the limit value $k_5{}^*/k_4$. The value of k_5 is adjusted only approximately so that the assumption of $HOS_2O_3^-$ being an unstable intermediate is fulfilled.

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(24) Moore, W. J. *Physical Chemistry*, 4th ed.; Prentice-Hall: New Jersey, 1972.

(25) Davies, C. W. *J. Chem. Soc.* **1938**, *140*, 2093−2098.

(26) Mader, P. M. *J. Am. Chem. Soc.* **1958**, *80*, 2634−2639.

(27) Abel, E. *Monatsh. Chem.* **1907**, *28, 1239−1312.*

(28) Schiller, J. E. *Inorg. Chem.* **1987**, *26*, 948−950.

Table 1. Reaction Rates and Rate Coefficients of the Steps R1−R10

rate equations	rate constants at 25 °C	ref
$v_1 = k_1[S_4O_6^{2-}][H_2O_2][OH^-]$	$k_1 = 1.5 \times 10^2\ (M^2\ s)^{-1}$	this work
$v_2 = k_2[S_4O_6^{2-}][SO_3^{2-}]$	$k_2 = f(k_0, I)$	see eq 6
	$k_0 = 0.27\ (M\ s)^{-1}$	this work
$v_3 = k_3[S_2O_3^{2-}][H_2O_2]$	$k_3 = 2.3 \times 10^{-2}\ (M\ s)^{-1}$	27, 28
$v_4 = k_4[HOS_2O_3^-][H_2O_2]$	$k_5/k_4 = 0.2$	28, see text
$v_5 = (k_5 + k_5^*[H^+])[HOS_2O_3^-][S_2O_3^{2-}]$	$k_5 = 10\ (M\ s)^{-1}$	this work
	$k_5^*/k_4 = 5 \times 10^7\ M^{-1}$	28, see text
$v_6 = k_6[SO_3^{2-}][H_2O_2]$	$k_6 = 0.2\ (M\ s)^{-1}$	26
$v_7 = (k_7 + k_7^*[H^+])[HSO_3^-][H_2O_2]$	$k_7 = 7.0\ (M\ s)^{-1}$	14
	$k_7^* = 1.48 \times 10^7\ (M^2\ s)^{-1}$	14
$v_8 = k_8[H_2O] - k_{-8}[H^+][OH^-]$	$k_8[H_2O] = 1 \times 10^{-3}\ Ms^{-1}$	14
	$k_{-8} = 1 \times 10^{11}\ (M\ s)^{-1}$	14
$v_9 = k_9[HSO_3^-] - k_{-9}[H^+][SO_3^{2-}]$	$k_9 = 3 \times 10^3\ s^{-1}$	14
	$k_{-9} = 5 \times 10^{10}\ (M\ s)^{-1}$	14
$v_{10} = k_{10}[H_2O_2] - k_{-10}[H^+][HO_2^-]$	$k_{10}/k_{-10} = 2.5 \times 10^{-12}\ M$	6, 29
	$k_{-10} = 1 \times 10^{10}\ (M\ s)^{-1}$	

A more detailed scheme for the oxidation of thiosulfate by hydrogen peroxide was published by Rábai and Hanazaki[7,30] to describe the complex oscillatory dynamics of the hydrogen peroxide−thiosulfate−sulfite reaction. This model has been taken from ref 30 without modifications, including the rate constants for 26 °C. In addition to the rate laws for R1 and R2, we tried to use both the Schiller model based on reactions R3−R10 and the Rábai−Hanazaki model[7,30] for the prediction of our experimental results on the oxidation of thiosulfate by hydrogen peroxide in the batch reactor. The results shown in Figure 13 surprisingly indicate that the batch experiments are better described by the original simple model by Schiller. Therefore, rather than adding R1 and R2 to the detailed model,[7,30] below, we use the scheme R1−R10.

As mentioned above, Figure 12 shows the experimental results of the time evolution of all measured species during the oxidation of tetrathionate by hydrogen peroxide in an alkaline solution. Under these conditions, the transient formation of thiosulfate as well as the formation of a significant amount of trithionate, which we attribute to reactions R1 and R2, is clearly visible. Figure 14 displays the results of simulation of the experiments from Figure 12 according to the model scheme R1−R10 with the use of data from Table 1. When Figures 12 and 14 are compared, the agreement of the experimental data with the model is complete in all qualitative aspects, including the occurrence of a minimum in the waveform of tetrathionate. Likewise, low concentrations of sulfite agree with the observation that its concentration did not reach the detection limit.

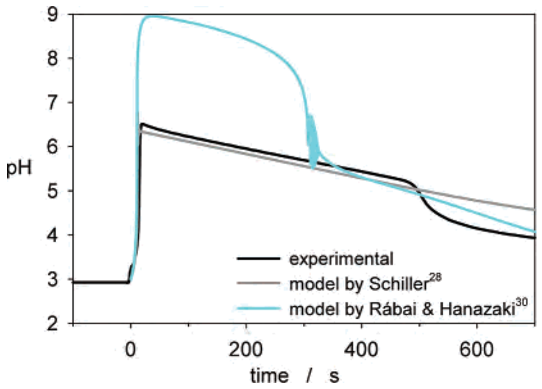

Figure 13. Comparison of the calculated pH from the two models indicated in the text with the measured pH over the course of the reaction of 0.01 M thiosulfate with 0.2 M hydrogen peroxide in 1×10^{-3} M HCl.

Kinetic measurements in the batch reactor were monitored by measuring pH with typical waveforms of the curves shown in Figure 1. Calculated curves of pH corresponding to the measurements in Figure 1 (with no cupric ions added) are shown in Figure 15. The agreement in the alkaline region is satisfactory; more pronounced differences occur only in the second stage of the reaction (pH < 7) where a sudden drop of pH is observed experimentally in both tetrathionate and thiosulfate oxidations (compare with Figure 13). This

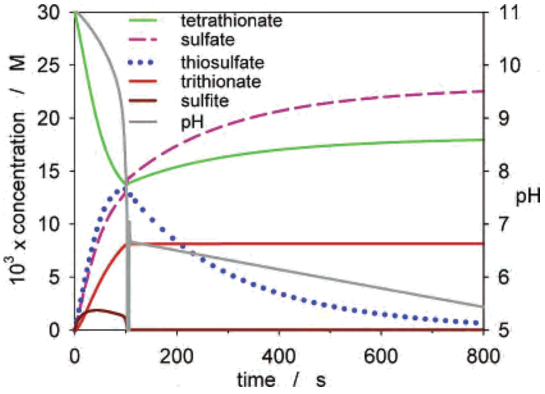

Figure 14. Calculated time evolution of the concentration of indicated reacting species simulating the course of the reaction of 0.03 M tetrathionate with 0.169 M hydrogen peroxide and with 3.8×10^{-2} M NaOH (see Figure 12).

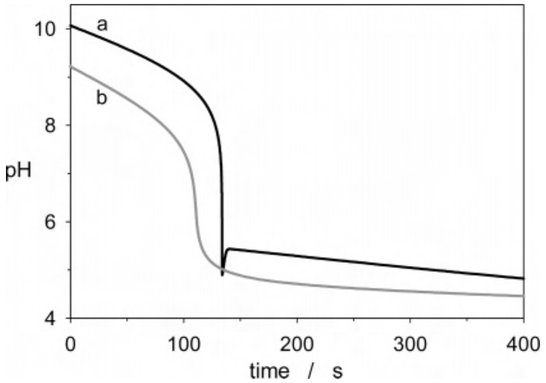

Figure 15. Kinetic pH curves simulated with the use of the model R1−R10 for conditions corresponding to the experiments in Figure 1.

feature is not modeled by any of the presented models and needs further research.

Discussion

The rate-determining step R1 is not elementary as suggested by the empirically found third-order kinetics in this work. On the basis of the known facts, we cannot firmly state what the elementary steps are. However, certain possibilities can be rather safely ruled out. One of them is a combination of the symmetric cleavage of tetrathionate by hydrogen peroxide[6] with a subsequent decomposition of peroxothiosulfate and its oxidation:

$$S_4O_6{}^{2-} + H_2O_2 \rightleftarrows 2HOS_2O_3{}^{-} \tag{2}$$

$$HOS_2O_3{}^{-} + OH^{-} \rightleftarrows S_2O_3{}^{2-} + H_2O_2 \tag{7}$$

$$H_2O_2 + HOS_2O_3{}^{-} \rightarrow 2HSO_3{}^{-} + H^{+} \tag{R4}$$

Equation 7 is also assumed by Rábai and Hanazaki.[30] It is a reverse step to thiosulfate oxidation by peroxide, which should slow the overall thiosulfate oxidation in an alkaline solution. This is, however, in contrast with experimental observations by Schiller.[28] Such a scheme does not lead to stoichiometry of the process R1 found in this work nor does it correspond to the observed third order of the tetrathionate oxidation, see eq 4. In addition, reactions 2, 7, and R4 do not explain the experimentally found stability of tetrathionate in the presence of hydrogen peroxide at pH < 7.

Another possibility is a combination of process R4 with the reversible reaction of tetrathionate and hydroxide ions:

$$S_4O_6{}^{2-} + OH^{-} \rightleftarrows S_2O_3{}^{2-} + HOS_2O_3{}^{-} \tag{8}$$

Reaction 8 could be the initial step in the decomposition of tetrathionate in an alkaline solution[22] and tetrathionate oxidation by hydrogen peroxide. Upon assuming a quasi-steady-state for $HOS_2O_3{}^{-}$ and expressing its concentration, we obtain for the initial rate of tetrathionate oxidation, according to eqs 8 and R4, the relation

$$\frac{d[S_4O_6{}^{2-}]}{dt}\Big|_{t=0} \cong \frac{k_8[S_4O_6{}^{2-}]_0[H_2O_2]_0[OH^{-}]_0}{k_{-8}/k_4[S_2O_3{}^{2-}]_0 + [H_2O_2]_0} = k_8[S_4O_6{}^{2-}]_0[OH^{-}]_0 \tag{9}$$

where $[S_2O_3{}^{2-}]_0 = 0$. However, this is in contradiction with the empirical eq 4.

As the most likely detailed reaction scheme for the overall process R1, we suggest the following:

$$H_2O_2 + OH^{-} \rightleftarrows HO_2{}^{-} + H_2O \tag{10}$$

$$S_4O_6{}^{2-} + HO_2{}^{-} \rightarrow S_2O_3{}^{2-} + S_2O_5{}^{2-} + H^{+} \tag{11}$$

$$H_2O_2 + S_2O_5{}^{2-} \rightarrow SO_4{}^{2-} + SO_3{}^{2-} + 2H^{+} \tag{12}$$

Depending on experimental conditions, hydrolysis of disulfite may compete with step 12:

$$S_2O_5{}^{2-} + H_2O \rightarrow 2SO_3{}^{2-} + 2H^{+} \tag{13}$$

Hydrogen peroxide is in excess under the given conditions, which apparently favors disulfite oxidation in agreement with the observed stoichiometry of the process R1. The rate-determining step in the sequence eqs 10−12 is probably a nucleophilic attack of the peroxide anion at the disulfidic bridge of the tetrathionate ion in step 11. We can use the value of the dissociation constant $K_c = k_{10}/k_{-10}$ in the equilibrium R10 (see Table 1) and the initial concentration of hydrogen peroxide to express the concentration of dissociated hydrogen peroxide. Taking into account the experimental pH range ($8 < \text{pH} \ll \text{p}K_c \cong 11.6$) and substituting it into the rate expression for step 11, we obtain the relation eq 4 with the slope a given by

$$a = 4k_1 \cong 4k_{11}K_c/K_W \tag{14}$$

where K_W is ionic product of water. From eq 14, we obtain $k_{11} \cong 0.65$ (M s)$^{-1}$. This rate coefficient depends, in general, on ionic strength according to eq 6. The product of charges of the reactants is half the earlier value ($z_{TT}z_P = 2$); therefore, the ionic strength dependence is less pronounced and can be neglected.

Our measurements confirm the kinetic relation for the oxidation of tetrathionate by hydrogen peroxide assumed by Kurin-Csörgei et al.[6] However, Figure 5 implies that the rate constant for the oxidation of tetrathionate in an acidic solution, where OH^{-} ions do not affect the reaction rate, should be smaller than the value 5×10^{-4} (M s)$^{-1}$. On the other hand, in most simulations with the HPTCu model,[6] much higher values for this reaction were used: $k_6 = (5-7) \times 10^{-2}$ (M s)$^{-1}$ for the acidic range and $k_6' = 1 \times 10^{5}$ (M^{2} s)$^{-1}$ for the alkaline range in the notation of ref 6. Both of these parameters were treated as adjustable and set to correspond with the experiments of Orbán and Epstein.[5] Nevertheless, the used values were apparently overestimated by one or more orders of magnitude. Moreover, the stoichiometry of reaction R1 shows that the entire second autocatalytic process in the HPTCu model combining reactions 2 and 3 is probably unrealistic. The actual cause of the observed oscillatory and bistable dynamics then remains unanswered, and the model will likely have to be rebuilt from scratch. In particular, despite experimental evidence in refs 12 and 13, the crucial step—OH^{-}-autocatalytic oxidation of thiosulfate by hydrogen peroxide catalyzed by Cu^{2+}—was, in ref 6, proposed as an analogy with a similar oxidation of hydrazine or hydroxylamine.[31] However, in those reactions, the increase of reaction rate with pH clearly relates to the dissociation of positively charged amino groups at pH ≈ 6, which cannot be assumed in the case of the Cu^{2+}-catalyzed oxidation of thiosulfate.

We were not able to confirm a secondary catalytic effect of Cu^{2+} on tetrathionate oxidation in the alkaline region (see

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(29) Perrin, D. D. *Ionization Constants of Inorganic Acids and Bases in Aqueous Solution*; Pergamon Press: Oxford, U. K., 1982.

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Figure 6), which was predicted in ref 5 and not included in the HPTCu model.[6] On the other hand, some secondary role of cupric ions does occur in neutral and weakly acidic media, probably at a low concentration of thiosulfate only, and leads to a faster decrease of pH, see Figure 1. This is very likely the effect which should replace the hypothetical autocatalytic loops involving OH^- in the current model of the HPTCu reaction and which may well account for the occurrence of the observed oscillations. Therefore, work on its elucidation is in progress.

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Appendix—Calculation of the Initial Reaction Rate from pH Measurements

For the study of chemical reaction kinetics accompanied by pH variations, a pH stat is usually employed to compensate for changes in the concentration of H^+ ions by continually adding the proper amount of acid or base of a known concentration; this amount is measured during the experiment. When the pH stat is not available, it is still possible, in some cases, to determine the initial rate on the basis of the measurement of the pH variation. However, the data processing is more involved than the pH-stat experiments because, in addition to the examined reaction, it is necessary to take into account fast acid—base reactions in the system. Even though there may be a large number of such protolytic equilibria, their actual effect depends on the concentration of a particular species, which corresponds to the dissociation constant and pH in the solution. Taking this into consideration, it is often possible, in a given situation, to include only the most important protolytic equilibria without losing accuracy of the results.

We will show this approach for the case where the effects of dissociation equilibria

$$\mathrm{HX} \overset{K_c}{\rightleftharpoons} \mathrm{H}^+ + \mathrm{X}^- \tag{A1}$$

$$\mathrm{H_2O} \overset{K_W}{\rightleftharpoons} \mathrm{H}^+ + \mathrm{OH}^- \tag{A2}$$

prevail in the measured range of pH. Because of a fast motion of H^+ and OH^- ions as a consequence of interactions with the solvent,[20,24] the equilibration of acid—base processes in aqueous solutions is extremely fast compared to that of other chemical reactions. Such processes can be reliably described as pseudo-equilibrium processes satisfying the equations

$$K_W = [\mathrm{H}][\mathrm{OH}] \tag{A3}$$

$$K_c = \frac{[\mathrm{H}][\mathrm{X}]}{[\mathrm{HX}]} \tag{A4}$$

The parameters K_W and K_c represent the ionic product of water and the dissociation constant, respectively, provided that the activity coefficients are close to unity. The dynamics of the protolytically active components can be described by the differential equations

$$\frac{d[\mathrm{HX}]}{dt} = r^*_{\mathrm{HX}} + \Delta_{\mathrm{HX}} + p_{\mathrm{HX}} \tag{A5}$$

$$\frac{d[\mathrm{X}]}{dt} = r^*_{\mathrm{X}} - \Delta_{\mathrm{HX}} + p_{\mathrm{X}} \tag{A6}$$

$$\frac{d[\mathrm{OH}]}{dt} = r^*_{\mathrm{OH}} - \Delta_{\mathrm{W}} + p_{\mathrm{OH}} \tag{A7}$$

$$\frac{d[\mathrm{H}]}{dt} = r^*_{\mathrm{H}} - \Delta_{\mathrm{HX}} - \Delta_{\mathrm{W}} + p_{\mathrm{H}} \tag{A8}$$

The symbols r^*_{HX}, r^*_X, r^*_{OH}, and r^*_H represent the sum of reaction rates in the molar balance of the corresponding species without the protolytic effects, whereas the terms Δ_{HX} and Δ_W involve contributions to the overall reaction rate by the reactions A1 and A2, respectively. The terms p_{HX}, p_X, p_{OH}, and p_H represent transport (in an open system). Equilibrium concentrations of OH^- and HX can be expressed from A3 and A4

$$[\mathrm{OH}] = K_W/[\mathrm{H}] \tag{A9}$$

$$[\mathrm{HX}] = [\mathrm{H}][\mathrm{X}]/K_c \tag{A10}$$

By formal differentiation with respect to time, we obtain

$$\frac{d[\mathrm{OH}]}{dt} = -\frac{K_W}{[\mathrm{H}]^2}\frac{d[\mathrm{H}]}{dt} \tag{A11}$$

$$\frac{d[\mathrm{HX}]}{dt} = \left([\mathrm{X}]\frac{d[\mathrm{H}]}{dt} + [\mathrm{H}]\frac{d[\mathrm{X}]}{dt}\right)/K_c \tag{A12}$$

By substituting from eqs A7 and A8 to A11, and from eqs A5, A6, and A8 to A12, we obtain a system of linear algebraic equations for the unknowns Δ_{HX} and Δ_W

$$(1 + [\mathrm{H}]^2/K_W)\Delta_W + \Delta_{HX} = r^*_H + p_H + [\mathrm{H}]^2/K_W(r^*_{OH} + p_{OH}) \tag{A13}$$

$$[\mathrm{X}]\Delta_W + (K_c + [\mathrm{H}] + [\mathrm{X}])\Delta_{HX} = [\mathrm{X}](r^*_H + p_H) + [\mathrm{H}](r^*_X + p_X) - K_c(r^*_{HX} + p_{HX}) \tag{A14}$$

By solving A13 and A14, we get

$$\Delta_W = \{K_c(r^*_{HX} + p_{HX}) - [\mathrm{H}](r^*_X + p_X) + ([\mathrm{H}] + K_c)(r^*_H + p_H) + ([\mathrm{H}] + [\mathrm{X}] + K_c)(r^*_{OH} + p_{OH})[\mathrm{H}]^2/K_W\}/\{[\mathrm{H}] + K_c + ([\mathrm{H}] + [\mathrm{X}] + K_c)[\mathrm{H}]^2/K_W\} \tag{A15}$$

$$\Delta_{HX} = r^*_H + p_H + (r^*_{OH} + p_{OH})[\mathrm{H}]^2/K_W - (1 + [\mathrm{H}]^2/K_W)\Delta_W \tag{A16}$$

Finally, upon substitution from eqs A15 and A16 to the relation for the rate of [H] change A8, we obtain an equation describing the effect of acid—base equilibria:

$$\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} = \left\{ r^*_{\mathrm{H}} + p_{\mathrm{H}} - r^*_{\mathrm{OH}} - p_{\mathrm{OH}} + \frac{K_{\mathrm{c}}(r^*_{\mathrm{HX}} + p_{\mathrm{HX}}) - [\mathrm{H}](r^*_{\mathrm{X}} + p_{\mathrm{X}})}{[\mathrm{H}] + K_{\mathrm{c}}} \right\} \Big/ \left\{ 1 + \frac{K_{\mathrm{W}}}{[\mathrm{H}]^2} + \frac{[\mathrm{X}]}{[\mathrm{H}] + K_{\mathrm{c}}} \right\} \quad \text{(A17)}$$

In the case of a closed system, the transport terms in eq A17 vanish, and for $t = 0$, we have $[\mathrm{HX}] = [\mathrm{HX}]_0$, $[\mathrm{X}] = [\mathrm{X}]_0$, $[\mathrm{H}] = [\mathrm{H}]_0$, and $c_0 = [\mathrm{HX}]_0 + [\mathrm{X}]_0$. From this, taking eq A4 into account, the resulting relation for the initial rate v_0 is

$$v_0 = \frac{\mathrm{d}[\mathrm{H}]_0}{\mathrm{d}t}\left\{ 1 + \frac{K_{\mathrm{W}}}{{[\mathrm{H}]_0}^2} + \frac{K_{\mathrm{c}}c_0}{([\mathrm{H}]_0 + K_{\mathrm{c}})^2} \right\} = r^*_{\mathrm{H}} - r^*_{\mathrm{OH}} + \frac{K_{\mathrm{c}}r^*_{\mathrm{HX}} - [\mathrm{H}]_0 r^*_{\mathrm{X}}}{[\mathrm{H}]_0 + K_{\mathrm{c}}} \quad \text{(A18)}$$

The derivative in eq A18 can be expressed with the use of the definition relation $\mathrm{pH} = -\log\,[\mathrm{H}]$

$$\frac{\mathrm{d}[\mathrm{H}]_0}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t}\Big|_{t\to 0} = -\ln(10)\,[\mathrm{H}]_0 \frac{\mathrm{dpH}}{\mathrm{d}t}\Big|_{t\to 0} \quad \text{(A19)}$$

and evaluated from the numerical first derivative of the time series of measured pH.

For the reaction of tetrathionate with hydrogen peroxide in the range of $\mathrm{pH} \in [8.5, 10.5]$, it is sufficient to consider the dissociation constant of hydrogen peroxide[6,29] with $\mathrm{p}K_{\mathrm{c}} \cong 11.6$ and the ionic product of water[24,29] $\mathrm{p}K_{\mathrm{W}} = 14.0$. The external parameter c_0 in eq A18 can be seen as a total concentration of hydrogen peroxide in the reaction mixture, while X_0 and HX_0 represent its ionized ($\mathrm{HO_2}^-$) and nondissociated ($\mathrm{H_2O_2}$) parts, respectively. Finally, when $\mathrm{pH}_0 \leq 10.5$, the relation A18 can be reduced to a simple form $v_0 \cong r^*_{\mathrm{H}} - r^*_{\mathrm{OH}}$ (or equivalently $v_0 \cong r^*_{\mathrm{H}} - r^*_{\mathrm{X}}$ when we consider $\mathrm{HO_2}^-$ reacting instead of $\mathrm{H_2O_2}$ and OH^-).

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