Unexpected Formation of Higher Polythionates in the Oxidation of Thiosulfate by Hypochlorous Acid in a Slightly Acidic Medium

3 AUTHORS, INCLUDING:

Attila K Horváth
University of Pécs
54 PUBLICATIONS   536 CITATIONS

SEE PROFILE

István Nagypál
University of Szeged
86 PUBLICATIONS   1,455 CITATIONS

SEE PROFILE

Unexpected Formation of Higher Polythionates in the Oxidation of Thiosulfate by Hypochlorous Acid in a Slightly Acidic Medium

**Dénes Varga, Attila K. Horváth,* and István Nagypál**

University of Szeged, Department of Physical Chemistry, Szeged, P.O. Box 105, H-6701, Hungary

Received: November 23, 2005; In Final Form: January 9, 2006

It has been clearly shown that not only tetrathionate but also pentathionate or even higher polythionates is formed in the oxidation of thiosulfate by hypochlorous acid in a slightly acidic medium. In thiosulfate excess, the absorbance−time curves registered at 250 nm may go through a maximum followed by a minimum, suggesting the presence of a short-lived absorbing intermediate proposed to be $S_2O_3OCl^{3-}$. Matrix rank analysis (MRA) studies have revealed that altogether five independent absorbing species are present in the wavelength range 240−400 nm. A kinetic model is suggested to take all of the experimental observations into account.
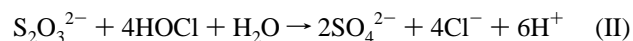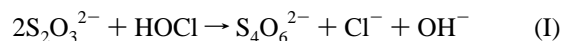
The chlorite−thiosulfate reaction exhibits a wide range of "exotic" kinetic phenomena, such as complex periodic, aperiodic oscillation[1,2] and chaos[3] in continuously fed stirred tank reactor (CSTR), and shows extreme sensitivity to fluctuations and stirring rate effects in batch condition.[4] So far, no attempt has been made to unravel the mechanism of this reaction because of its complexity. At least three long-lived intermediates and/or end products—tetrathionate, hypochlorous acid, and chlorine dioxide—participate in it, and they can react not only with both of the reactants but also with each other, making the mechanism particularly complicated. Since the last decade of the 20th century, the kinetics and mechanisms of several subsystems have been elucidated such as those of hypochlorous acid−chlorite,[5] thiosulfate−chlorine dioxide,[6] tetrathionate−hypochlorous acid,[7] tetrathionate−chlorine dioxide,[8] and the decomposition of chlorous acid.[9] As a sequence of the systematic mechanism revelation, here we report the preliminary results of the kinetics and mechanism of the hypochlorous acid−thiosulfate system. So far, no detailed kinetic study is available on this system.

The experiments were conducted in acetic acid−acetate buffer at constant ionic strength ($I = 0.5$ M adjusted with 0.3 M sodium perchlorate taking the pK of acetic acid 4.55 and the concentration of sodium acetate 0.2 M). The reaction was followed between 240 and 400 nm at $T = 25.0 \pm 0.2$ °C by a Zeiss S10 diode-array spectrophotometer attached to a Hi-Tech SFA-20 rapid kinetic accessory, allowing us to mix the reactants within 10 ms. The light path of the quartz cell was 2 mm. As a preliminary study, the initial concentration of the reactants was varied between 0.0008 and 0.0064 M in the case of thiosulfate and 0.001 237 and 0.006 34 M in the case of hypochlorous acid. Altogether, 17 kinetic runs were executed at a constant pH of 3.95. The fitting was carried out by ZiTa,[10] a comprehensive program package developed recently for simultaneous determination of the kinetic parameters of chemical reaction mechanisms. The kinetic parameters were determined at a single wavelength chosen to be 250 nm, where significant absorbance changes could be registered and none of the absorbance values
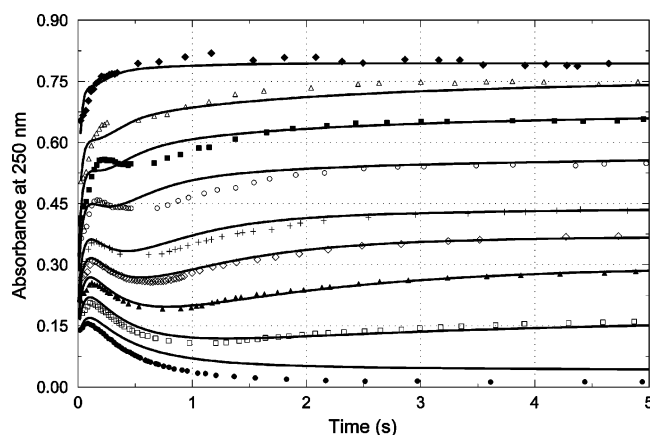
Figure 1. Measured (symbols) and calculated (solid lines) kinetic curves at 250 nm and pH 3.95 with constant hypochlorous acid concentration ($[HOCl]_0 = 0.004\ 021$ M). $[S_2O_3^{2-}]_0$ (M) = 0.0008 (●), 0.0012 (□), 0.0016 (▲), 0.002 (◇), 0.0024 (+), 0.0032 (○), 0.004 (■), 0.0048 (△), 0.0064 (♦).

reached 1.2, where the relative error of the absorbance measurement increases significantly. Generally the stoichiometry of the reaction was thought to be a linear combination of the following equations:

$$2S_2O_3^{2-} + HOCl \rightarrow S_4O_6^{2-} + Cl^- + OH^- \qquad \text{(I)}$$

$$S_2O_3^{2-} + 4HOCl + H_2O \rightarrow 2SO_4^{2-} + 4Cl^- + 6H^+ \qquad \text{(II)}$$

Tetrathionate ion, however, can react further with hypochlorous acid more slowly than thiosulfate ion can, giving sulfate and chloride ions as final products.[7] Since the molar absorbance of tetrathionate is much larger at 250 nm than that of the reactants, a single maximum was predicted to be measured at the kinetic runs.

The surprising results of our preliminary investigation are illustrated in Figure 1 and Table 1. Instead of a single maximum,

2468 *J. Phys. Chem. B, Vol. 110, No. 6, 2006*

Letters

TABLE 1: Measured and Calculated Final Absorbance at Different Initial Concentrations of the Reactants[a]

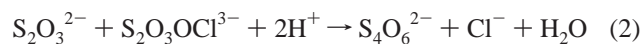| $[S_2O_3^{2-}]_0$ (mM)	$[HOCl]_0$ (mM)	A_∞^{meas}	A_∞^{calcd} with SI	A_∞^{calcd} with SII
2.0	1.237	0.236	0.211	0.098
2.0	1.546	0.298	0.216	0.093
2.0	2.474	0.354	0.231	0.080
2.0	3.247	0.374	0.243	0.069
2.0	4.021	0.376	0.256	0.057
2.0	4.794	0.378	0.268	0.046
2.0	5.567	0.372	0.281	0.035
2.0	6.340	0.327	0.293	0.024
0.8	4.021	0.011	0.141	0.013
1.2	4.021	0.172	0.179	0.011
1.6	4.021	0.298	0.218	0.034
2.4	4.021	0.436	0.294	0.080
3.2	4.021	0.547	0.370	0.127
4.0	4.021	0.652	0.447	0.173
4.8	4.021	0.746	0.523	0.219
5.6	4.021	0.780	0.600	0.265
6.4	4.021	0.790	0.676	0.311

[a] The fourth column of the table is in regard to that value which could be calculated if stoichiometry I (SI) alone is taken into consideration. The last column is in regard to that value which could be calculated if only stoichiometry II (SII) alone is taken into consideration.

some of the absorbance–time curves (see Figure 1) go through a maximum followed by a minimum before reaching the final absorbance value. Moreover, Table 1 compares the calculated final absorbance to the measured value if either only tetrathionate (in stoichiometry I) or only sulfate (in stoichiometry II) is formed. If there is no other absorbing species besides thiosulfate, hypochlorous acid, and tetrathionate and the final sulfur-containing oxyanions are a mixture of sulfate and tetrathionate, then the measured absorbance must be between the corresponding values calculated in the fourth and fifth columns of Table 1. Those values are hypothetical ones; the absorbance calculated in the fourth column of Table 1 assumes that no reaction takes place between tetrathionate ion and hypochlorous acid, while that of the fifth column of Table 1 supposes that the reaction between tetrathionate ion and hypochlorous acid is much faster than the thiosulfate–hypochlorous acid reaction. In reality, the thiosulfate more rapidly reacts with hypochlorous acid than tetrathionate does, meaning that the final absorbance must be between the values calculated in the fourth and fifth columns of Table 1. In some cases, however, the measured final absorbance is significantly higher than the calculated one even if all of the thiosulfate ions are converted to tetrathionate. It clearly means that another highly absorbing species must be formed, whose molar absorbance is much higher than that of tetrathionate at the given wavelength. Among the known sulfur-containing oxyanions, only the pentathionate and hexathionate ions are able to satisfy this criterion.[11,12] The longer the S-chain of the polythionate is, the higher its molar absorbance is at a given wavelength. To calculate the number of independent absorbing species, we have also carried out matrix rank analysis (MRA).[13] This study has yielded five independent absorbing species in the wavelength range used in the experiments; among them, the molar absorbances of thiosulfate, hypochlorous acid, and tetrathionate can independently be measured. From the stoichiometric considerations, the formation of pentathionate (or higher polythionates) as the fourth absorbing species seems to be feasible. The fifth absorbing species is proposed to be an adduct of thiosulfate and hypochlorous acid by analogies of other nonmetal redox reactions.[14-16] Our aim here is to provide a quantitative explanation for the observed behavior of the kinetic curves. After examining many candidate kinetic models, we
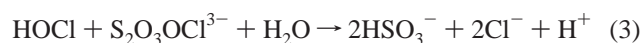
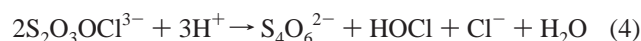propose the following one for the thiosulfate–hypochlorous acid reaction:

$$S_2O_3^{2-} + HOCl \rightarrow S_2O_3OCl^{3-} + H^+ \qquad (1)$$

$$r_1 = k_1[S_2O_3^{2-}][HOCl]$$

$$S_2O_3^{2-} + S_2O_3OCl^{3-} + 2H^+ \rightarrow S_4O_6^{2-} + Cl^- + H_2O \qquad (2)$$

$$r_2 = k_2[S_2O_3^{2-}][S_2O_3OCl^{3-}]$$

$$HOCl + S_2O_3OCl^{3-} + H_2O \rightarrow 2HSO_3^- + 2Cl^- + H^+ \qquad (3)$$

$$r_3 = k_3[HOCl][S_2O_3OCl^{3-}]$$

$$2S_2O_3OCl^{3-} + 3H^+ \rightarrow S_4O_6^{2-} + HOCl + Cl^- + H_2O \qquad (4)$$

$$r_4 = k_4[S_2O_3OCl^{3-}]^2$$

$$S_4O_6^{2-} + HOCl \rightarrow S_2O_3Cl^- + S_2O_3OH^- \qquad (5)$$

$$r_5 = k_5[S_4O_6^{2-}][HOCl]$$

$$S_2O_3^{2-} + S_2O_3OH^- + H^+ \rightarrow S_4O_6^{2-} + H_2O \qquad (6)$$

$$r_6 = k_6[S_2O_3^{2-}][S_2O_3OH^-]$$

$$HOCl + S_2O_3OH^- + H_2O \rightarrow 2HSO_3^- + Cl^- + 2H^+ \qquad (7)$$

$$r_7 = k_7[HOCl][S_2O_3OH^-]$$

$$HSO_3^- + HOCl \rightarrow SO_4^{2-} + Cl^- + 2H^+ \qquad (8)$$

$$r_8 = k_8[HSO_3^-][HOCl]$$

$$S_4O_6^{2-} + S_2O_3Cl^- + H_2O \rightarrow S_5O_6^{2-} + SO_4^{2-} + Cl^- + 2H^+ \qquad (9)$$
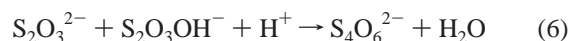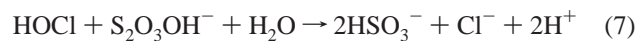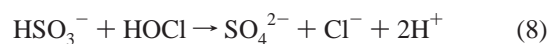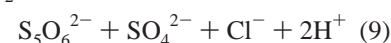
$$r_9 = k_9[S_4O_6^{2-}][S_2O_3Cl^-]$$

Step 1 is the initialization of the reaction in which the absorbing adduct $S_2O_3ClO^{3-}$ is formed. Although the back reaction is also conceivable chemically, inclusion of this step in the final model was unsuccessful. Our fitting procedure has also yielded a reasonable (1075 ± 19 M^{-1} cm^{-1}) molar absorbance to this intermediate. Steps 2–4 are the further reactions of $S_2O_3ClO^{3-}$ with the reactants and its second-order decay. Steps 2 and 4 produce tetrathionate ion, while step 3 leads directly to hydrogen sulfite ion that can rapidly react further with hypochlorous acid (see step 8), giving sulfate ion as a final product. Step 5 is the well-known oxidation of tetrathionate by hypochlorous acid which was studied recently in a slightly alkaline medium.[7] This reaction has already been well-established,[7] giving the two intermediates $S_2O_3OH^-$ and $S_2O_3Cl^-$. Steps 6 and 7 are the further reactions of $S_2O_3OH^-$ by the reactants. These reactions were found to be rapid, so only their ratio could be calculated. Therefore, k_6 was fixed to a feasible and fast value of 10^6 M^{-1} s^{-1} and the k_7/k_6 ratio was determined. These rapid second-order reactions also support the fact that $S_2O_3OH^-$ and/or its deprotonated form are quite reactive species. Step 8 is the well-known fast reaction between sulfite and hypochlorous acid. This rate coefficient was determined by Fogelman et al.;[14] we directly adopted their 7.6×10^8 M^{-1} s^{-1} value into our fitting procedure. Step 9 has already

Letters

J. Phys. Chem. B, Vol. 110, No. 6, 2006 **2469**

TABLE 2: Fitted and Fixed Rate Coefficients and Molar Absorbances at 250 nm Used in the Fitting Procedure

| parameter	value
k_1 (M^{-1} s^{-1})	3915 ± 140
k_2 (M^{-1} s^{-1})	1480 ± 166
k_3 (M^{-1} s^{-1})	746 ± 23
k_4 (M^{-1} s^{-1})	369 ± 30
k_5 (M^{-1} s^{-1})	390 ± 42
k_7/k_6	0.306 ± 0.067
k_8 (M^{-1} s^{-1})	7.6×10^8 (fix)
k_9 (M^{-1} s^{-1})	6583 ± 433
$\epsilon(S_2O_3{}^{2-})$	288.52 (fix)
$\epsilon(S_4O_6{}^{2-})$	1036 (fix)
$\epsilon(HOCl)$	80.43 (fix)
$\epsilon(S_2O_3OCl^{3-})$	1075 ± 19
$\epsilon(S_5O_6{}^{2-})$	$11\,682 \pm 716$

been proposed in the later phase of the tetrathionate ion–hypochlorous acid reaction at a slightly alkaline pH.[7] It was also suggested that the importance of this reaction increases with decreasing pH. The formation of pentathionate in thiosulfate excess is responsible for the measured final absorbance being higher than it could be calculated if all the thiosulfate was transformed to tetrathionate. Altogether, seven rate coefficients and two molar absorbances were fitted; additionally, two other rate coefficients and of course three other molar absorbances (that of the thiosulfate, tetrathionate, and hypochlorous acid) were fixed during the fitting procedure and are summarized in Table 2. The ability of the model proposed here is illustrated in Figures 1 and 2. The average deviation between the measured and calculated values was found to be 0.016 absorbance units, which is close to the experimentally achievable limit of error of the absorbance measurements under our experimental conditions.

To obtain spectral information from the intermediates involved in this reaction, we have also carried out the fitting procedure at every 5 nm of the 250–300 nm wavelength range. The logarithm of the calculated molar absorbances can be seen in Figure 3.

One important drawback of the model has to be mentioned as well. The fitting procedure has provided a significantly (3–4 times) higher molar absorbance for pentathionate than what was measured 40 years ago by other workers.[11,12] At this point, we are unable to give a proper answer to this question, but it seems likely that the separation of higher polythionates (penta-, hexa-, etc.) from each other is still not resolved entirely. A mixture of higher polythionates, however, might lead to an apparently high molar absorbance designated to pure pentathionate. It is hoped that further experiments planned in our lab will provide additional important information to this point.

Despite the drawback outlined above, the kinetic model, which is working properly within the range of the reactants used in the experiments, has an interesting feature. The hypochlorous acid not only oxidizes the thiosulfate (and the tetrathionate) ion, meanwhile it is uniquely reduced to chloride ion, but also assists in the generation of higher polythionates through the formation of $S_2O_3Cl^-$.

It has been reported that the use of a diode-array spectrophotometer produces photochemical oscillatory decomposition of tetrathionate in a longer time scale.[17] It is also well-known that a diode-array spectrophotometer can induce photochemical reactions and therefore might make a significant contribution to the kinetics of the reaction studied as well.[18] To check whether the polychromatic light beam has a significant effect or not, we have repeated some experiments with a Hi-Tech SF-61 stopped-flow instrument attached to a single wavelength spectrophotometer that provides monochromatic light at 250 nm.
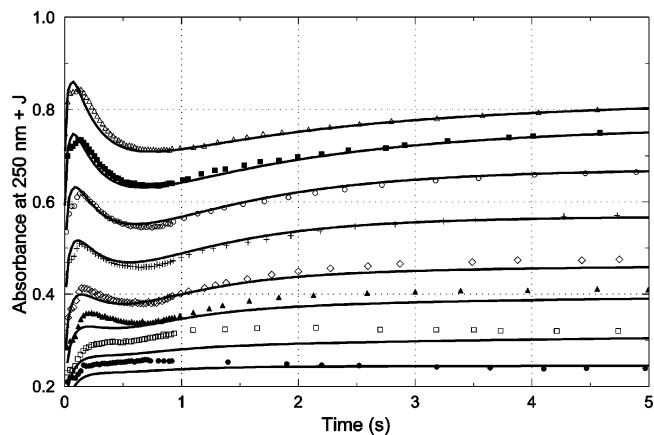
Figure 2. Measured (symbols) and calculated (solid lines) kinetic curves at 250 nm and pH 3.95 with constant thiosulfate concentration ($[S_2O_3{}^{2-}]_0 = 0.002$ M). $[HOCl]_0$ (mM) = 1.237 (●), 1.546 (□), 2.474 (▲), 3.247 (◇), 4.021 (+), 4.794 (○), 5.567 (■), 6.340 (△). Note that the measured and calculated absorbance–time curves are shifted along the Y-axis in order to see the trends better. The corresponding absorbance shifts are $J = 0$ (●), 0.02 (□), 0.05 (▲), 0.1 (◇), 0.2 (+), 0.3 (○), 0.4 (■), and 0.5 (△), respectively.
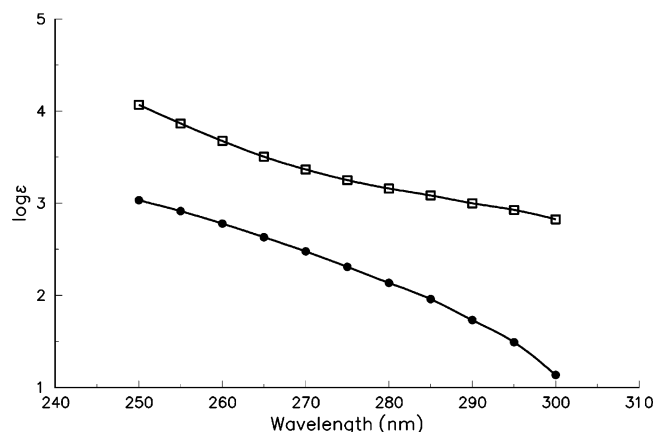
Figure 3. Logarithm of the calculated molar absorbances of pentathionate (□) and $S_2O_3OCl^{3-}$ (●) in the 250–300 wavelength range.

The characteristics of the kinetic curves did not change at all; therefore, we concluded that any photochemical reaction that may be involved in the reaction cannot have a significant effect.

It should also be emphasized that the rate coefficients given here were determined at a single pH. Further investigations will be carried out in our lab to unravel the pH dependence of the rate coefficients and to strengthen the role of pentathionate or even higher polythionates involved in the reaction between thiosulfate (and/or tetrathionate) ion and hypochlorous acid.

References and Notes

(1) Orbán, M.; De Kepper, P.; Epstein, I. R. *J. Phys. Chem.* **1982**, *86*, 431.

(2) Orbán, M.; Epstein, I. R. *J. Phys. Chem.* **1982**, *86*, 3907.

(3) Maselko, J.; Epstein, I. R. *J. Chem. Phys.* **1984**, *80*, 3175.

(4) Nagypál, I.; Epstein, I. R. *J. Phys. Chem.* **1986**, *90*, 6285.

(5) Peintler, G.; Nagypál, I.; Epstein, I. R. *J. Phys. Chem.* **1990**, *94*, 2954.

(6) Horváth, A. K.; Nagypál, I. *J. Phys. Chem. A* **1998**, *102*, 7267.

(7) Horváth, A. K.; Nagypál, I. *Int. J. Chem. Kinet.* **2000**, *32*, 395.

2470 *J. Phys. Chem. B, Vol. 110, No. 6, 2006*

Letters

(8) Horváth, A. K.; Nagypál, I.; Epstein, I. R. *J. Phys. Chem. A* **2003**, *107*, 10063.

(9) Horváth, A. K.; Nagypál, I.; Peintler, G.; Epstein, I. R.; Kustin, K. *J. Phys. Chem. A* **2003**, *107*, 6966.

(10) Peintler, G. *ZiTa*, version 5.0; a comprehensive program package for fitting parameters of chemical reaction mechanisms; Attila József University: Szeged, Hungary, 1989−1998.

(11) Goldsmith, R. M. *J. Chem. Phys.* **1960**, *33*, 1666.

(12) Schmidt, M.; Sand, T. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1173.

(13) Peintler, G.; Nagypál, I.; Jancsó, A.; Kustin, K.; Epstein, I. R. *J. Phys. Chem. A* **1997**, *101*, 8013.

(14) Fogelman, K. D.; Walker, D. M.; Margerum, D. W. *Inorg. Chem.* **1989**, *28*, 986.

(15) Liu, R. M.; McDonald, M. R.; Margerum, D. W. *Inorg. Chem.* **1995**, *34*, 6093.

(16) Perrone, T. F.; Huff-Hartz, K. E.; Wang, L.; Margerum, D. W. *Inorg. Chem.* **2003**, *42*, 5818.

(17) Horváth, A. K.; Nagypál, I.; Epstein, I. R. *J. Am. Chem. Soc.* **2002**, *124*, 10956.

(18) Lente, G.; Espenson, J. H. *J. Photochem. Photbiol., A* **2004**, *163*, 249.