# UNIVERSITY OF PÉCS

Doctoral School of Chemistry

# Kinetics and Mechanism of the Reactions of Pentathionate Ion by Different Halogen-Containing Oxidizing Agents

Ph.D. Thesis

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# 1 Introduction

Polythionates ($S_xO_6^{2-}$, $x \geq 3$), also known as polysulfane disulfonic acids or polysulfane disulfonates, are sulfur-based molecules in which the sulfur chain is terminated at both ends by $SO_3^-$ groups. These compounds, in particular trithionate, tetrathionate, pentathionate and hexathionate are important intermediates in redox transformation of sulfur containing compounds in several environmentally or industrially important processes and the metabolism of sulfur-oxidizing and sulfur-reducing microorganisms. A review and recent advances in the sampling and analysis of sulfur-oxygen species including polythionates have facilitated their direct identifications and studies in many environments. A notable application of polythionates is the formation of copper sulfide, $Cu_xS$ thin film on the polyamide surface, markedly promoting the optoelectrical efficiency of transportation, where the polythionate is used as a precursor of polymer sulfurization in acidic conditions as a result of its polysulfur chain.

As we know, the cyanidation process was used in leaching of copper, silver, gold and other noble metal from their ores beside the fact that the toxicity of cyanide ion has long been known. Recently, there are considerable efforts to find alternative and less harmful processes to exchange the cyanidation technology. Thiosulfate solution, as a nontoxic alternative, seems to be a promising opportunity to replace that cyanidation process. However, several problems arose during the procedure of the thiosulfatolysis process. One of them is the generation of polythionates from the oxidation of thiosulfate, which are detrimental to the subsequent metal recovery process with ion-exchange resin at low concentrations.

It is generally well-known that oxidations of thiosulfate ion by different oxidizing agents lead finally to sulfate ion via formation of different sulfur–containing intermediates (mainly polythionates with a considerably long half–lives ). These reactions of thiosulfate, for example, with bromate, chlorite, iodate and periodate, exhibit several exotic nonlinear dynamical phenomena such as autocatalysis under batch condition, bistability and complex periodic and aperiodic behavior in a continuously stirred tank reactor (CSTR), and an appearance of varieties of different reaction-diffusion patterns (chemical waves and chemical reaction fronts) in unstirred system. Recent investigations have shown that not only chemical but also electrochemical oxidation of thiosulfate leads to the formation of higher poly-

thionates. Moreover, the kinetic studies of hydrogen peroxide–thiosulfate, chlorite–thiosulfate, and hypochlorous acid–thiosulfate systems have clearly demonstrated that besides sulfate ion, polythionates such as trithionate, tetrathionate and pentathionate are also produced in detectable amounts. These intermediates will further react with the corresponding oxidants (like chlorite, periodate, iodate *etc.*) and intermediates of corresponding oxidants (like hypochlorous and chlorine dioxide) sometimes displaying fascinating kinetics and may thus contribute to the appearance of a rich variety of kinetic phenomena found experimentally in the oxidation of thiosulfate. Therefore, systematic investigation on the kinetics and mechanism of the oxidations of polythionates by different oxidants seems to be expected as a crucial part of the studies of oxidations of thiosulfate. A firm knowledge of the oxidation of polythionates may accelerate further researches on the detailed kinetics and mechanism of oxidation of thiosulfate.

Pentathionate, as one of important polythionates generated in the oxidation of thiosulfate and other sulfur compounds reacting further with the oxidants, may play a crucial role in the appearance of the exotic nonlinear dynamical phenomena. A good understanding of the oxidation of pentathionate will accelerate the researches of oxidation of other polythionates as well as deeper understanding about oxidation of thiosulfate. Compared to trithionate and tetrathionate, however, significantly less information is available in the literature about the oxidation of pentathionate apart from only a few studies that directly investigate the oxidation of pentathionate by ferrate ion as well as the decomposition of pentathionate at an alkaline medium.

## 2  Objectives

The objectives of my dissertation are to investigate the kinetic behaviors of oxidation of pentathionate by different halogen-containing oxidizing agents to obtain deeper insight into the nature of sulfur-chain-breaking reactions of polythionates and for better descriptions of nonlinear exotic phenomena observed in oxidation of thiosulfate in which polythionates, mainly trithionate, tetrathionate and pentathionate, are seriously involved. Unfortunately, as mentioned previously, no information of oxidation of pentathionate by halogen-containing oxyanions is available in the literature. Thus first we chose the relatively simple iodine–

pentathionate reaction as a beginning of the series of studies on the redox transformation of pentathionate. This study was followed by three more complex reaction systems such as chlorine dioxide–pentathionate, iodate–pentathionate and periodate–pentathionate.

# 3  Methods

The iodine–pentathionate and chlorine dioxide–pentathionate reactions were studied in a slightly acidic medium in acetic acid/acetate buffer. The iodate–pentathionate and periodate–pentathionate reactions were investigated at lower pH ranges adjusted by phosphoric acid/dihydrogen phosphate buffer. All kinetic measurements were carried out at $25.0 \pm 0.1$ °C and at 0.5 M ionic strength.

All the iodine–pentathionate, chlorine dioxide–pentathionate, iodate–pentathionate and periodate–pentathionate reactions were found to be slow enough under the present experimental conditions that allowed us to monitor the kinetics by a diode array spectrophotometer (Zeiss S600) in the visible range without using the deuterium lamp. Raman spectroscopy was also carried out to check the end-products of chlorine dioxide–pentathionate reaction by an NXR FT-Raman spectrometer.

Simultaneous evaluation of the kinetic curves was carried out by the Chem-Mech/Zita program package developed to fit basically unlimited experimental series. For computational of theoretical calculations, the Firefly 7.1.G quantum chemical package was used. Natural bond orbital(NBO) analysis have been performed by the module NBO 5.G implemented in Firefly.

# 4  Results

Results of all reaction systems can be summarized as follows:

**The iodine–pentathionate reaction system:**

1. It is found that the rate of the reaction is independent of pH within the pH range studied and exhibits strong iodide autoinhibition[*]. The kinetic curves and theoretical evaluations also support the fact that iodide inhibition cannot be simply explained by the fast equilibrium formation of the unreactive triiodide ion and $S_5O_6I^-$ along with the iodide ion has to be involved in the initiating rapid equilibrium between the reactants being shifted far to the left:

$$S_5O_6^{2-} + I_2 \; \rightleftharpoons \; S_5O_6I^- + I^-$$
(1)
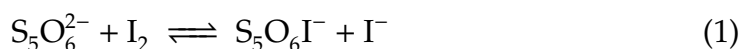
   These properties of the given system can be treated as general phenomena of the corresponding polythionate–iodine reaction systems.

2. The stoichiometry of the reaction was established experimentally to be:

$$S_5O_6^{2-} + 10I_2 + 14H_2O \; = \; 5SO_4^{2-} + 20I^- + 28H^+$$
(2)
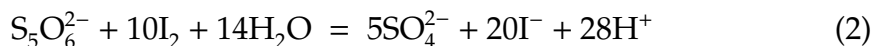
   and the apparent rate equation is:

$$-\frac{1}{10} \cdot \frac{d[T_{I_2}]}{dt} = k_{\text{app}} \frac{[S_5O_6^{2-}][T_{I_2}]}{[I^-]}$$
(3)

   where the $[T_{I_2}] = [I_2] + [I_3^-]$. This stoichiometry with the apparent rate equation is valid both in excess of iodine and that of pentathionate.

3. On the basis of the experiments, a nine-step kinetic model with two fitted parameters is proposed by a nonlinear parameter estimation and discussed. The complex iodide ion inhibition and the pH independent behavior were adequately explained by the proposed kinetic model and the correlation between the rate coefficients was interpreted by derivation of a formal rate equation deduced from the proposed kinetic model.

**The iodate–pentathionate reaction system:**

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[*]The autoinhibition is defined as a process where one of the product formed during the course of the reaction slows down the rate of its formation, which is a negative feedback. The species causes this phenomenon is called as an autoinhibitor.

4. The kinetic measurements showed that clock species iodine appears only after a fairly long time lag before complete consumption of substrate pentathionate and the inverse of time necessary to produce a certain amount of iodine ($t_i$) is linearly proportional to the initial concentration of iodate ion and the square of the hydrogen ion concentration meanwhile depending complexly on the concentration of substrate pentathionate. It is also found that the substrate pentathionate and the clock species iodine coexist for a relatively long time— due to their relatively slow direct reaction—depending on the experimental circumstances, which differs from the Landolt-type clock reactions in which the clock species appears at exactly the same time point when the substrate (bisulfite or thiosulfate) is depleted. The accelerating effect of the increase of ionic strength and significant catalytic effect of buffer composition and the autocatalytic effect of iodide ion have also been observed.

5. A 14-step plausible kinetic model with four fitted rate coefficients was proposed in which the mechanisms of the pentathionate–iodine, bisulfite–iodate and the well-known Dushman reactions are combined. It is revealed that the direct pentathionate–iodate reaction plays a role only to produce iodide ion via a finite sequence of reactions and once its concentration reaches a certain level, the reaction is almost exclusively governed by the pentathionate–iodine and Dushman reactions. In other words, the dependence of $t_i$ on concentration of pentathionate, iodate and hydrogen ion can be well explained by the proposed mechanism. It is also found that the strong catalytic effect of the buffer composition can readily be explained by its well-known catalytic influence on the original Dushman reaction and the autocatalytic effect of iodide ion can be explained by the proposed kinetic model as well.

**The periodate–pentathionate reaction system:**

6. The observations indicate that iodine also appears only after a well-defined but fairly long time lag and the reciprocal of time necessary to produce a certain amount of iodine depends complexly with respect to the concentration of the reactants as well as the pH. Iodide ion was proven to be an autocatalyst of the reaction. A significant influence of the ionic strength and the total buffer concentration on the reaction indirectly prove that the pentathionate–iodate and the Dushman reactions play a key role in determining the kinetic behavior

of the title system due to their strong influence on the pentathionate–iodate and the Dushman reactions.

7. A 24-step kinetic model is proposed in which the mechanisms of pentathionate–iodine, pentathionate–iodate, hydrogen-sulfite–periodate, hydrogen-sulfite–iodate, iodide–periodate and the well-known Dushman reactions are combined. A thorough analysis revealed that the direct pentathionate–periodate reaction plays a role only to produce iodide ion via a finite sequence of reactions and once its concentration reaches a certain level, the reaction is almost exclusively governed by the pentathionate–iodine, the iodide–periodate and the Dushman reactions.

**The chlorine dioxide–pentathionate reaction system:**

8. A series of qualitative tests revealed that the thermodynamically most favorable stoichiometry is

$$S_5O_6^{2-} + 4ClO_2 + 6H_2O = 5SO_4^{2-} + 4Cl^- + 12H^+ \tag{4}$$
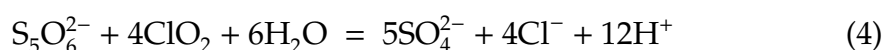
but at higher chlorine dioxide excess, the stoichiometric ratio (SR defined as SR = $([ClO_2]_0 - [ClO_2]_\infty)/[S_5O_6^{2-}]_0$) exceeds 4 and is shifted to almost 10. The Raman spectrum of the end products including chlorate suggests that the reaction

$$6ClO_2 + 3H_2O = 5ClO_3^- + Cl^- + 6H^+ \tag{5}$$

also plays a significant role in determining the stoichiometry of the reaction. The highest SR near 10 can easily be obtained by an algebraic sum of eq. 4 and eq. 5:

$$S_5O_6^{2-} + 10ClO_2 + 9H_2O = 5SO_4^{2-} + 5ClO_3^- + 5Cl^- + 18H^+ \tag{6}$$
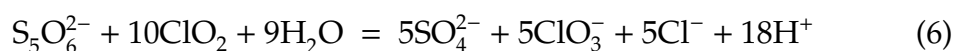
It is clearly demonstrated that the initial conditions such as the concentration of the reactants, chloride ion and pH shifts the balance between eq. 4 and eq. 6

9. Kinetics of the reaction was found to be more complex than that of chlorine dioxide–trithionate and chlorine dioxide–tetrathionate because initial rate studies revealed that neither the formal kinetic order of the reactants nor that of $H^+$ is an integer number. (In the previous reactions the formal kinetic order of at least one reactant is unity.) It is also found that the chloride

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ion has significant catalytic effect on the reaction which is the same as the observations in the previous reactions indicating a general phenomenon in all the polythionate–chlorine dioxide reactions.

10. On the basis of our observations and simultaneous evaluation of the kinetic curves, an 11-step kinetic model with 6 fitted rate coefficients was established. The changing stoichiometry was soundly explained and the kinetic curves at different initial conditions were adequately described by this kinetic model. A relatively simple rate equation describing the correlation between the rate coefficients has also been derived from proposed mechanism.

# 5  Future Perspectives

Combined with the previous studies, it looks to be worth mentioning some perspectives of the present works:

1. The studies of pentathionate–iodine reaction supports an additional information about the similar phenomena of redox reactions of polythionate (such as a general pathway of sulfur-chain-breakage of polythionate and iodide inhibition), which may inspire some further theoretical investigations of redox reactions of higher polythionates to obtain deeper insight into the nature of sulfur-chain-breaking reactions of polythionates.

2. The pentathionate–iodate and pentathionate–periodate reactions are defined as "autocatalysis-driven clock reactions[†]" and Landolt reaction is suggested to be classified as "substrate-depletive clock reactions[‡]". Therefore, we would like to mention the facts that precise clarification of a definition of the term "clock reaction" as well as reclassification of these systems is eagerly expected. We hope that our suggestion here may pave the way to clarify the meaning of the generally used term "clock reaction".

3. The autocatalysis-driven clock reactions (such as the pentathionate–iodate and pentathionate–periodate reaction) may be used in studying spatiotemporal phenomena. As seen these systems are painfully slow reactions above pH = 3, therefore strongly acidic condition is a necessary requirement for a possible production of spatiotemporal structures. At this condition the key to control the reaction is the concentration level of the autocatalyst iodide ion. It straightforwardly means that the main driving force of the reaction is rather the autocatalytic buildup of iodide ion than that of the increase of $H^+$ observed in the original Landolt reaction. Since the diffusion constant of iodide ion is significantly lower compared to that of hydrogen ion, it may provide an inherent control for a slower diffusion of the autocatalyst. It may therefore be anticipated that several different spatiotemporal structures might

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[†]A reaction featuring clock behavior emerged from the concurrent consumption of a substrate and an appearance of a clock species is called as a *substrate-depletive clock reactions*

[‡]A system featuring a clock behavior emerging from the autocatalytic build-up of the clock species without depleting the substrate is called as an *autocatalysis-driven clock reaction.*

be observed without binding part of autocatalyst reversibly of irreversibly to decrease its mobility.

4. Finally, the pentathionate–chlorine dioxide may be treated as a subsystem of pentathionate–chlorite reaction which is also worth studying as a subsystem of thiosulfate–chlorite reaction, which may be helpful for better descriptions of nonlinear exotic phenomena of oxidation of thiosulfate with chlorite.

# 6 Publications, presentation

**I. Publications forming the basic of Ph.D. dissertation:**

1. **L. Xu,** Gy. Csekő, T. Kégl, A. K. Horváth: General Pathway of Sulfur-Chain Breakage of Polythionates by Iodine Confirmed by the Kinetics and Mechanism of the Pentathionate–Iodine Reaction. *Inorg. Chem.,* **2012,** *51,* 7837-7843. **IF: 4.593**

2. **L. Xu,** Gy. Csekő, A. Petz, A. K. Horváth: Kinetics and Mechanism of the Oxidation of Pentathionate Ion by Chlorine Dioxide in a Slightly Acidic Medium. *J. Phys. Chem. A,* **2014,** *118,* 1293-1299. **IF: 2.775**

3. **L. Xu,** A. K. Horváth: A Possible Candidate To Be Classified as an Autocatalysis-Driven Clock Reaction: Kinetics of the Pentathionate–Iodate Reaction. *J. Phys. Chem. A,* **2014,** *118,* 6171-6180. **IF: 2.775**

4. **L. Xu,** A. K. Horváth: Autocatalysis-Driven Clock Reaction II: Kinetics of the Pentathionate–Periodate Reaction. *J. Phys. Chem. A,* **2014,** *118,* accepted for publication, DOI: 10.1021/jp507925e. **IF: 2.775**

**II. Other publications:**

1. X. F. Hu, J. X. Xie, **L. Xu,** H. M. Liu, X. L. Lv, Q. Y. Gao: Deposition Dynamics of Sulfur in the Electrochemical Oxidation of Sulfide on Pt Electrode. *Sciencepaper Online,* **2009,** *4,* 453-458. **IF: 0.000**

2. **L. Xu,** J. H. Zheng, Y. Hu, Y. C. Lu, Q. Y. Gao: Separation and Analysis of Chlorite and Sulfur Oxyanions in Mixture Using High Performance Liquuid Chromatography. *Chinese J. Anal. Chem.,* **2010,** *4,* 537-541. **IF: 0.790**

3. Y. C. Lu, Q. Y. Gao, **L. Xu,** Y. M. Zhao, I. R. Epstein: Oxygen-Sulfur Species Distribution and Kinetic Analysis in the Hydrogen Peroxide–Thiosulfate System. *Inorg. Chem.,* **2010,** *49,* 6026-6034. **IF: 4.325**

4. **L. Xu,** A. K. Horváth, Y. Hu, C. Ji, Y. M. Zhao, Q. Y. Gao: High Performance Liquid Chromatography Study on the Kinetics and Mechanism of Chlorite–Thiosulfate Reaction in Slightly Alkaline Medium. *J. Phys. Chem. A,* **2011,** *115,* 1853-1860. **IF: 2.946**

5. Y. Hu, J. M. Feng, Y. W. Li, Y. Y. Sun, **L. Xu,** Y. M. Zhao, Q. Y. Gao: Kinetic Study on Hydrolysis and Oxidation of Formamidine Disulfide in Acidic Solutions. *Sci. Chin. Chem.,* **2012,** *55,* 235-241. **IF: 1.330**

6. Csekő Gy., **Xu L.,** Horváth A. K.:A kénlánc oxidációjának kinetikája a politionát– jód reakciókban. *Magyar Kémiai Folyóirat,* **2013,** *119*, 88-92. **IF: 0.000**

**III. Presentation:**

1. **L. Xu,** Gy. Csekő, A. K. Horváth: Kinetics and mechanism of the pentathionate–iodine reaction. CECE 2013 10$^{th}$ International Interdisciplinary Meeting on Bioanalysis, Pécs, 2013. April 25-27.