

UNIVERSITY OF PÉCS

Doctoral School of Chemistry

**Kinetic studies of some redox
reactions of trithionate ion**

Ph.D. Thesis

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1. Introduction

Spatial or temporal nonlinear processes that meet difficulties to be observed in nature are generally studied by the help of chemical reactions to be capable of mimicking these features in laboratorial circumstances. For example, the one-dimensional propagating reaction front is analogous to the movement of flames in a thin detonating chord and the two-dimensional movement of the reaction front is analogous to the spread of wildfires.

Many different chemical reactions are known to be able to model these phenomena. One of the well-studied systems is the tetrathionate–chlorite (CT) reaction, which was first investigated in 1986 by Nagypál *et. al.* Although the complete kinetic model of this system being capable of describing the kinetic behaviour on the whole timescale of the reaction was not available at that time, several important characteristics have already been resolved. One of the most important observations was that the reaction is supercatalytic with respect to hydrogen ion. Intensive researches of this system törtlendő helyette have been being carried out since 1996, when Tóth *et. al.* observed the appearance of cellular structures in the unstirred CT-reaction, if part of the hydrogen ions was immobilized. Later the CT-reaction was used to study several interesting nonlinear chemical phenomena in connection with front-propagation such as pattern formation, 2D-front instability, 3D-front instability, spatial bistability, excitation waves and oscillation by several independent research groups. The kinetic model originally suggested by Nagypál *et. al.* was used almost exclusively in majority of these studies. It was, however, found that the rate coefficient has to be modified significantly most probably due to the complexity of CT reaction. Thus it appears to be inevitable that a simple kinetic rate equation having a single rate coefficient is not sufficient to describe quantitatively the phenomena observed.

In 2010 Peintler *et. al.* attempted to improve the kinetic model, which is routinely used in unstirred circumstances. They used the latest results published on the mechanism of CT-reaction, and suggested that the thermodynamically most favourable stoichiometry of CT-reaction should be supple-

mented with the decomposition of chlorite ion in acidic medium in slight excess of chlorite ion. It should be emphasized that this is the most common experimental condition used in the investigations of spatial periodic phenomena. Moreover a new rate equation has also been proposed consisting of two terms including the concentration of hydrogen ion both in the second and third power as well. Thus this system is very sensitive to the concentration of hydrogen ion, therefore to prevent the spontaneous initiation of front propagation the pH of reaction solution has to be kept at the alkaline region. This, however, gives a rise to a further problem, namely the alkaline decomposition of tetrathionate to produce thiosulfate, trithionate, sulfate and sulfite ions. The kinetics of thiosulfate–chlorite and sulfite–chlorite reactions has already been studied, so these reactions can easily be taken into account to model quantitatively the unstirred CT-reaction. Unfortunately, no information has yet been available in the literature about the kinetics and mechanism of the trithionate–chlorite reaction. Furthermore, we have only found one relevant article on the reactions of trithionate, namely its vanishingly slow decomposition at alkaline medium, but redox transformations of this species are completely unknown.

2. Objectives

The initial objective of my dissertation was to interpret the kinetic behaviour of trithionate–chlorite reaction to further improve the kinetic model of CT-reaction for achieving a better quantitative agreement in that complex system. Previously it is mentioned that thorough kinetic studies on oxidation of trithionate by any oxidizing agents are missing. Due to the lack of any relevant kinetic information and being aware of the complexity of the chlorite–trithionate reaction obtained by preliminary investigations we decided to start these series of studies with the less complex iodine–trithionate reaction followed by that of the possible subsystems such as hypochlorous acid–trithionate and chlorine dioxide–trithionate reactions.

3. Methods

The iodine–trithionate, chlorine dioxide–trithionate and the chlorite–trithionate reactions have been studied in a slightly acidic medium in acetic acid/acetate buffer. The HOCl–trithionate reaction has been studied at a broad pH range, at a nearly neutral condition, the pH was adjusted by dihydrogen phosphate/hydrogen phosphate buffer, while around pH = 12 by hydrogen phosphate/phosphate buffer. All the kinetic measurements have been investigated at 25.0 ± 0.1 °C and at 0.5 M ionic strength. In case of the front propagation experiments the temperature was kept constant at 25 ± 1 °C.

The kinetics of majority of the reactions has been recorded spectrophotometrically, the iodine–trithionate, chlorine dioxide–trithionate and the chlorite–trithionate reactions are slow enough in the whole pH range that allows us to follow them by a diode array spectrophotometer (Zeiss S600 or Zeiss S10). The HOCl–trithionate reaction was also investigated by a diode array spectrophotometer around pH = 12, but at nearly neutral pH range this reaction is relatively fast. Since usual reaction times were found to be less than 10 s stopped-flow technique has been employed to study this reaction. Raman spectroscopy was also carried out to check the end-products by an NXR FT-Raman spectrometer. 1D-front propagation studies were executed in a thin 50 cm long capillary tube having an inner diameter of 0.733 ± 0.006 mm.

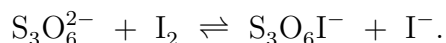
The number of absorbing species was determined by the program package MRA. Simultaneous evaluation of the kinetic curves was carried out by the program package ZiTa. The partial differential equation system of the 1D-front propagation was numerically integrated using BDF2 formula at the 1D-front calculations.

4. Results

Results can be summarized as follows:

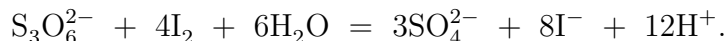
The iodine–trithionate system:

1. It is shown that consumption of iodine is inhibited by iodide ion, but it cannot be simply explained via the fast equilibrium formation of triiodide ion that is usually known to be more sluggish towards any redox transformation. We have proven both experimentally and theoretically that a relatively fast equilibrium exists between the reactants to produce iodide ion and $\text{S}_3\text{O}_6\text{I}^-$ and this equilibrium is shifted far to the left:



We have also found this system to be independent of pH. These properties of the given system can be treated as complete analogies of the corresponding polythionate–iodine reactions.

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

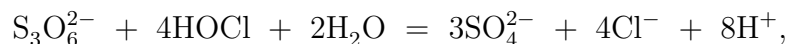


This stoichiometry is valid both in excess of iodine and trithionate.

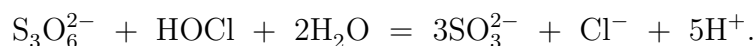
3. On the basis of the experiments, a 5-step kinetic model with 4 fitted kinetic parameters is proposed by a nonlinear parameter estimation. The complex iodide ion inhibition and the pH independent behavior were adequately explained by the proposed kinetic model. The correlation between the rate coefficients was interpreted by derivation of a formal rate equation from the proposed kinetic model.

The HOCl–trithionate system:

4. The stoichiometry of reaction in an excess of HOCl was determined to be



but in an excess of trithionate ion the following limiting stoichiometry can also be taken into consideration:

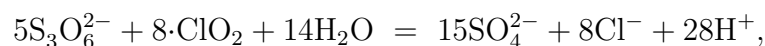


A suitable linear combination of these equations adequately describes the actual stoichiometry of the reaction in the concentration ranges of the reactants studied. Sulfite ion was detected indirectly by standard iodometry after successfully masking it by formaldehyde.

5. A 6-step plausible kinetic model with 4 fitted kinetic parameters is proposed by a nonlinear parameter estimation that is able to take into account the changing stoichiometry and the characteristics of the measured kinetic curves between pH 6.6 and 12.2. It was also demonstrated that both forms of Cl(I) are kinetically active species.

The chlorine dioxide–trithionate system:

6. In an excess of trithionate ion the stoichiometry of the chlorine dioxide–trithionate reaction was measured to be



but an excess of chlorine dioxide shifts this stoichiometric ratio to 1:4 according to the following equation:



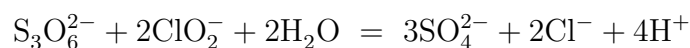
We have also shown that a suitable linear combination of these equations accounts well the shifts in the stoichiometric ratio as a function of the concentration of the reactants and that of pH. Formation of chlorate ion was further verified by Raman spectroscopy.

7. As a result of the simultaneous evaluation of the kinetic curves a 13-step kinetic model with 6 fitted kinetic parameters was established. The changing stoichiometry was soundly explained and the measured

kinetic curves between pH = 4.35–5.70 were adequately described by this kinetic model. It was also demonstrated that both hydrogen ion and chloride ion may act as autocatalysts of the reaction. The correlation between the rate coefficients was as well interpreted on the basis of the formal kinetics.

The chlorite–trithionate system:

8. Systematic investigations at wide concentration ranges of the reactants suggested that the actual stoichiometry of the chlorite–trithionate reaction can be described by an appropriate linear combination of the following equations:



9. Detailed initial rate studies have clearly revealed the formal kinetic orders of hydrogen ion and chlorite ion to be strictly two and one, respectively, but that of trithionate ion can be approximated by 0.5 that allowed us to establish the following rate equation*:

$$-\frac{d[\text{ClO}_2^-]}{dt} = k_{27}[\text{S}_3\text{O}_6^{2-}]^{1/2}[\text{ClO}_2^-][\text{H}^+]^2.$$

10. A simple model was proposed in unstirred conditions, that can describe quantitatively the concentration dependence of the front velocity between 1:3–1:6 trithionate:chlorite ratio. Within this region a maximum of front velocity was found experimentally.

*The original label of this rate coefficient is preserved from dissertation.

11. It is clearly demonstrated that specific acid catalysis also appears in the chlorite–trithionate system. Taking this effect into account a relatively huge difference between the rate coefficients (k_{27}) obtained from the initial rate studies and fitting of the concentration dependence of front propagation studies can easily be reconciled.

5. Publication, presentations

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

1. **Gy. Csekő**, A.K. Horváth: Non-Triiodide Based Autoinhibition by Iodide Ion in the Trithionate–Iodine Reaction. *J. Phys. Chem. A*, **2010**, *114*, 6521. **IF: 2.732**
2. **Gy. Csekő**, A.K. Horváth: Kinetics and Mechanism of the Chlorine Dioxide–Trithionate Reaction. *J. Phys. Chem. A*, **2012**, *116*, 2911. **IF: 2.771**
3. **Gy. Csekő**, E. Rauscher, A.K. Horváth: Kinetics and Mechanism of the Hypochlorous Acid–Trithionate Reaction. *J. Phys. Chem. A*, **2013**, *117*, 8836. **IF: 2.771**
4. **Gy. Csekő**, L. Ren, Y. Liu, Q. Gao, A.K. Horváth: A New System for Studying Spatial Front Instabilities: The Supercatalytic Chlorite–Trithionate Reaction. *J. Phys. Chem. A*, **2014**, *118*, 815. **IF: 2.771**

II. Other publication:

1. **Gy. Csekő**, D. Varga, A.K. Horváth, I. Nagypál: Simultaneous Investigation of the Landolt and Dushman Reactions. *J. Phys. Chem. A*, **2008**, *112*, 5954. **IF: 2.871**
2. A.K. Horváth, I. Nagypál, **Gy. Csekő**: Theoretical Investigation on the Concentration Dependence of the Landolt Time. *J. Phys. Chem. A*, **2008**, *112*, 7868. **IF: 2.871**
3. G. Peintler, **Gy. Csekő**, A. Petz, A.K. Horváth: An improved chemical model for the quantitative description of the front propagation in the tetrathionate–chlorite reaction. *Phys. Chem. Chem. Phys.*, **2010**, *12*, 2356. **IF: 3.453**

4. E. Rauscher, **Gy. Csekő**, A. K. Horváth: On the Complexity of Kinetics and the Mechanism of the Thiosulfate-Periodate Reaction. *Inorg. Chem.*, **2011**, *50*, 5802. **IF: 4.601**
5. 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. **IF: 4.593**
6. **Csekő Gy.**, Xu L., Horváth A. K.: A kénlánc oxidációjának kinetikája a politionát–jód reakciókban. *Magyar Kémiai Folyóirat*, **2013**, *119*, 88. **IF: 0.000**
7. **Gy. Csekő**, Y. Hu, Y. Song, R. T. Kégl, Q. Gao, S. V. Makarov, A. K. Horváth: Kinetic Evidence of Tautomerism of Thiourea Dioxide in Aqueous Acidic Solutions. *Eur. J. Inorg. Chem.*, **2014**, *11*, 1875. **IF: 3.120**
8. 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. **IF: 2.771**

III. Other presentations:

1. A. K. Horváth, I. Nagypál, **Gy. Csekő**, D. Varga: A Landolt-reakció: újabb eredmények. MTA Reakciókinetikai és Fotokémiai Munkabizottsági ülés, Gyöngyöstarján, 2008. November 6-7.
2. E. Rauscher, **Gy. Csekő**, A. K. Horváth: A tioszulfát–perjodát reakció kinetikája. MTA Reakciókinetikai és Fotokémiai Munkabizottsági ülés, Siófok, 2011. May 5-6.
3. L. Xu, **Gy. Csekő**, T. Kégl, A. K. Horváth: Kinetics and mechanism of the pentathionate–iodine reaction. CECE 2013 10th International Interdisciplinary Meeting on Bioanalysis, Pécs, 2013. April 25-27.