Final Report for OTKA Project K116591

Introduction

The main scope of the present research proposal was to understand how the ageing process of thiourea dioxide affects its reducing and oxidizing capability. To achieve this goal, the kinetics and mechanism of several reactions of thiourea dioxide and its corresponding reaction partners have been thoroughly and systematically studied. Although an unambiguous answer is yet to be given, the published results may serve as a solid background for future investigations. The publications supported by the OTKA project K116591 may be divided into three groups, six articles and one book directly related to answering the original questions raised by the research proposal (group no. 1.), twelve publications are closely, but not entirely connected to the nonlinear dynamical behavior of the reaction partner of thiourea dioxide in aqueous solutions (group no. 2.). From the remaining four publications, two is not tightly related to answer the original question (group no. 3.), and only in the case of two publications it is difficult to identify some connections of the research proposal (group no. 4.), though these two results were important to support a strong international cooperation with Sergei V. Makarov, who is a well-known international expert in thiourea oxide chemistry or to establish a new cooperation with István T. Horváth.

<u>Summary of the results achieved by publications group no. 1.:</u>

1. *<u>Explaining the autocatalytic behahavior of the thiourea dioxide-chlorine dioxide reaction (Ref. 1. of list of publications):</u>* We have elaborated the kinetics and mechanism of the chlorine dioxide-thiourea dioxide system by the help of an international cooperation of prof. Q. Gao's group in China and prof. Sergei Makarov. The main outcome of this result is that hypochlorous acid, chlorite and bisulfite play substantial role in the appearance of sigmoidal shaped profile of the kinetic curves. As a result, a sixteen-step kinetic model including a slow first order transformation of the less reactive form of thiourea dioxide into a more reactive form has been published to describe quantitatively the measured concentration-time profiles of chlorine dioxide. It has been proposed that the controlling the concentration level of bisulfite ion, hypochlorous acid and chlorite ion at certain experimental conditions is responsible for the appearance of the autocatalytic nature of the reaction.
2. *<u>Review book about the chemistry and application of dithionite, rongalite and thiourea oxides (Ref. 5. of list of publications):</u>* This book summarizes the most important chemical feature of dithionite, rongalite and thiourea oxides (synthesis, reactivity, stability and application). Although these compounds seem to be independent of each other, they are connected with other in the fact the alkaline hydrolysis of rongalite and thiourea dioxide will lead to the formation sulfoxylic acid, a strong reducing agent that s also formed from dithionite under some experimental condition.
3. *<u>About the kinetics and mechanism of the thiourea dioxide-iodine reaction (Ref. 6. of the list of publications):</u>* It was also confirmed that the slow rearrangement of thiourea dioxide in aqueous acidic solution to produce a key species having significantly different kinetic activity toward iodine is also an indispensable part of the kinetic model. Iodine reacts with both the fresh and the aged thiourea dioxide in a halonium

ion and a possible electron transfer process, respectively. The reaction was found to be strongly inhibited by iodide ion; a nine-step kinetic model with four fitted parameters is suggested and discussed to account for all the observed concentration-time profiles. This proposed model was later implemented in describing the nonlinear dynamical feature of thiourea dioxide-iodate and thiourea dioxide-periodate reactions.

4. *Review article about the reactivity of small oxoacids of sulfur (Ref. 16. of the list of publications):* We have reviewed the recent developments on the reactivity and structure of small oxoacids of sulfur, such as sulfenic and sulfoxylic acids. The major source of the latter compound is the alkaline decomposition of thiourea dioxide, thus comparing the kinetic behavior of the oxidation reactions of small oxoacids may reveal such an important difference that may shed light on the aging process of thiourea dioxide in aqueous solutions. In this review we thoroughly overviewed the mechanism of sulfide oxidation where small oxoacids of sulfur may appear as key intermediates. Later, it provided a substantial impact of reporting the kinetic model of the sulfide-chlorine dioxide reaction.
5. *Revising the erroneous kinetic model of the thiourea dioxide-iodate reaction (Ref. 17. of the list of publications):* We have revised the kinetic model of the thiourea dioxide-iodate reaction published more than 25 years ago by Mambo and Simoyi. Their proposed model suffered from serious shortcomings like violating the principle of detailed balancing, and at the same time it contains two improbable reactions between the sluggish triiodide ion and thiourea dioxide (TDO), as well as between thiourea trioxide and iodine. The latter one was explicitly ruled out to occur by Makarov et al (J. Phys. Chem. A, 1998, 102,6786). Furthermore, we have shown that aging of thiourea dioxide solution has a great impact on the kinetic traces, the longer the age of the thiourea dioxide solution is, the shorter the induction period to be observed. We have elucidated a 16-step kinetic model including the kinetic model of the TDO-iodine reaction as well as the well-known Dushman reaction. The proposed kinetic model was able to describe the main characteristics of the title system, quantitatively.
6. *Elucidation of the kinetic model of the thiourea dioxide-bromate reaction (Ref. 18. of the list of publication):* We have shown that the thiourea dioxide-bromate reaction may be classified as a substrate-depletive clock reaction, because the TDO-bromine reaction is rapid. It is also unambiguously demonstrated that bromide ion acts as an autocatalyst, and the concentration of the buffer components seriously affects the Landolt time to be measured. In contrast to all the other oxidation reactions of TDO, however, we found that unless the age of TDO solution is no longer than 3 days, the age does not have any effect on the Landolt time and on the shape of the kinetic traces. This fact may easily be explained by the rapid TDO-bromine reaction leaving no further room to shorten the induction period by the slow rearrangement of thiourea dioxide to yield a more reactive species. As shown previously TDO-iodine reaction is significantly slower than the TDO-bromine one, and even inhibited by the product iodide ion as well as by H^+. Since the more reactive form of TDO reacts very rapidly with iodine eventually it results in shorten Landolt time due to increasing autocatalyst

concentration (iodide ion). In addition to that a general formula on the concentration dependence of the Landolt was also derived.

7. *Elucidation of the kinetic model of the thiourea dioxide-periodate reaction (Ref. 19. of the list of publication):* We have established the kinetic model of thiourea dioxide-periodate reaction, a system that has not yet been studied. According to the characteristics of the absorbance-time profiles measured in this system the thiourea dioixde-periodate reaction may be classified as an autocatalysis-driven clock reaction. The kinetic model consisting of 21 reactions was systematically built up from the mechanism of the thiourea dioxide-iodine and thiourea dioxide iodate reactions supplemented by the necessary reactions of periodate. As it was shown the Landolt time measured is affected by the age of the TDO solution, like in the case of the majority of the oxidation reactions of TDO. Thus, the model must also include a faster reaction of periodate with the aged TDO. It interesting to mention that the rate coefficients of the subsystems were directly adopted in this study meaning that the overall model is also capable of sound description of the kinetic traces measured independently in the TDO-iodine and the TDO-iodate systems.

Summary of the results achieved by publications group no. 2.:

8. *Main result of the simplified kinetic model of the arsenous acid-iodate reaction (Ref. 2. of the list of publications):* A simplified kinetic model of the reaction between iodate and arsenous acid has been reported. It was a general belief that no direct reaction takes place between arsenous acid and iodate and the title reaction is rather initiated by small iodide impurities of the iodate stock solution. Our recent results, however, provide a direct evidence that indeed slow direct reaction must exist. Of course, this publication was quite important to show that even though trace amount of iodide impurity may exist in iodate solution, the direct reductant-iodate reaction (like in the case of thiourea dioxide) must also be considered when quantitative description of the concentration-time profiles on the given reaction is performed.
9. *Result of the chlorite-periodate reaction (Ref. 3. of the list of publications):* The kinetics and mechanism of the title reaction has been studied for the first time. It was found that the stoichiometry of the reaction may be described by a linear combination of two limiting stoichiometries. The kinetic traces can conveniently be described by a four-step kinetic model including the formation of an asymmetric short-lived intermediate $OClOIO_3$ and a direct oxygen-transfer process in between the reactants. This information contributed to the kinetic feature of periodate in its oxidation reactions.
10. *Result on the compatible mechanism of the arsenous acid-iodate reaction (Ref. 4. of the list of publications):* We have reported a comprehensive kinetic model to describe simultaneously the kinetic behavior of the iodate-arsenous acid system, the Dushman reaction (iodide-iodate system) and the Roebuck reaction (iodine-arsenous acid reaction). Because the iodate-iodide reaction is a central part of the kinetic model of all the systems where iodate or periodate is the oxidizing agent, it was important to establish this mechanism under the experimental circumstances when thiourea dioxide was oxidized by these species.

11. *Results on the equilibrium speciation of periodate ion (Ref. 10. of the list of publications):* The equilibrium speciation of aqueous periodate solution has been clarified. It is a general belief that in aqueous solution there is an equilibrium between the ortho and the meta forms of periodate ion having an equilibrium constant of approximately 29. It would, however, indicate that both forms may be found in appreciable amount. Our comprehensive Raman, UV-vis and gravimetric studies gave no clear evidence for neither this equilibrium process nor the frequently invoked dimerization. All the experiments can be readily be explained by the successive protonation and deprotonation processes of ortho-periodate ion, thus the meta form of periodate is not likely to play any crucial role in the oxidation reaction of periodate ion. This result has been used to propose an adequate kinetic model in the thiourea dioxide-periodate reaction.
12. *Proposing a new, more stable system to study convection-induced fingering fronts (Ref. 11. of the list of publications):* It was also shown that the trithionate-chlorite reaction in a Hele-Shaw cell exhibits fingering patterns. The main advantage of the present system over the well-studied tetrathionate-chlorite one is that trithionate is much more stable in alkaline condition than tetrathionate thus no side reaction occurs disturbing the pattern formation. This result was also important to understand the kinetic role a sulfur-containing species by chlorite ion as an oxidant. Based on this study the experiments to unravel the kinetics and mechanism of the trithionate-chlorite reaction were also performed, although the construction of its kinetic model is still under evaluation. The measured kinetic curves obtained are much more complex than those of found in the corresponding tetrathionate-chlorite reaction. Another kinetic model is also under construction that intends to describe the nonlinear behavior of the thiourea dioxide-chlorite reaction.
13. *Kinetics and mechanism of the autocatalytic oxidation of trithionate ion by iodate (Ref. 12. of the list of publications):* The trithionate-iodate reaction was found to be subject of autocatalysis and the kinetic behavior of the system resembles quite well on the thiourea-dioxide-iodate reaction. It was also found to be classified as an autocatalysis-driven clock reaction. A simple Landolt-type kinetic model is proposed to describe the measured concentration-time series.
14. *Discovery of a new system exhibiting crazy clock behavior I (Ref. 14. of the list of publications):* We have found that beside the arsenous acid-iodate reaction the arsenous acid periodate reaction also exhibits crazy-clock behavior. Although the previous reaction is a subsystem of the reaction studied here, we have shown both experimentally and numerically that the stochastic feature is mainly originated from the imperfect mixing process. Furthermore, we have provided an evidence that a less efficient may either accelerate or decelerate a nonlinear autocatalytic reaction at a macroscopic level. This behavior differs from the one observed in a microfluidic channel, where the imperfect mixing just accelerated the nonlinear reaction.
15. *Results in the crazy clock behavior in the Briggs-Rauscher reaction (Ref. 13. of the list of publications):* A new system involving iodate (Briggs-Rauscher) has been first proven to exhibit crazy-clock-behavior. We have shown that the time lag necessary for transition from low iodide and iodine concentration state (state I) to high iodide and

iodine concentration state (state II) after the system leaves the well-reproducible oscillatory phase may vary significantly. We have also proven experimentally that surprisingly better stirring conditions does not make this time lag reproducible, but it simply does not allow this transition to occur. The proposed mechanism, additional explanation and proposal for this irreproducibility of state I state II transition have been presented.

16. *Kinetics and mechanism of the sulfide-chlorine dioxide reaction (Ref. 15 of the list of publications):* We have elucidated the kinetics and mechanism of the two-stage oxidation of sulfide by chlorine dioxide. The first stage proceeds very rapidly and leads to the parallel formation of polysulfide and sulfate. The second stage, however, can readily be measured by conventional UV-vis spectroscopy. The surprising feature of the second stage is that the measured kinetic traces can only be described adequately by the direct oxidation of tetrasulfide by chlorine dioxide and the tetrasulfide-catalyzed decomposition of chlorine dioxide, simultaneously. These results may be useful in understanding the kinetic feature of small sulfur-containing oxoacids in several oxidation reactions, where sulfoxylic acid and its subsequent reactions are involved.
17. *Elucidating the kinetics and mechanism of the methionine-iodine reaction (Ref. 20 of the list of publications):* We have revised the kinetics and mechanism of the methionine-iodine reaction published by Chikwana et al. (Can. J. Chem, 2009, 87, 689-697). It was clearly shown that the system is autoinhibitory with respect to iodide ion, and this autoinhibition appears quite prominently when initially iodide ion is added (in the mM concentration range) to the reactants. We have also proved that instead of hypoiodous acid iodine is the kinetically active species in the system since hydrogen ion has only a slightly inhibitory effect. It also means that the methionine-iodate reaction deserves to be reinvestigated as well because the mechanism and the rate coefficients of the above cited paper contain serious problems. It looks to be reasonable that the oxidation reactions of methionine (being one of the sulfur-containing amino acid) by strong oxidizing agents (like iodate, periodate and bromate) in acidic conditions are closely related to the oxidation reactions of thiourea dioxide, thus it may also contribute to the better understanding of the aging problem of thiourea dioxide.
18. *Results on the law of mass action type kinetic models in interpreting autocatalysis and hypercycles (Ref. 22 of the list of publications):* The core mechanisms of the autocatalytic reactions studied in this OTKA project led us to extend the scope of this project and to find biological and especially evolutional relevance. It is generally accepted that autocatalytic systems might have play a crucial role in controlling the origin and spreading of Life on our entire planet. We have shown that the simplest autocatalytic loop involving reactions capable of self-replication and obeying law of mass action kinetics, the concentration growth of the autocatalyst may have to be characterized by parametrization of the direct and autocatalytic pathways rather than by simple the kinetic orders of the autocatalyst. We have also shown that in case of the simplest hypercycle (involving two autocatalytic reactions and cross-catalyzed by each other autocatalyst the selection of the self-replicating species depends on the

kinetic and flow parameters mimicking that the most adaptive loop of the hypercycle (but not the most efficient autocatalytic path!) eventually finds its wining way in the evolutionary race.

19. *Results on the correct classification and identification of autocatalysis (Ref. 23. of the list of publications):* It is generally accepted that autocatalysis is a kinetic phenomenon, where a product of a reacting system functions as a catalyst. Consequently, the reaction proceeds faster upon adding the corresponding product to the unreacted mixture of reactants providing an unequivocal possibility how a system may be identified either experimentally or theoretically as an autocatalysis. Once this is approved, it often results in sigmoidal concentration--time profiles, though it is neither necessary nor sufficient prerequisite because appropriate mechanistic and parametric conditions must be met to give rise the appearance of this kinetic feature. Several mass action type kinetic models producing sigmoidal concentration--time profiles are systematically analyzed to clarify their correct characterization and classification. This procedure has led us to refine the definitions of autocatalysis and autocatalyst. A kinetic phenomenon where a product of the overall chemical event serves as a catalyst for at least one of its subsystems or for the whole system itself is called autocatalysis. This definition makes it clear that in the case of autocatalysis, the concentration of autocatalyst necessarily increases during the course of any real overall chemical or biochemical reactions. The way how it is achieved thereby provides a suitable tool to classify autocatalytic processes by their elucidated and fine mechanistic details.

Summary of the results achieved by publications group no. 3.:

20. *Results on the reactions of halogenates with hydrogen peroxide (Ref. 8. of the list of publications):* We have shown that the halogenate-hydrogen peroxide reactions produce radical intermediates when chlorate and iodate used as reactants. We clarified by electron paramagnetic spin trapping technique that iodine-dioxide and hydroxyl radical appear when iodate and chlorate are used, respectively. Furthermore, it is also shown that in the case of chlorate-hydrogen peroxide reaction the source of the OH radical is the homolytic cleavage of chloric acid. In contrast to this the bromate-hydrogen peroxide reaction does not produce any EPR signal suggesting that the role of radical species in this reaction is not so relevant compared to the other halogenate reaction.
21. *Results on the photoactivity of periodate ion (Ref. 21 of the list of publications):* We have also show that periodate is a photoactive species meaning that its reactions may be followed by special circumspection when studied by spectrophotometry, especially in case of diode-array spectrophotometers. Quantitative simultaneous evaluation of kinetic curves in case of photoinduced reaction may require determining precisely the amount of light reaching the irradiated sample which of course may be different in the other compartments of the given instrument as well. It is therefore also important to track the technical factors influencing the emission spectrum of the light and their suitable utilization my provide the amount of photon reaching the sample. To illustrate its properness sodium periodate solution was used. We have shown that decomposition of periodate is not affected by the measured absorption signal meaning

that the quantitative evaluation of the kinetic curves may be performed by the eq. 1 of the manuscript, which is quite similar to the equation proposed by Lente and Fábián (Pure Appl. Chem., 2010, 82, 1957). The slight modification, namely the lack of direct involvement of the measured absorbance that may be replaced by the absorption signal given by the Lambert-Beer law (if it is valid) makes the simultaneous evaluation more tractable.

Summary of the results achieved by publications group no. 4.:

22. *Results on the oxidation of aquacobalamin and cob(II)alamin by chlorite and chlorine dioxide (Ref. 7. of the list of publications):* It was found that chlorite ion does not react with H_2O-Cbl(III), but oxidizes Cbl(II) to H_2O-Cbl(III) as a major product and corrin-modified species as minor products. The proposed mechanism of chlorite reduction involves formation of hypochlorous acid that modifies the corrin ringv during the course of reaction with Cbl(II). H_2O-Cbl(III) undergoes relatively slow destruction by chlorine dioxide via transient formation of oxygenated species, whereas reaction between Cbl(II) and chlorine dioxide proceeds extremely rapidly and leads to the oxidation of the cobalt center.
23. *Results on the stability of gamma-valerolactone in acidic, basic and neutral conditions (Ref. 9. of the list of publications):* Dry gamma-valerolactone is stable for several weeks, however, at higher temperature it reacts with in a ring-opening reaction to produce 4-hydroxyvaleric acid and reaches the equilibrium within a few days. In the presence of acids and bases the ring-opening process is significantly fastened but the reversible ring opening of gamma-valerolactone in the presence of hydrochloric acid and sodium hydroxide has no effect on the stability of the chiral center.

Conclusion

During the five-year project 22 scientific papers and one book are published by the help of OTKA project. Among them 6, 11 and 5 results appeared in D1, Q1 and Q2 journals, respectively. The sum of the impact factor was found to be 72.57.

List of publications supported by the OTKA project K116591:

1. Y. Hu, A. K. Horváth, S. Duan, Gy. Csekő, S. V. Makarov, Q. Gao: *Mechanism Involving Hydrogen Sulfite Ions, Chlorite Ions and Hypochlorous Acid as Key Intermediates of the Autocatalytic Chlorine Dioxide-Thiourea Dioxide Reaction.* Eur. J. Inorg. Chem., 2015, 12(30), 5011-5020. Q1, IF=2.686.
2. Gy. Csekő, L. Valkai, A. K. Horváth: *A Simple Kinetic Model for Description of the Iodate-Arsenous Acid Reaction: Experimental Evidence of the Direct Reaction*. J. Phys. Chem. A, 2015, 119(45), 11053-11058. Q1, IF=2.883
3. N. Baranyi, Gy. Csekő, L. Valkai, L. Xu, A. K. Horváth: *Kinetics and Mechanism of the Chlorite-Periodate System: Formation of a Short-Lived Key Intermediate $OClOIO_3$ and Its Subsequent Reactions.* Inorg. Chem., 2016, 55(5), 2436-2440. D1/Q1, IF=4.857
4. L. Valkai and A. K. Horváth: *Compatible Mechanism for a Simultaneous Description of the Roebuck, Dushman, and Iodate-Arsenous Acid Reactions in an Acidic Medium.* Inorg. Chem., 2016, 55(4), 1595-1603. D1/Q1, IF=4.857

5. S. V. Makarov, A. K. Horváth, R. Silaghi-Dumitrescu, Q. Gao: *Sodium Dithionite, Rongalite and Thiourea Oxides: Chemistry and Applications.* World Scientific Publishing Co. Pte. Ltd., Singapore, 2016, 244 pages. ISBN: 9781786340955.
6. L. Xu, L. Valkai, A. A. Kuznetsova, S. V. Makarov, A. K. Horváth: *Kinetics and Mechanism of Thiourea Dioxide by Iodine in a Slightly Acidic Medium.* Inorg. Chem., 2017, 56(8), 4679-4687. D1/Q1, IF=4.700
7. I. A. Dereven'kov, N. I. Shpagilev, L. Valkai, D. S. Salnikov, A. K. Horváth, S. V. Makarov: *Reactions of Aquacobalamin and Cob(II)alamin with Chlorite and Chlorine Dioxide.* J. Biol. Inorg. Chem., 2017, 22(4), 453-459. Q1, IF=2.952
8. M. C. Pagnacco, M. D. Mojovic, A. D. Popovic-Bijelic, A. K. Horváth: *Investigation of the Halogenate-Hydrogen Peroxide Reactions using the Electron Paramagnetic Resonance Spin Trapping Technique.* J. Phys. Chem. A, 2017, 121(17), 3207-3212. Q1, IF=2.836
9. C. Y. Y. Wong, A. W-T. Choi, M. Lui, B. Fridrich, A. K. Horváth, L. T. Mika, I. T. Horváth*: Stability of Gamma-Valerolactone under Neutral, Acidic, and Basic Conditions.* Struc. Chem. 2017, 28(2), 423-429. Q2, IF=2.018
10. L. Valkai, G. Peintler, A. K. Horváth: *Clarifying the Equilibrium Speciation of Periodate Ions in Aqueous Medium.* Inorg. Chem., 2017, 56(18), 11417-11425. D1/Q1, IF=4.700
11. Y. Liu, W. Zhou, T. Zheng, Y. Zhao, Q. Gao, C. W. Pan, A. K. Horváth: *Convection-Induced Fingering Fronts in the Chlorite-Trithionate Reaction.* J. Phys. Chem. A, 2016, 120(16), 2514-2520. Q1, IF=2.847
12. Gy. Csekő, C. W. Pan, Q. Gao, C. Ji, A. K. Horváth: *Autocatalytic Oxidation of Trithionate by Iodate in a Strongly Acidic Medium.* J. Phys. Chem. A, 2017, 121(43), 8189-8196. Q1, IF=2.836
13. M. C. Pagnacco, J. P. Maksimovic, N. I. Potkonjak, B. D. Bozic, A. K. Horváth: *Transition from Low to High Iodide and Iodine Concentration States in the Briggs-Rauscher Reaction: Evidence on Crazy Clock Behavior.* J. Phys. Chem. A, 2018, 122(2), 482-491. Q1, IF=2.641
14. L. Valkai, A. K. Horváth: *Imperfect Mixing as a Dominant Factor Leading to Stochastic Behavior: A New System Exhibiting Crazy Clock Behavior.* Phys. Chem. Chem. Phys., 2018, 20(20), 14145-14154. D1/Q1, IF=3.567.
15. Gy. Csekő, C. W. Pan, Q. Gao, A. K. Horváth: *Kinetics of the Two-Stage Oxidation od Sulfide by Chlorine Dioxide.* Inorg. Chem., 2018, 57(16), 10189-10198. D1/Q1, IF=4.850
16. S. V. Makarov, A. K. Horváth, A. S. Makarova: *Reactivity of Small Oxoacids of Sulfur. Molecules*, 2019, 24(15), 2768. Q1, IF=3.060
17. Gy. Csekő, Q. Gao, L. Xu, A. K. Horváth: *Autocatalysis-Driven Clock Reaction III: Clarifying the Kinetics and Mechanism of the Thiourea Dioxide-Iodate Reaction in an Acidic Medium.* J. Phys. Chem. A, 2019, 123(9), 1740-1748. Q2, IF=2.600
18. Gy. Csekő, Q. Gao, A. Takács, A. K. Horváth: *Exact Concentration Dependence of the Landolt Time in the Thiourea Dioxide-Bromate Substrate-Depletive Clock Reaction.* J. Phys. Chem. A, 2019, 123(18), 3959-3968. Q2, IF=2.600
19. Gy. Csekő, Q. Gao, C. W. Pan, L. Xu, A. K. Horváth: *On the Kinetics and Mechanism of the Thiourea Dioxide-Periodate Autocatalysis-Driven Iodine Clock Reaction.* J. Phys. Chem. A, 2019, 123(35), 7582-7589. Q2, IF=2.600
20. L. Xu, Gy. Csekő, A. K. Horváth: *Autoinhibition by Iodide Ion in the Methionine-Iodine Reaction.* J. Phys. Chem. A, 2020, 124(29), 6029-6038. Q2, IF=2.600
21. L. Valkai, A. Marton, A. K. Horváth: *Some Physical Parameters Influencing the Comprehensive Evaluation of Kinetic Data in Photochemical Reactions and Its Application in the Periodate-Chemistry.* J. Photochem. PhotoBiol. A, 2020, 388, 112021. Q1, IF=3.306

22. A. K. Horváth: *Law of Mass Action Type Chemical Mechanisms for Modeling Autocatalysis and Hypercycles: Their Role in the Evolutionary Race.* ChemPhysChem, 2020, 21(15), 1703-1710, Q1, IF=3.144
23. A. K. Horváth: *Correct Classification and Identification of Autocatalysis.* Phys. Chem. Chem. Phys., 2021, accepted for publication, doi: 10.1039/D1CP00224D, Q1, IF=3.430.