# UNIVERSITY OF PÉCS
## Doctoral School of Chemistry

Ph.D. Thesis

# Crazy-Clock Behavior and deterministic kinetic description of the Iodate–Arsenous Acid reaction

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supervisor:
**Dr. Horváth Attila**
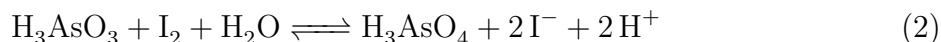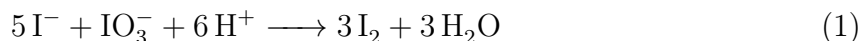*associate professor*

Pécs

2018

**Principal definitions of the field of dissertation**

**clock reaction (n.)**  *collective noun.*   A class of chemical reaction systems. In case of these reactions, the change of concentration can be detected after a well-defined time lag (called Landolt time). This pehnomenon is originated from either stochiometric or kinetic constraint(s).

**crazy-clock reaction (n.)**  *collective noun.*   A special type of clock reactions, where the measured Landolt time is not identical in case of individual experiments performed under the same experimental conditions. It consequently means that the system can be characterized by a Landolt time distribution curve.

## 1. Introduction

The iodate–arsenous acid reaction is a suitable candidate to demonstrate various kinds of nonlinear dynamic phenomena. The kinetic description of the system is usually implemented by a two-step kinetic model, which consists of the Dushman (iodate–iodide) and Roebuck (iodine–arsenous acid) reactions. Both reactions mentioned above were named by a scientist reporting first the most important chemical characteristics of the given system. The stoichiometry of these are (1) and (2), respectively.

$$5\,\mathrm{I^-} + \mathrm{IO_3^-} + 6\,\mathrm{H^+} \longrightarrow 3\,\mathrm{I_2} + 3\,\mathrm{H_2O} \tag{1}$$

$$\mathrm{H_3AsO_3} + \mathrm{I_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3AsO_4} + 2\,\mathrm{I^-} + 2\,\mathrm{H^+} \tag{2}$$

It is easily seen if reactions (1) and (2) are alone considered to describe the kinetic behavior of the iodate–arsenous acid system then the reaction cannot take place without iodide or iodine impurity. It is generally accepted that iodate always contains some iodide impurity originated from the manufacturing process, thus there is no need to take the direct attack of iodate on arsenous acid into account.

The rate law of the Dushman reaction is the following:

$$R_\alpha = -\frac{\mathrm{d[IO_3^-]}}{\mathrm{d}t} = (k_1 + k_2[\mathrm{I^-}])[\mathrm{I^-}][\mathrm{IO_3^-}][\mathrm{H^+}]^2,$$

where $k_1 = 4.5 \cdot 10^3$ M$^{-3}$ s$^{-1}$ and $k_2 = 10^8$ M$^{-4}$ s$^{-1}$. While in case of the Roebuck reaction the rate law is

$$R_\beta = -\frac{\mathrm{d[I_2]}}{\mathrm{d}t} = \frac{k_3[\mathrm{I_2}][\mathrm{H_3AsO_3}]}{[\mathrm{I^-}][\mathrm{H^+}]},$$

where $k_3 = 3.2 \cdot 10^{-2}$ M s$^{-1}$.

Despite the fact that enormous number of publications can be found on the system, the crazy-clock behavior (*see* page 1) was not noticed.

## 2. Experimental section

### 2.1. Chemicals

All of the chemicals used were of the highest purity commercially available and used without further purification. Potassium and sodium iodate, arsenic trioxide, sodium arsenite, anhydrous sodium sulfate, iodine, sodium iodide, sodium hydrogen carbonate, phenophtaleine, and methyl red was produced by Reanal. The ortho-phosphoric acid, sodium hydroxide, sodium perchlorate monohydrate, and absolute ethanol was purchased from Merck. Sodium monohydrogen phosphate monohydrate, sodium dihydrogen phosphate dodecahydrate, and sodium perchlorate monohydrate was manufactured by the Sigma-Aldrich company. The perchloric acid was produced by Germed.

### 2.2. Equipments and instruments

Volume measurement was carried out by an Eppendorf Reference automatic pipette with adjustable volume up to 1.000 mL, a volumetric pipette with the volume of 10.00 mL, or 5.00, or 10.00 mL graduated pipettes, or by a 25.00 mL Witeg burette equipped with solid glass plug.

The UV-Vis spectra were recorded by an AnalytikJena SPECORD S600 diode array spectrophotometer. The sample compartment was thermostatted during all of the measurements by circulating $(25.0\pm0.1)°C$ water. The samples were thoroughly stirred during the course of all the experiments. The photometric measurements were carried out in a Hellma quartz cuvet, made from Suprasil, having a pathlength of 1.000 cm, sealed air-tight by a Teflon stopper. The cuvet contained a plastic coated micro stirrer bar to homogenize the solution. The only exception was the serial of experiments when a more robust cylindrical stirrer was applied in a wide-mouth quartz cuvet during the investigation of the crazy-clock behavior of the reaction.

Reactions, faster than three minutes were followed by an Applied Photophysics SX20 stopped-flow instrument. All driving processes were carried out with a pressure of 4 bar. The lamp housing was purged by a slow, constant nitrogen flow to avoid the production of ozone. The Sample Handling Unit (including drive syringes) and the optical cell were thermostatted by circulating $(25.0 \pm 0.1)°C$ water.

Potentiometric titrations were carried out by a Boeco Germany pH meter attached to a combined pH-electrode filled with an appropriate liquid electrolyte.

Stirring of the solutions was carried out by IKA and Dragonlab stirring apparatus with digital display and controlled stirring speed.

## 2.3. Calculation methods and applied program packages

The kinetics of the reaction was followed by absorbance measurement at the wavelength of 468 nm, the isosbestic point of the iodine–triiodide system, where the value of molar absorbance is 747 $M^{-1}$ $cm^{-1}$.

For the simulation and the parameter estimation, the version 5.99c of ChemMech program package was used with an orthogonal fitting procedure. By this way the uncertainty of our experimental data can be handled both of the applied axes. The necessity of this handling process was originated from the naked-eye detection of the Landolt times, which caused higher uncertainty in the time scale than the instrumental measurements.

DVODE (Double precision Variable-coefficient Ordinary Differential Equation solver) program package, Spline Calculus program of Peintler Gábor, the software of each instruments, the wxMaxima, Graphics Layout Engine (GLE), GhostScript, Ghost View, LaTeX, TeXstudio, TeXLive softwares, and numerous in-house programs were also applied.

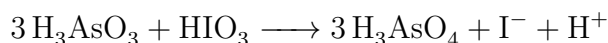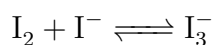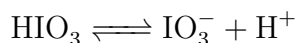## 3. Novel scientific results

### 3.1. Crazy-clock behavior of the iodate–arsenous acid reaction
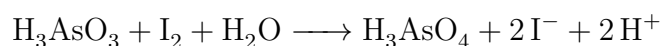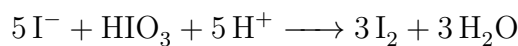
1. The crazy-clock behavior of the iodate–arsenous acid reaction was experimentally proven in 1:1 phosphoric acid–dihydrogen phosphate buffer in case of iodate excess.
2. It was experimentally proven, that a more effective mixing process results longer Landolt times, while the width of the distribution curve shows no systematic change. The distribution curves are mainly determined by initial inhomogeneities existing in the time period from initiation up to the homogenization* of the solution.

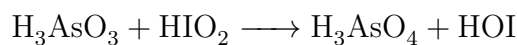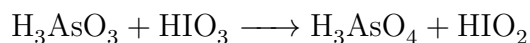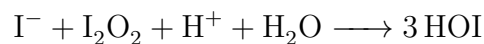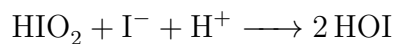### 3.2. Deterministic kinetic description of the iodate–arsenous acid reaction

3. The crazy-clock behavior of the iodate–arsenous acid system can be ceased at low pHs in iodate excess by applying stopped-flow apparatus that provides far the most efficient mixing process at initiation available in our laboratory.
4. A five-step kinetic model was established, that along with its simplicity, provides an adequate description of the most relevant characteristics of the system. It consists of two rapidly established preequilibria, a direct reaction between the iodate and arsenous acid, the Roebuck and Dushman reactions ((1) and (2)).

$$HIO_3 \rightleftharpoons IO_3^- + H^+$$

$$I_2 + I^- \rightleftharpoons I_3^-$$

$$3\,H_3AsO_3 + HIO_3 \longrightarrow 3\,H_3AsO_4 + I^- + H^+$$

*Inhomogeneities and poorly stirred parts exist in the solution during the whole time of the reaction.

$$5\,\text{I}^- + \text{HIO}_3 + 5\,\text{H}^+ \longrightarrow 3\,\text{I}_2 + 3\,\text{H}_2\text{O}$$

$$\text{H}_3\text{AsO}_3 + \text{I}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{AsO}_4 + 2\,\text{I}^- + 2\,\text{H}^+$$

5. It was proven that the appropriate kinetic description of the kinetic curves measured in case of the iodate–arsenous acid reaction can be done without the assumption of any iodide impurity in the stock solutions.

6. The description of the Roebuck (iodine–arsenous acid) reaction was performed by a six-step kinetic model providing a sound explanation of the iodide and proton inhibition of the system based on simple chemical considerations.

7. After determination of the medium dependent chemical kinetic parameters of the Dushman (iodate–iodide) reaction, and implementing the kinetic model of the Roebuck reaction, a thirteen-step kinetic model was established to describe the name reaction:

$$\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$$

$$\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$$

$$\text{I}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOI} + \text{I}^- + \text{H}^+$$

$$\text{H}_2\text{OI}^+ \rightleftharpoons \text{HOI} + \text{H}^+$$

$$\text{H}_3\text{AsO}_3 + \text{HOI} \longrightarrow \text{H}_3\text{AsO}_4 + \text{I}^- + \text{H}^+$$

$$\text{H}_3\text{AsO}_3 + \text{H}_2\text{OI}^+ \longrightarrow \text{H}_3\text{AsO}_4 + \text{I}^- + 2\,\text{H}^+$$

$$\text{H}_3\text{AsO}_3 + \text{I}_2 \rightleftharpoons \text{H}_2\text{AsO}_3\text{I} + \text{I}^- + \text{H}^+$$

$$\text{H}_3\text{AsO}_3\text{I} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_4 + \text{H}^+ + \text{I}^-$$

$$\text{HIO}_3 \rightleftharpoons \text{IO}_3^- + \text{H}^+$$

$$\text{I}^- + \text{HIO}_3 + \text{H}^+ \rightleftharpoons \text{I}_2\text{O}_2 + \text{H}_2\text{O}$$

$$\text{I}^- + \text{I}_2\text{O}_2 + \text{H}^+ \longrightarrow \text{I}_2 + \text{HIO}_2$$

$$\text{I}_2\text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{HIO}_2 + \text{HOI}$$

$$\text{HIO}_2 + \text{I}^- + \text{H}^+ \longrightarrow 2\,\text{HOI}$$

$$\text{I}^- + \text{I}_2\text{O}_2 + \text{H}^+ + \text{H}_2\text{O} \longrightarrow 3\,\text{HOI}$$

$$\text{H}_3\text{AsO}_3 + \text{HIO}_3 \longrightarrow \text{H}_3\text{AsO}_4 + \text{HIO}_2$$

$$\text{H}_3\text{AsO}_3 + \text{HIO}_2 \longrightarrow \text{H}_3\text{AsO}_4 + \text{HOI}$$
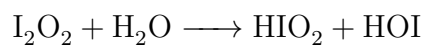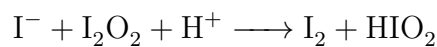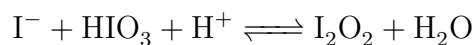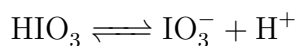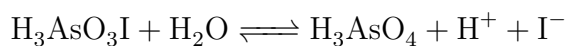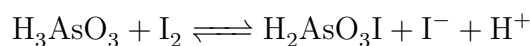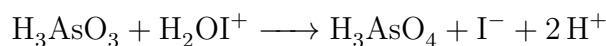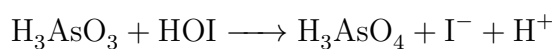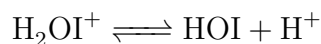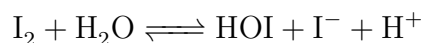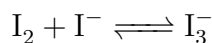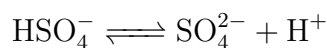
## 4. List of Publications

### 4.1. Papers related to the Theses published in refereed journals

- Valkai L., Horváth A. K., Compatible mechanism for a simultaneous Description of the Roebuck, Dushman, and Iodate–Arsenous Acid Reactions in an Acidic Medium. *Inorganic Chemistry*
  55, (4) **2016**, 1595-1603. IF: 4.86
- Valkai L., Csekő, Gy., Horváth A. K., Initial Inhomogeneity-induced Crazy-clock Behavior in the Iodate–Arsenous Acid Reaction in a Buffered Medium Under Stirred Batch Conditions. *Physical Chemistry Chemical Physics* 17, **2015**, 22187-22194. IF: 4.45
- Csekő Gy., Valkai L., Horváth A. K., A Simple Kinetic Model for Description of the Iodate–Arsenous Acid Reaction: Experimental Evidence of the Direct Reaction. *The Journal of Physical Chemistry A* 119, (45) **2015**, 11053-11058. IF: 2.87

### 4.2. Other papers published in refereed journals

- Valkai L., Horváth A. K., Imperfect Mixing as a Dominant Factor Leading to Stochastic Behavior: A New System Exhibiting Crazy Clock Behavior , *Physical Chemistry Chemical Physics* 20, **2018**, 14145-14154. IF: 4.12
- Valkai L., Peintler G., Horváth A. K., Clarifying the Equilibrium Speciation of Periodate Ions in Aqueous Medium, *Inorganic Chemistry* 56, (18) **2017**, 11417-11425. IF: 4.86
- Xu L., Valkai L., Kuznetsova A. A., Makarov S. V., Horváth A. K., Kinetics and Mechanism of the Oxidation of Thiourea Dioxide by Iodine in a Slightly Acidic Medium, *Inorganic Chemistry* 56, (8) **2017**, 4679-4687. IF: 4.86
- Dereven'kov I. A., Shpagilev N. I., Valkai L., Salnikov D. S., Horváth A. K., Makarov S. V., Reactions of aquacobalamin and cob(II)alamin with chlorite and chlorine dioxide, *Journal of Biological Inorganic Chemistry* 22, (4) **2017**, 453-459. IF: 2.89
- Baranyi N., Csekő Gy., Valkai L., Xu L., Horváth A. K., Kinetics and Mechanism of the Chlorite–Periodate System: Formation of a Short-Lived Key Intermediate $OClOIO_3$ and Its Subsequent Reactions, *Inorganic Chemistry* 55, (5) **2016**, 2436-2440. IF: 4.86
- Csankó K., Kozma G., Valkai L., Kukovecz Á., Kónya Z., Sipos P., Pálinko I., Self-assembling of 2,3-phenyl/thienyl-substituted acrylic acids over polycrystalline gold, *Journal of Molecular Structure* 1044, Supp. C **2013**, 32-38. IF: 1.40

### 4.3. Conference lectures

– Valkai L., Horváth A. K., Bolondórareakciók kinetikai leírása, Új Nemzeti Kiválósági Program Intézményi Konferencia, Pécs, 2018. V. 23.

– Valkai L., Horváth A. K., Meglepő jelenségek az arzénessav–perjodát reakcióban, Reakciókinetikai és Fotokémiai Munkabizottsági Ülés, 2017. XI. 2.

– Valkai L., Horváth A. K., A perjodát ionok oldategyensúlyai, XL. Kémiai Előadói Napok, (összefoglaló: ISBN 978-963-9970-83-0), Szeged, 2017. X. 16-18.

– Valkai L., Horváth A. K., A perjodát–arzénessav rendszer kinetikai leírása, PTE Grastyán Endre Szakkollégiumának és a PTE TTK Szentágothai János Szakkollégiumának közös Ph.D. és TDK hallgatói konferencia, 2016. X. 27-28.

– Valkai L., Horváth A. K., A perjodát–arzénessav rendszer kinetikai leírása, XXXIX. Kémiai Előadói Napok, (összefoglaló: ISBN 978-963-9970-73-1), Szeged, 2016. X. 17-19.

– Valkai L., Csekő Gy., Horváth A. K., Sztochasztikus kinetika a jodát–arzénessav rendszerben, Fizikai-kémiai Munkabizottsági Ülés, 2015. XI. 20., Pécs

– Valkai L., Csekő Gy., Horváth A. K., A Roebuck, a Dushman és az arzénessav–jodát reakciók szimultán kinetikai vizsgálata, Reakciókinetikai és Fotokémiai Munkabizottsági Ülés, 2015. XI. 5.

– Valkai L., Peintler G., Protonálódási mellékreakciók hatása kémiai hullámok terjedésére, XXXVI.Kémiai Előadói Napok, (összefoglaló: ISBN:978-963-315-145-7), Szeged, 2013. X. 28-30.

### 4.4. Poster presentations

– Valkai L., Marton A., Koshman Y., Horváth A. K., Crazy-clock Behavior in the Periodate–Arsenous Acid Reaction, 1st International Conference on Reaction Kinetics, Mechanism and Catalysis,Budapest, 2018. VI. 6-9.

– Valkai L., Horváth A. K., Stochastic kinetics or imperfect mixing driven irreproducibility?, XXXVII Dynamics Days / Dynamics Days Europe International Conference, Szeged, 2017. VI. 5-9.

– Csankó K., Kozma G., Valkai L., Kukovecz Á., Kónya Z., Sipos P., Pálinkó I., Supramolecular organisation of 2/3-phenyl/thienyl-substituted acrylic acids over polycrystalline Au surface, International Symposium on Macrocyclic and Supramolecular Chemistry, 2012., New Zealand, Dunedin, I. 29 - II. 2.