

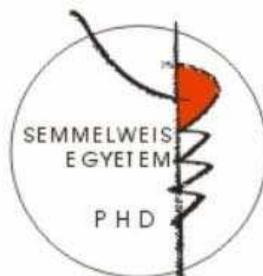
# **Studies on the dynamical behavior and the mechanism of new oscillatory chemical systems**

PhD Thesis

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## Summary

In my thesis the results of my research work on the field of nonlinear chemical dynamics are summarized. These results are related to three areas of nonlinear chemical dynamics: my aim was to study temporal and spatial oscillations observed in chemical systems, to develop mechanisms and to model known oscillators, and to produce new chemical oscillating systems based on design.

For studying the oscillations and the pattern formation the bromate – dual substrate (hypophosphite and acetone) – dual catalyst (Mn(II) and Ru(II)) system have been used. Our goal was to develop a mechanism which explains the experimentally observed temporal and spatial behavior of the system. The total system was broken up to subsystems which were separately studied. The bromate – Ru(II) – bromoacetone subsystem was identified as core oscillator which is capable of producing similar dynamics observed in the total system. The unknown rate constant of some reactions were measured and used in the mechanism. A 14-step mechanism was suggested to simulate both the dynamics of the subsystems and the oscillations observed in the total system. [1], [2]

A recently published design method for producing oscillations in the concentrations of ions possessing only a single stable

non-zero oxidation state was used to induce oscillations in the concentration of  $F^-$  by coupling the pH dependent hydrolysis of  $Al^{3+}$  and the consecutive aluminium-fluoride complex formation to the  $BrO_3^- - SO_3^{2-} - Mn^{2+}$  pH-oscillator. [3]

A slight modification of the original method enabled us to extend the number of cations which participate in oscillatory process. With the new version of the method, which is based on coupling a redox core-oscillator to irreversible chemical reactions, we successfully induced oscillations in the concentrations of some divalent metal ions like  $Ca^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ . [4]

## I. Introduction

Oscillatory chemical reactions fall within the scope of periodic phenomena that widely occur in nature. Periodicity in general means the repetitive appearance of a pattern in time and/or space. Planets orbiting the Sun, the pendulum, some composite reactions of the glycolysis, the patterns in the coat of animals and the population-dynamics are known examples of periodicity. Periodic behavior can occur in non-linear systems which are far from equilibrium. In a non-linear system the effect of a flux results in a non-linear (quadratic, cubic, logarithmic etc.) response which, if coupled to other processes, may trigger exotic dynamical behaviors. Periodicity can also be observed in chemical systems. The non-linearity in their mechanism may give rise to regular changes in the concentration of intermediates in time and space, and “exotic chemical phenomena”, such as *temporal oscillations* in a well stirred system, *pattern formation* in an unstirred layer of a reaction mixture, *chaos*, *complex oscillations*, *multistability*, *excitability*, etc. in a continuously fed stirred tank reactor can appear. The main goal of the research in the field of non-linear chemical dynamics is *to produce* and *to study* “exotic phenomena” in chemical systems, *to reveal* their mechanism and *to simulate* these temporal and spatial patterns. The

oscillatory chemical reactions represent the simplest systems in which non-linear chemical dynamics can be studied. The conclusions drawn from the studies at molecular level (i.e. in chemical systems) will hopefully lead to establish some general rules and help us to understand similar phenomena observed in more complex biological systems or in technological processes or in prediction of periodically occurring crisis in society, etc.

## II. Objectives

The objective of my research was to gain new information on the field of nonlinear chemical dynamics by studying *oscillating chemical reactions* (periodicity in time) and *chemical pattern formation* (periodicity in space).

One of my aims was to clarify the chemical origin of the *concentration waves* and *patterns* developed in the thin layer of the mixture of “ $\text{BrO}_3^-$  – dual substrate – dual catalyst” system by the interaction of the oscillatory kinetics and diffusion. This reaction is ideal for studying oscillations both in time and space, because it offers some advantages over the widely used “ $\text{BrO}_3^-$  – malonic acid – catalysator” (BZ) and “chlorite – iodide – malonic acid” (CIMA) systems when spatial oscillations are studied. The patterns are homogenous (no precipitate or gaseous byproduct form), they show sensitivity to physical perturbations and have long lifespan (several hours). The serious drawback of using it to study pattern formation was the lack of a proper mechanism.

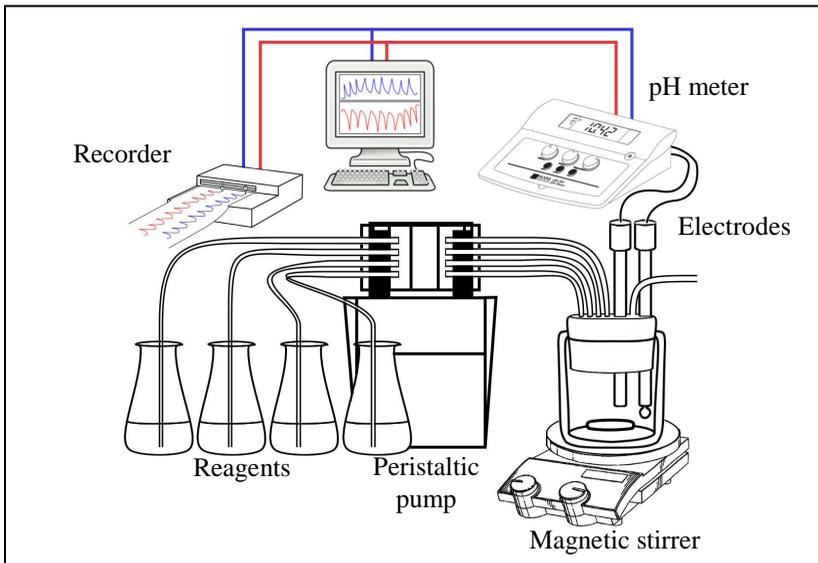
The second objective of my research was to describe the chemical background of the oscillatory “ $\text{BrO}_3^-$  – dual substrate – dual catalyst” system, namely to suggest a *mechanism* and to build a model which is capable of simulating its dynamical features.

The third objective of my research was to *develop new oscillating chemical reactions*. Although lots of chemical systems are known – 9 oscillator family including about 150 variants – the design of new oscillating chemical reactions is still a demand. My aim was to design and develop such oscillatory systems in which periodic changes in the concentration of non-redox species take place. These systems are interesting because it is known that non-redox species (ions and molecules) can participate in periodic processes in living organisms but their direct participation in the oscillatory cycle has never been demonstrated in laboratory. A design method published earlier by our group was used to induce oscillations in the concentration of non-redox ions. The method involves coupling of the target species to a known redox-oscillator using a complex or precipitate formation equilibrium reaction in which the target ion participates. My goal was to *design and produce* experimentally oscillations in the concentrations of non-redox ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{F}^-$ , etc.), so the group of elements that participate in induced oscillations would be extended with new members.

In my thesis I summarize the results of my research regarding these objectives.

### III. Methods

Depending on the system under study experiments were carried out in either a closed system (batch reactor) or in an open system (continuously stirred tank reactor, CSTR). When a closed system was used, the reactants were initially introduced into the reactor in a predetermined order afterwards the reactor was closed from transport of matter. In open system the reactants were continuously fed at a defined rate into the reactor using a peristaltic pump. The reactor was first filled with the reagents and an optimal flow-rate ( $k_0$ ) was then maintained to generate oscillations.



*Figure 1.: Experimental setup*

The excess of the reaction mixture was continuously removed with an other peristaltic pump through a hole drilled into the cap of the reactor. The changes in potential of electrodes (glass, platinum and ion-selective electrodes were used) was monitored and recorded with an analog recorder and a personal computer simultaneously.

The *pattern formation* was studied at room temperature in a thin layer of the reaction mixture spread in a covered Petri-dish.

*Spectroscopic measurements* were carried out using Milton Roy 3000 diode array spectrophotometer equipped with quartz cells. The reactants were introduced to the cells and the absorbance of the stirred reaction mixture was recorded at fixed wavelength. The data were evaluated using Origin software package.

The *unknown kinetic parameters* of some composite reactions were determined by stopped flow technique using Agilent 8452 diode array spectrophotometer. The parameter estimations were carried out by the MULTIMRQ program using the Marquardt method.

The *simulations* of the dynamics were done with the program XPPAUT. The distribution of species vs. pH curves were calculated using MEDUSA software package.

## IV. Results

Below I summarize new scientific results of my doctoral work regarding the objectives described earlier.

1. The  $BrO_3^-$  – dual substrate ( $H_2PO_2^-$ , acetone) – dual catalyst ( $Mn^{2+}$ ,  $Ru(bpy)_3^{2+}$ ) system was proven to be ideal for studying both oscillations and chemical pattern formation. By studying the dynamics of the total system and its subsystems the  $BrO_3^-$  – bromoacetone –  $Ru(bpy)_3^{2+}$  subsystem was found to be capable of oscillations and to form patterns in a thin layer of its reaction mixture. The dynamic features and the *pattern formation* observed in this subsystem are similar to those in the total system. These findings support the idea that the oscillatory behavior of the total system is the result of the interaction between two internally coupled oscillators.

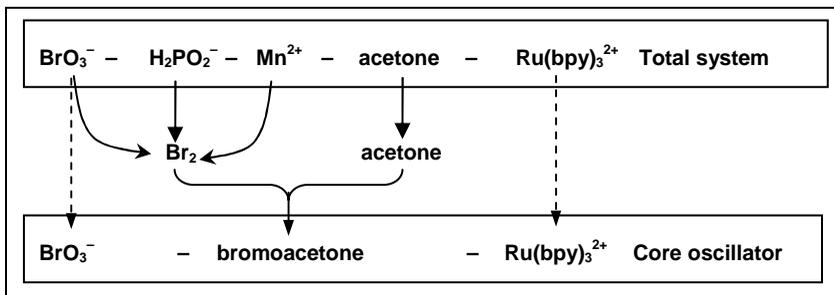


Figure 2.: The development of the  $BrO_3^-$  – bromoacetone –  $Ru(bpy)_3^{2+}$  core oscillator from the  $BrO_3^-$  –  $H_2PO_2^-$  – acetone –  $Mn^{2+}$  –  $Ru(bpy)_3^{2+}$  total system

2. A detailed mechanism which can explain the dynamical features of the  $BrO_3^- - H_2PO_2^- - Mn^{2+} - acetone - Ru(bpy)_3^{2+}$  system was proposed. The model based on this mechanism is capable of simulating the dynamical behavior observed in both the total system and its subsystems. The unknown kinetic data of some composite reactions were determined and included in the mechanism.
3. New oscillating chemical systems were designed and produced:
  - a) Oscillations in the concentration of  $F^-$  were induced in a CSTR by coupling two consecutive pH dependent equilibrium reactions to a pH oscillator. The  $BrO_3^- - SO_3^{2-} - Mn^{2+}$  system was used as a redox core oscillator. In this system – under oscillatory conditions – the pH changes between 2.5 and 7.5 with a period of 30 minutes. The pH dependent equilibrium reaction was either the hydrolysis of  $Al^{3+}$  followed by the complex formation with  $F^-$  or the complex formation between  $Ca^{2+}$  and EDTA followed by the consecutive formation of  $CaF_2$  precipitate. By optimizing some experimental control parameters (input concentrations and their ratios, flow rate, temperature) periodic changes in  $[F^-]$  with a magnitude of 1-3 were induced. In these coupled systems bistability (the

appearance of two stationary states under the same experimental conditions) was also shown to exist. The chemical background of these oscillations has been clarified in detail and calculations of the distribution of species vs. pH have been carried out.

- b) The method suggested for generating oscillations in non-redox species published by our group in 2005 in *Nature* has been slightly modified. Oscillations in the concentration of non-redox divalent metal ions ( $M^{2+} = Cd^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}$  and  $Ni^{2+}$ ) were induced using the  $BrO_3^- - SO_3^{2-}$  pH system as core redox oscillator. Besides pH oscillations periodic changes in the concentration of  $SO_3^{2-}$  was also observed. The target ion was coupled to the core oscillator by its precipitate formation reaction with  $SO_3^{2-}$ . The amplitude of the oscillations in free  $[M^{2+}]$  was shown to depend on the amount of the  $M^{2+}$  bound in the precipitate. It is depends on both the solubility product ( $K_{sp}$ ) of the  $MSO_3$  precipitate and the actual concentration of the  $SO_3^{2-}$  in the CSTR. By optimizing some experimental control parameters oscillations in the concentration of the metal ions with a magnitude of 1-2 were induced in the  $BrO_3^- - SO_3^{2-} - M^{2+}$  systems.

## V. Conclusions

Long lasting oscillations were initiated and maintained in the initially non-oscillatory mixture of  $BrO_3^- - H_2PO_2^- - acetone - Mn^{2+}$ , when an uncovered reactor and very intensive stirring were used. The appearance of the oscillations was attributed to the physical removal of the intermediate  $Br_2$ , which is known to be an inhibitor in the bromate oscillators. A conclusion may be made that in non-linear chemical systems, if volatile intermediates are formed, the intensity of stirring may be a determining factor (constraint) in bringing about or eliminating the oscillatory behavior.

Target pattern was shown to develop and oscillations were observed in the  $Ru(bpy)_3^{2+}$  catalyzed  $BrO_3^- - bromoacetone$  reaction which can be regarded as core oscillator in the previously discovered  $BrO_3^- - H_2PO_2^- - acetone - Mn^{2+} - Ru(bpy)_3^{2+}$  “dual substrate – dual catalyst” bromate oscillator. These results represent an other example when both temporal and spatial structures can appear in a nonlinear chemical system. From these findings we may conclude that all oscillatory batch reactions are capable of forming spontaneous self-organized spatial patterns, if the mechanical mixing in the system is excluded. Up to date the  $Cu^{2+}$  catalyzed  $H_2O_2 - SCN^-$  batch oscillator seems to be the only exception from this rule.

A detailed mechanism was suggested that describes the dynamical behavior observed in the  $BrO_3^- - H_2PO_2^- - acetone - Mn^{2+} - Ru(bpy)_3^{2+}$  batch system and its subsystems. Beside this oscillator many more double substrate BZ-type oscillatory reactions were reported where one of the substrate was acetone, but its exact role in the oscillatory mechanism has never been clarified. Here we demonstrated – both experimentally and in the model – that the long lasting batch oscillations in the total system are due to the continuous formation of bromoacetone in the  $Mn^{2+}$  catalyzed  $BrO_3^- - H_2PO_2^- - acetone$  subsystem which serves as substrate in the  $Ru(bpy)_3^{2+}$  catalyzed  $BrO_3^- - bromoacetone$  oscillator. It is fair to conclude that similar sequence of reactions takes place in all reported  $BrO_3^- - substrate - acetone - catalyst$  type oscillators, in fact the catalysed  $BrO_3^- - bromoacetone$  reaction is responsible for the oscillatory kinetics in all ones.

Oscillations and multiple steady states were induced in the concentration of non-redox anions and cations, like  $F^-$ ,  $Ca^{2+}$ ,  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$ . Since these ions possess only one stable oxidation state, they are not able to participate directly in the generally accepted redoxreaction-based oscillatory mechanism. Here we have successfully generated oscillations in the concentration of many non-redox ions by coupling them

to a core pH-oscillator through their pH-dependent equilibria. These (and earlier) results support the idea that coupling a reaction of the target element to a core redox oscillator may represent a way how the concentrations of the non-redox species (ions or molecules) undergoes periodic changes in living systems.

## VI. Publications related to the dissertation

1. Horváth V., Kurin-Csörgei K., Epstein I. R., Orbán M.,  
Oscillatory concentration pulses of some divalent metal  
ions induced by a redox oscillator (2010)  
Phys. Chem. Chem. Phys., 12: 1248-1252 IF: 4,064
2. Horváth V., Kurin-Csörgei K., Epstein I. R., Orbán M.,  
Oscillations in the concentration of fluoride ions induced  
by a pH oscillator (2008)  
J. Phys. Chem. A, 112: 4271-4276 IF: 2,871
3. Kurin-Csörgei K., Horváth V., Orbán M.,  
Chemical origin of the sustained-like pattern formation  
observed in the bromate - dual substrate - dual catalyst  
oscillatory batch system (2007)  
React. Kinet. Catal. Lett., 90: 405-411 IF: 3,047
4. Szalai I., Kurin-Csörgei K., Horváth V., Orbán M.,  
New experimental data and mechanistic studies on the  
bromate - dual substrate - dual catalyst batch oscillator  
(2006)  
J. Phys. Chem. A., 110: 6067-6072 IF: 0,584