



**Temperature dependence of the dynamical behavior and
temperature-compensation in oscillatory chemical
reactions**

PhD thesis

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Introduction

The most important aim of my PhD research work was to find or design temperature-compensated chemical oscillators. Temperature-compensation means that the period length of an oscillation is little or not affected by environmental temperature changes which occur within a certain range. Many biological rhythms can exhibit such a phenomenon, because timing of numerous periodic processes should be independent of environmental factors, such as temperature. On the contrary, temperature-compensation is not a general phenomenon in chemical oscillators: characteristically the period length and the amplitude decrease with increasing temperature. The first experimental example of the temperature-compensation in a chemical oscillator has been reported only quite recently. Taking into account that the mechanism of chemical oscillators is supposed to be easier to understand, chemical examples of temperature-compensation may help to decipher the controlling mechanism of the phenomenon. For this reason, it seems to be justified to investigate this problem.

I have carried out experiments in four different reacting systems. Accordingly, the results are presented in four separate chapters. According to the original aim, first I studied the temperature dependence in these systems, but when I discovered a new oscillatory reaction I investigated the dynamics of the reaction in detail under different conditions and proposed a mechanism for simulating the experimental behavior.

New scientific results

1. Temperature sensitivity of the $\text{H}_2\text{O}_2\text{-SO}_3^{2-}\text{-S}_2\text{O}_3^{2-}$ oscillatory flow system

I. I have discovered that a change in the environmental temperature affected the period length of pH-oscillations in the $\text{H}_2\text{O}_2\text{-SO}_3^{2-}\text{-S}_2\text{O}_3^{2-}$ flow system in a complex way: *i.* Under certain experimental conditions, the period length increased with increasing temperature, *ii.* Under some other conditions, it decreased with increasing temperature, *iii.* As a result of these two opposing effects, one could observe temperature-compensation (i.e. no temperature effect on the period length) under optimized conditions. For example, changing the input concentration of SO_3^{2-} had a significant influence on the temperature dependence of the period length of the oscillations (Figure 1.).

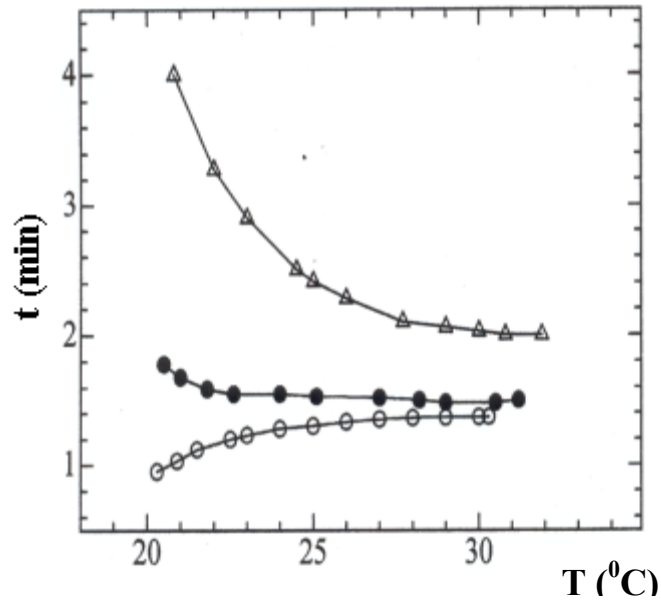


Figure 1. Period length as a function of temperature at different input sulfite ion concentrations. $[\text{H}_2\text{O}_2]_0 = 0.0135 \text{ M}$; $[\text{S}_2\text{O}_3^{2-}]_0 = 5.0 \times 10^{-3} \text{ M}$; $[\text{H}^+]_0 = 5.0 \times 10^{-4} \text{ M}$; $k_0 = 3.0 \times 10^{-3} \text{ s}^{-1}$; $[\text{SO}_3^{2-}]_0 = 0.0018 \text{ (}\Delta\text{)}$, $0.0017 \text{ (}\bullet\text{)}$, $0.0015 \text{ M (}\circ\text{)}$.

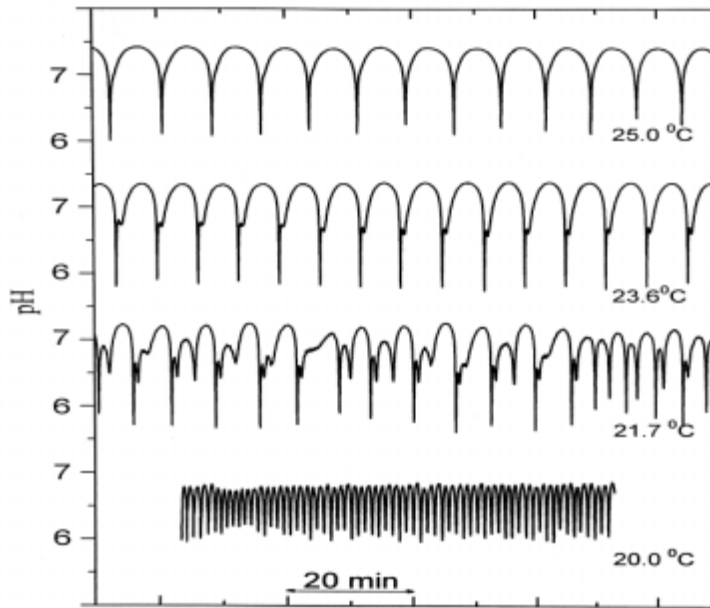


Figure 2. The effect of temperature in $\text{H}_2\text{O}_2\text{-SO}_3^{2-}\text{-S}_2\text{O}_3^{2-}\text{-CSTR}$ system. $[\text{H}_2\text{O}_2]_0 = 0.01 \text{ M}$; $[\text{SO}_3^{2-}]_0 = 2.5 \times 10^{-3} \text{ M}$; $[\text{S}_2\text{O}_3^{2-}]_0 = 4.0 \times 10^{-3} \text{ M}$; $[\text{H}^+]_0 = 7.0 \times 10^{-4} \text{ M}$; $k_0 = 8.76 \times 10^{-4} \text{ s}^{-1}$.

II. A significant temperature sensitivity of the dynamical behavior was noticed when the experiments were carried out under another input concentrations of the reactants: I observed transitions between different dynamic states of this system when the environmental

temperature was changed only by 1-2 °C. Figure 2. shows this remarkable temperature sensitivity. One can follow how the traces develop from simple oscillations with high frequency through complex periodic oscillation and chaos to low-frequency oscillations by increasing the temperature step by step.

III. The mechanism of this reacting system have already revealed. I used this mechanism with estimated activation energies to simulate both the experimentally observed temperature-compensation and the remarkable temperature sensitivity. The hydrogen sulfite ion had a key role to simulate the temperature dependence. The length of the neutral region of a period is determined by the time required for the consumption of HSO_3^- . Since HSO_3^- was produced in step M2 (92.2 kJ/mol) with high activation energy and consumed in steps M5 (31.0 kJ/mol), M5' (34.2 kJ/mol) with low activation energies, its production rate increase more rapidly than its consumption rate, causing an increase in its average lifetime. As a result, the high pH stage increased with increasing temperature and, at the same time, the low pH stage decreased. This opposing influence compensated each other under certain conditions leading to a constant period length at different temperatures.

Table 1. The mechanism of the $\text{H}_2\text{O}_2\text{-SO}_3^{2-}\text{-S}_2\text{O}_3^{2-}$ -system.

$\text{H}_2\text{O}_2 + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{HOS}_2\text{O}_3^- + \text{OH}^-$	M1 M-1
$\text{H}_2\text{O}_2 + \text{HOS}_2\text{O}_3^- \rightarrow 2\text{HSO}_3^- + \text{H}^+$	M2
$\text{S}_2\text{O}_3^{2-} + \text{S}_2\text{O}_3 \rightarrow \text{S}_4\text{O}_6^{2-}$	M3
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	M4 M-4
$\text{H}_2\text{O}_2 + \text{HSO}_3^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} + \text{H}^+$	M5
$\text{H}_2\text{O}_2 + \text{HSO}_3^- + \text{H}^+ \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} + 2\text{H}^+$	M5'
$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	M6 M-6
$\text{HOS}_2\text{O}_3^- + \text{H}^+ \rightleftharpoons \text{S}_2\text{O}_3 + \text{H}_2\text{O}$	M7 M-7

IV. I have disclosed theoretical possibility (mechanistic and parametric conditions) of temperature-compensation in a general model of pH-oscillators. Simulations indicated that there were two possibility of the evolution of the temperature-compensation:

- (a) The increasing rate of the negative feedback loop (N3) increased the period length. At the same time, an increasing rate of the autocatalytic composite reaction (N2) should lead to

shorter periods. The two opposing effects may compensate each other if the negative feedback reaction had higher activation energy than the other component reactions did.

- (b) If the protonation equilibrium (N1) were shifted to the production of the protonated form of reactant, the rate of the positive feedback cannot increase significantly because of the lower concentration of free H^+ at elevated temperature. As a result, the period length remains constant despite of increasing temperature.

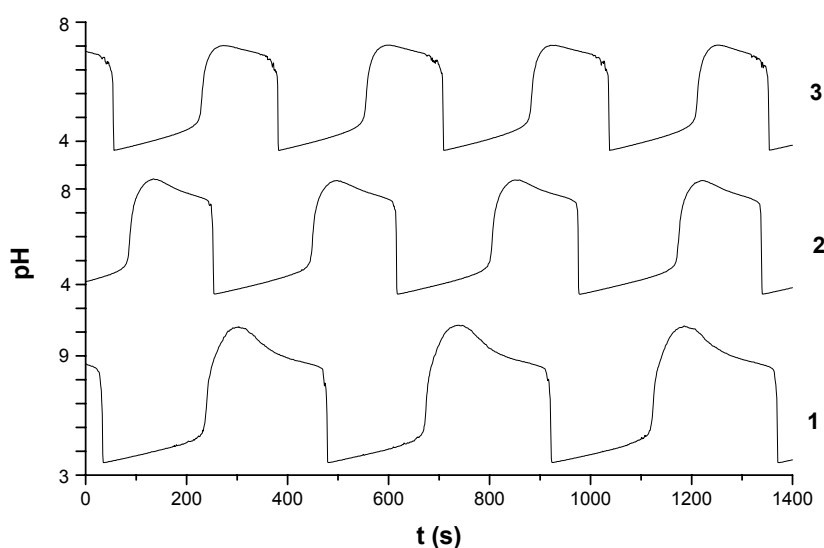
Table 2. General scheme for pH-oscillators:

$A^- + H^+ \rightleftharpoons AH$	(N1)
$AH + H^+ + \{B\} \rightarrow 2H^+ + P$	(N2)
$H^+ + \{C\} \rightarrow CH$	(N3)

2. The H_2O_2 - $S_2O_4^{2-}$ - OH^- -system

V. I discovered a new pH oscillatory reaction in the H_2O_2 - $S_2O_4^{2-}$ - OH^- -system in a CSTR. The oscillation was very sensitive to the changing experimental constraints. The temperature dependence of the frequency and the amplitude were also remarkable.

Figure 4. The temperature dependence of the oscillation. $[H_2O_2]_0 = 0.0105$ M; $[Na_2S_2O_4]_0 = 0.00375$ M; $pH_i = 11.5$; $k_0 = 2.7 \times 10^{-3} s^{-1}$; $T_1 = 20.4$ °C; $T_2 = 22.4$ °C; $T_3 = 25.9$ °C. pH_i - the initial pH value of the dithionite solution before the addition of H_2O_2 .



The periodic behavior occurred within a narrow range of parameters. I also investigated the effect of experimental conditions on the kinetics in a closed reactor where no oscillations took place. The measured pH-time traces showed multiple inflection points in a closed reactor.

VI. I have propose a very simple mechanism consisting of three protonation equilibria and three redox reactions. Formation of sulfate was assumed to take place in two stages (P1 and P2). Reaction (P1) led to the transient accumulation of hydrogen sulfite ions. Further oxidation of hydrogen sulfite ions in reaction (P2) is known to be autocatalytic in H^+ . (P3) was the negative feedback loop. The results of calculations were in a good agreement with experiments.

Table 3. The model of the H_2O_2 - $S_2O_4^{2-}$ - OH^- -system:

$H_2O_2 + S_2O_4^{2-} \rightarrow 2 HSO_3^-$	(P1)
$H_2O_2 + HSO_3^- \rightarrow SO_4^{2-} + H^+ + H_2O$	(P2)
$2 H_2O_2 + S_2O_4^{2-} + H^+ \rightarrow HS_2O_6^- + 2 H_2O$	(P3)
$H^+ + SO_3^{2-} \rightleftharpoons HSO_3^-$	(P4)
$H^+ + S_2O_6^{2-} \rightleftharpoons HS_2O_6^-$	(P5)
$H^+ + OH^- \rightleftharpoons H_2O$	(P6)

3. The kinetics and mechanism of the decomposition of the dithionite ion

VII. The decomposition of the dithionite ion at initial $pH \approx 7$ had autocatalytic kinetics in a closed reactor: an early induction period was followed by a fast decomposition. I revealed the oscillatory dynamics of the decomposition in a flow reactor, which occurred in a wide range of experimental parameters. The experimental data showed complex pH-time curves consisting of double peak periods. The parameters of the oscillation were very sensitive to the changing of constraints.

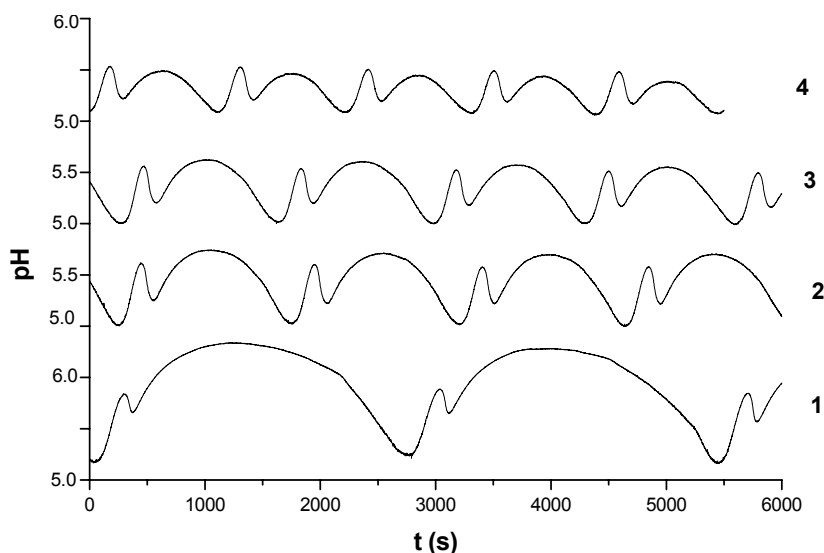


Figure 5. Measured double peak pH-oscillation at different input concentration of hydrogen ion . $[\text{Na}_2\text{S}_2\text{O}_4]_0 = 0.016 \text{ M}$; $[\text{NaOH}]_0 = 0.0182 \text{ M}$; $T = 39.6 \text{ }^\circ\text{C}$; $k_0 = 7.52 \times 10^{-4} \text{ s}^{-1}$; $[\text{H}^+]_{01} = 1.75 \times 10^{-2} \text{ M}$; $[\text{H}^+]_{02} = 1.85 \times 10^{-2} \text{ M}$; $[\text{H}^+]_{03} = 1.91 \times 10^{-2} \text{ M}$; $[\text{H}^+]_{04} = 1.95 \times 10^{-2} \text{ M}$.

VIII. I could describe the most important features of dynamic behavior of the dithionite ion decomposition with a detailed mechanism. This mechanism contained three protonation equilibria and seven redox reactions between different sulfur species. I could model the effect of decreasing pH, which increased the rate of the decomposition. I simulated the double peak pH-oscillations assuming two negative feedback reactions.

Table 4. The mechanism of the dithionite ion decomposition in aqueous solution:

$\text{S}_2\text{O}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HS}_2\text{O}_4^-$	(Q1)
$\text{SO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HSO}_3^-$	(Q2)
$\text{SO}_2^{2-} + \text{H}^+ \rightleftharpoons \text{HSO}_2^-$	(Q3)
$\text{S}_2\text{O}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{HSO}_3^- + \text{HSO}_2^-$	(Q4)
$2 \text{HSO}_2^- \rightarrow \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O}$	(Q5)
$\text{HSO}_3^- + \text{HS}_2\text{O}_4^- \rightarrow \text{S}_3\text{O}_6^{2-} + \text{H}_2\text{O}$	(Q6)
$\text{S}_3\text{O}_6^{2-} \rightarrow \text{S} + \text{S}_2\text{O}_6^{2-}$	(Q7)
$\text{S}_3\text{O}_6^{2-} + \text{H}_2\text{O} \rightarrow 2 \text{HSO}_3^- + \text{HSO}_2^- + \text{H}^+$	(Q8)
$\text{SO}_3^{2-} + \text{S} \rightarrow \text{S}_2\text{O}_3^{2-}$	(Q9)
$\text{HSO}_3^- + \text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{S} + \text{HSO}_2^-$	(Q10)

4. The effect of temperature on the dynamics of the Bray reaction

IX. I observed increasing, decreasing and temperature independent period length of the oscillation with increasing environmental temperature in a closed reactor. A previously proposed mechanism was used to simulate how temperature-compensation developed in this reacting system.

Table 5. The mechanism of the Bray reaction proposed by Schmitz:

$\text{IO}_3^- + \text{I}^- + 2\text{H}^+ \rightarrow \text{HIO} + \text{HIO}_2$	(R1)
$\text{HIO} + \text{HIO}_2 \rightarrow \text{IO}_3^- + \text{I}^- + 2\text{H}^+$	(R2)
$\text{HIO}_2 + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2\text{O} + \text{H}_2\text{O}$	(R3)
$\text{I}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HIO}$	(R4)
$2\text{HIO} \rightarrow \text{I}_2\text{O} + \text{H}_2\text{O}$	(R5)
$\text{HIO} + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O}$	(R6)
$\text{I}_2 + \text{H}_2\text{O} \rightarrow \text{HIO} + \text{I}^- + \text{H}^+$	(R7)
$\text{HIO} + \text{H}_2\text{O}_2 \rightarrow \text{I}^- + \text{H}^+ + \text{H}_2\text{O}$	(R8)
$\text{I}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{HIO} + \text{HIO}_2$	(R9)
$\text{HIO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}$	(R10)
$\text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{HIO}_2 + \text{O}_2 + \text{H}_2\text{O}$	(R11)
$\text{I}_2(\text{aq}) \rightarrow \text{I}_2(\text{g})$	(R12)

Calculations revealed that increasing the rate constants of R4, R6, R8 and R12 component processes increased the period length, while increasing the rate of the all remaining composite reactions resulted in a decreasing period length. So I could simulate the temperature-compensation giving adequate activation energies to the component reactions.

Publications in the topic of this dissertation:

1. **Klára M. Kovács** and Gyula Rábai: Large amplitude pH oscillations in the hydrogen peroxide-dithionite reaction in a flow reactor, *J. Phys. Chem. A*, 2001, **105**, 9183-9187.
2. **Klára M. Kovács** and Gyula Rábai: Mechanism of the oscillatory decomposition of the dithionite ion in a flow reactor, *Chem. Commun.*, 2002, 790-791.

3. **Klára M. Kovács** and Gyula Rábai: Temperature-compensation in pH-oscillator, *Phys. Chem Chem. Phys.*, 2002, 4, 5265-5269.

4. **Klára M. Kovács** and Gyula Rábai: Temperature-compensation in the Bray reaction, manuscript.

Publications not tightly connected to the topic of the dissertation:

5. Gyula Rábai and **Klára M. Kovács**: Photoinduced reaction between chlorine dioxide and iodine in acidic aqueous solution, *J. Phys. Chem. A*, **2001**, 105, 6167-6170.

Presentations and posters in the topic of the dissertation:

1. **Klára M. Kovács** és Gyula Rábai: Ditionition alapú pH oszcillációs reakciók MTA Reakciókinetikai és Fotokémiai Munkabizottsági Ülés, Kecskemét, 2001.

2. **Klára M. Kovács** és Gyula Rábai: pH-oszcillációk a ditionition reakcióiban, Erdélyi Magyar Műszaki Tudományos Társaság VII. Vegyész Konferencia, Nagyvárad, 2001.

3. **Klára M. Kovács** és Gyula Rábai: Hőmérséklet-kompenzáció a Bray reakcióban, Erdélyi Magyar Műszaki Tudományos Társaság VIII. Vegyész Konferencia, Kolozsvár, 2002.

4. **Klára M. Kovács** és Gyula Rábai: Temperature-compensation in the Bray reaction, Reactor workshop, Budapest, 2003.