

Experimental study of coupled chemical oscillators of the Belousov—Zhabotinskii type

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Dedicated to Professor L. Treindl, DrSc., in honour of his 60th birthday

The dynamic behaviour of oscillation reactions of the BZ type was investigated by using double-substrates and bubbling inert gas in a closed system. The oscillation reactions were chemically coupled *via* the common bromine-containing species. Some new phenomena which do not occur in simple noncoupled systems have appeared. The limiting cycles confirming the complexity of behaviour of the studied systems were measured.

Изучалось динамическое поведение осциллирующих реакций типа BZ с использованием двойных субстратов в закрытой системе с продуванием инертным газом. Осциллирующие реакции были химически сопряжены через общие содержащие бром частицы. В этих системах было обнаружено наличие нескольких новых явлений, не наблюдающихся в простых несопряженных системах. Были экспериментально измерены лимитные циклы, подтверждающие сложность поведения изучаемых систем.

The coupled chemical oscillators of the Belousov—Zhabotinskii (BZ) type have not been given hitherto great attention, but it appears that coupled oscillators are more a rule than an exception in living organisms.

The study of coupled chemical oscillators may be divided into two groups, *i.e.* it is concerned with physical coupling of oscillators in separated vessels and chemical coupling of chemically different oscillators by means of common reactant or intermediate in single vessel. The physical coupling usually involves equal oscillators working under different conditions, for instance with different inlet concentrations into continuous stirred tank reactor (CSTR). The coupling is achieved by joining the separated cells by means of mass transport [1—4] or electrical linkage [5]. The driving force for coupling is due to concentration differences between the cells. The chemically coupled oscillation reactions take place in closed systems where two or more organic substrates in simple BZ reaction [6] or in the Briggs—Rauscher oscillator [7] have been used. The first attempts to accomplish chemical coupling in CSTR were made by *Maselko* [8] who used the BZ reaction with mixed substrates. The coupling of oscillators gives rise to different new complex phenomena including chaos which are not

observed in simple systems. *Epstein* and coworkers [9—11] studied the dynamic behaviour of chemically coupled oscillators in CSTR and discovered birhythmicity, composite oscillations, and complex periodic and aperiodic oscillations.

If oxalic acid [12, 13], malonic acid [14], sodium hypophosphite [15] or glycerol [16] are used as substrates in the BZ reaction proceeding in a closed system with bubbling inert gas (pseudo CSTR system), simple oscillations characteristic of the used substrate can be measured. However, if we use a double-substrate obtained by combination of some above-mentioned substrates, we obtain complex oscillations which have been the topic of our experimental research.

Experimental

The course of the oscillation reaction was investigated potentiometrically and a polarograph OH-105 (Radelkis, Budapest) was used for registration. This polarograph served as a millivoltmeter which measured temporal changes in potential of a redox platinum electrode.

The oscillation reactions took place in a thermostated vessel in which a platinum electrode, fritted stoneware for homogeneous nitrogen bubbling, and agar salt (Na_2SO_4) bridge joining the reaction vessel with the reference electrode were dipped. A calomel electrode (Radelkis) dipped in saturated solution of NaCl was used as reference electrode. An ion-selective bromide electrode (CRYTUR) functioning as the second indication electrode was also put into the reaction solution for measuring the limiting cycles. Both indication electrodes were connected through operational amplifiers with a plane coordinate x — y recorder 4105 (Laboratorní přístroje, Prague). The chemicals used were anal. grade reagents. They were dissolved in redistilled water. The rate of nitrogen flow was measured with a laboratory flow meter TG 400 (GDR).

Results and discussion

First of all, we paid attention to the system oxalic acid (OA), NaBrO_3 , Mn(II) , H_2SO_4 , malonic acid (MA) which involved two independent oscillation reactions (BrO_3^- —MA and BrO_3^- —OA) chemically coupled *via* the common bromine-containing species. Malonic acid is a substrate which is able to be easily brominated, oxalic acid does not undergo bromination. The reaction system is bubbled by an inert gas which removes gaseous products, especially bromine from the system. The flow rate of inert gas is a bifurcation parameter. If the flow rate of inert gas varies, a series of bifurcations from one type of oscillation into another appears at constant concentrations and temperature.

The phase diagrams $c(\text{OA})_0$ —flow rate of N_2 and $c(\text{MA})_0$ —flow rate of N_2 were measured, other conditions were fixed. The first phase diagram (Fig. 1)

gives much more varying form of oscillations than the second one, which is due to the fact that oxalic acid used as substrate cannot undergo bromination and is much more sensitive to different rates of bromine removal than malonic acid. We can observe double oscillations, sharp oscillations with small and large amplitude, dual oscillations with or without induction period, and inhibition of oscillations. The great variety of the observed phenomena indicates a rather high degree of coupling in this system.

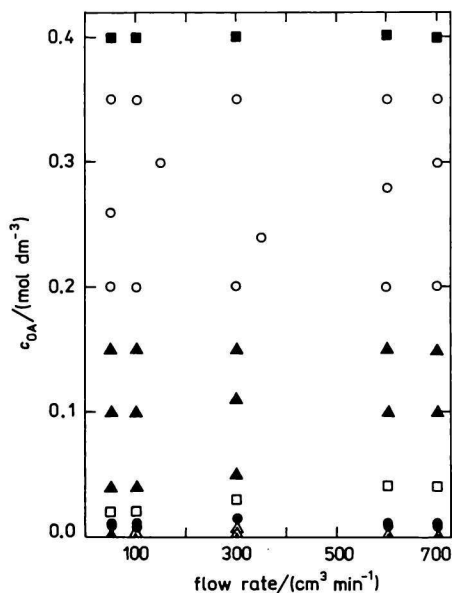


Fig. 1. Phase diagram of the system (1.5 M- H_2SO_4 , 3×10^{-2} M- NaBrO_3 , 2×10^{-3} M- MnSO_4 , 6×10^{-2} M-MA, 20°C , 20 cm^3) showing the regions of different oscillations as a function of oxalic acid concentration and flow rate of inert gas (N_2).

▲ Double oscillations, □ interrupted double oscillations, ● dual oscillations without induction period, ○ dual oscillations with induction period, ■ sharp oscillations with small amplitude, △ sharp oscillations with large amplitude.

An x—y recorder equipped with a selective bromide electrode and platinum redox electrode was used for obtaining two-dimensional phase portraits of oscillation waves. Fig. 2a shows the dependence of potential of the platinum electrode on time. The variations of potential usually correspond to changes in concentration of the Mn^{3+} ions. Fig. 2b represents the dependence of potential of the selective bromide electrode on potential of the platinum electrode, *i.e.* the projection of paths on the coordinates corresponding to the Mn^{3+} and Br^- concentrations. The points corresponding to each other are denoted with numerals. A simple limiting cycle corresponds to single oscillation while a limiting cycle with a loop or deflection corresponds to composite oscillation. It results from Fig. 2 how the course of oscillation reaction changes with time. The system passes from simple oscillations to double-oscillations, which is accompanied with changes in limiting cycles. The limiting cycle belonging to chaotic oscillation is still more complicated [17]. We may state that a complicated

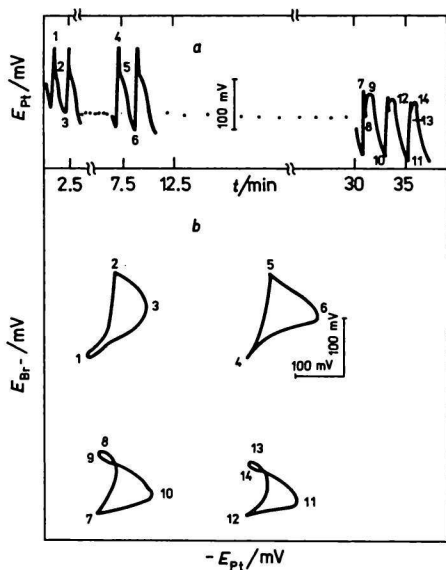


Fig. 2. Time change in potential of the Pt redox electrode (a). Dependence of potential of the selective bromide electrode on potential of the Pt redox electrode (b).

The record was simultaneously made on x-t and x-y recorders for equal solution (6×10^{-2} M-MA, 1.5 M- H_2SO_4 , 3×10^{-2} M- $NaBrO_3$, 2×10^{-3} M- $MnSO_4$, 8×10^{-2} M-OA, 20°C, flow rate of nitrogen $100 \text{ cm}^3 \text{ min}^{-1}$, 20 cm^3).

limiting cycle is to be regarded as an indicator of the existence of complex oscillations and aperiodicity.

Other chemically coupled oscillator studied by us contained oxalic acid, $NaBrO_3$, $Mn(II)$, H_2SO_4 , and glycerol (G) and involved two independent oscillation reactions, *i.e.* $BrO_3^- - OA$ and $BrO_3^- - G$. The used substrates differed in their reactivity with respect to bromine and hypobromous acid. While oxalic

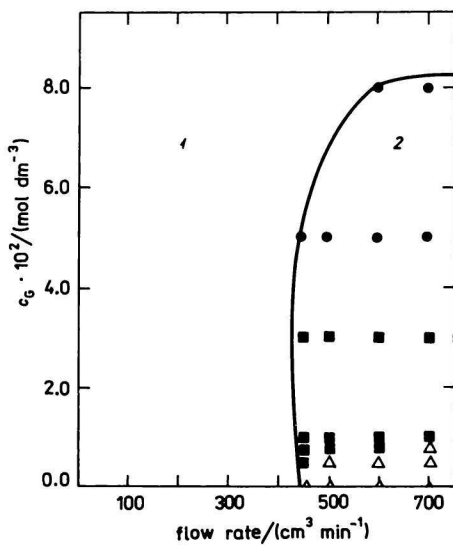


Fig. 3. Phase diagram of the system (1.5 M- H_2SO_4 , 2×10^{-3} M- $MnSO_4$, 1×10^{-3} M- $NaBrO_3$, 2.5×10^{-2} M-OA, 20°C, 20 cm^3) showing the region of stationary (1) and oscillation (2) state as a function of glycerol concentration and flow rate of nitrogen.

● Oscillations with small amplitude, ■ consecutive oscillations, at first one substrate and then the other substrate oscillates, ▲ oscillations with large amplitude.

acid reacts preferentially with HOBr ($k_{\text{HOBr}} = 15.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and rather slowly with Br_2 ($k_{\text{Br}_2} = 5.5 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) [18], glycerol reacts neither with bromine nor with HOBr [16]. It results from this fact that the system starts to oscillate only at higher rates of nitrogen flow in the presence of this pair of substrates under given concentration conditions (Fig. 3).

Merely consecutive oscillations can be observed. At first, one substrate oscillates and immediately or after a certain period the second substrate is used up. This second case is represented in Fig. 4. A similar course of oscillation reaction was observed by other authors [19—21]. During the quiet period free of oscillation the system was in state B of the Field—Körös—Noyes (FKN) mechanism [21], *i.e.* in the state attributed to low concentrations of the Br^- ions. In order to elucidate the influence of the Br^- ions on nonoscillation period, we added different amounts of NaBr in the course of the nonoscillation period.

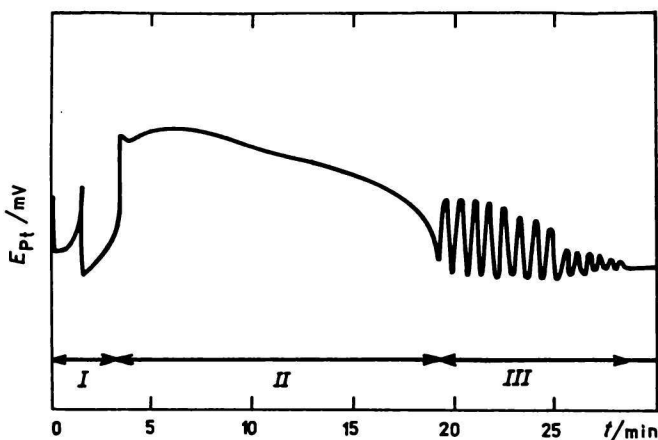


Fig. 4. Time change in potential of the Pt redox electrode (10^{-1} M glycerol, 1 M- H_2SO_4 , 3×10^{-3} M- MnSO_4 , 3×10^{-2} M- NaBrO_3 , 6×10^{-3} M-OA, 20°C , flow rate of nitrogen $500 \text{ cm}^3 \text{ min}^{-1}$, 20 cm^3).

According to the FKN mechanism the key intermediate of the BZ reaction are the Br^- ions [14, 22]. If their concentration exceeds the critical value $c(\text{Br}^-)_{\text{crit}} = 2 \times 10^{-5} c(\text{BrO}_3^-)_0$, which corresponds to the value $6 \times 10^{-7} \text{ mol dm}^{-3}$ in our system, the system passes from process B to process A of the FKN mechanism. When we determined the critical concentration of the Br^- ions by extrapolating the concentration of these ions to the zero time of the nonoscillation period [23], we obtained the value $10^{-3} \text{ mol dm}^{-3}$. This rather high value suggests that not only the Br^- ions but also another intermediate [24] affects the origination and length of the nonoscillation period. It is most probable that it is the radical

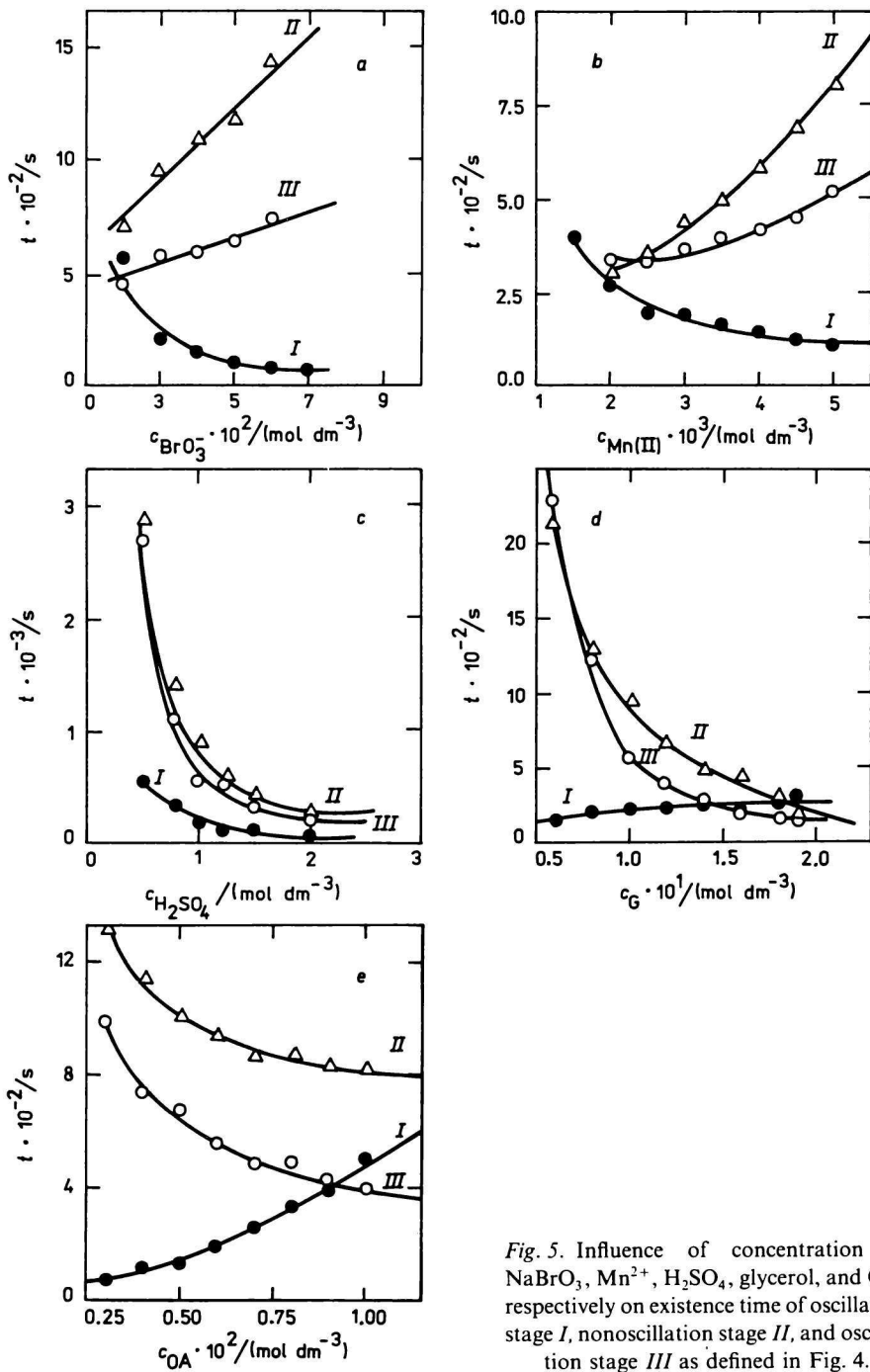


Fig. 5. Influence of concentration of NaBrO_3 , Mn^{2+} , H_2SO_4 , glycerol, and OA, respectively on existence time of oscillation stage I, nonoscillation stage II, and oscillation stage III as defined in Fig. 4.

arising from organic acid. Further experimental results are in agreement with this assumption. The nonoscillation period increases with concentration of the BrO_3^- ions and catalyst (Mn(II)) (Figs. 5*a*, *b*) and decreases with increasing concentration of H_2SO_4 , glycerol and oxalic acid (Figs. 5*c*, *d*, *e*). The assumption that the first oscillation stage (part *I* in Fig. 4) corresponds to oscillation of the system containing oxalic acid as dominant substrate is corroborated by Figs. 5*d*, *e*. It results from Fig. 5*d* that the influence of glycerol on the first oscillation stage is insignificant while Fig. 5*e* shows that the time of existence of these oscillations increases with concentration of oxalic acid. The measured limiting cycle is also in line with these facts (Fig. 6).

The last investigated chemically coupled oscillator consisted of OA, BrO_3^- , Mn(II) , H_2SO_4 , and NaH_2PO_2 and involved two oscillation reactions one of which was organic BrO_3^- —OA and the other inorganic BrO_3^- — NaH_2PO_2 .

As the partial redox reactions, *i.e.* reduction of bromate ions by hypophosphites and reduction of bromate ions by oxalic acid exhibit different dependence on concentration of the hydrogen ions, it could be assumed that the

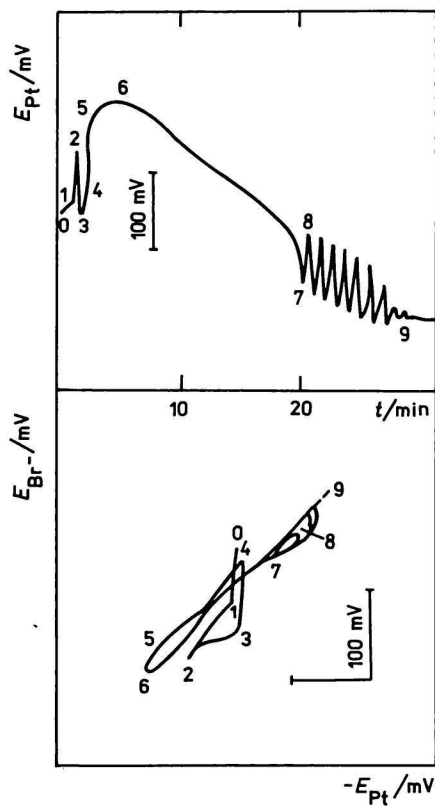


Fig. 6. Time change in potential of the Pt redox electrode and the corresponding trajectory in the phase plane (10^{-1} M glycerol, 1 M- H_2SO_4 , 3×10^{-3} M- MnSO_4 , 3×10^{-3} M- NaBrO_3 , 6×10^{-3} M-OA, 20°C, flow rate of N_2 500 $\text{cm}^3 \text{min}^{-1}$, 20 cm^3).

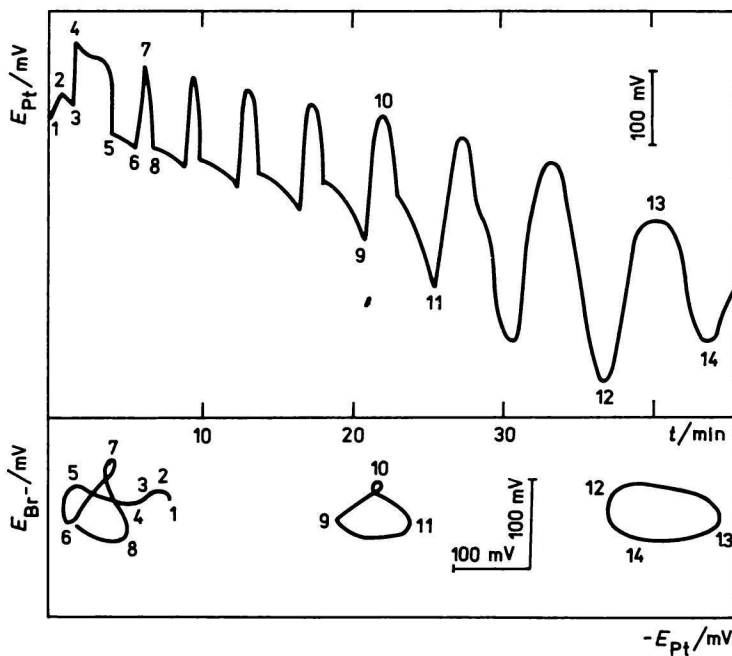
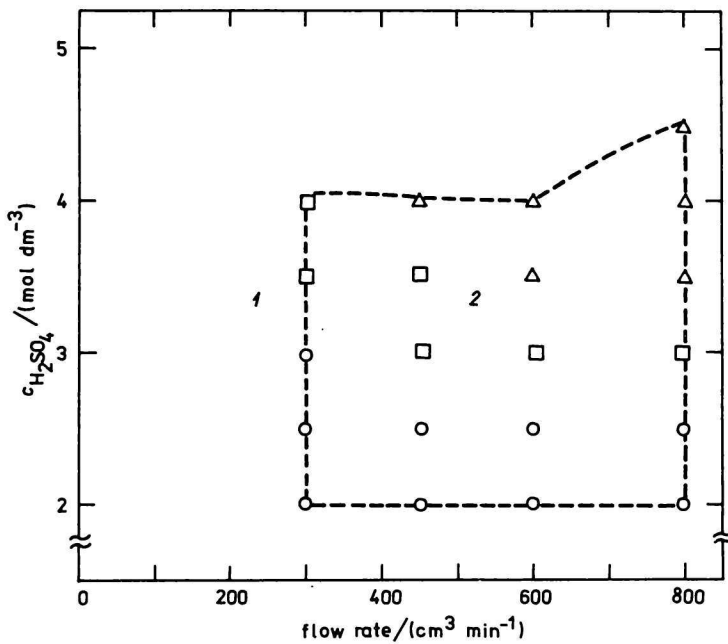


Fig. 7. Phase diagram of the system (2×10^{-2} M-OA, 2×10^{-3} M-MnSO₄, 10^{-2} M-NaBrO₃, 7×10^{-3} M-NaH₂PO₂, 20 °C, 20 cm³) as a function of concentration of H₂SO₄ and flow rate of nitrogen.

Δ, □, ○ Different types of very complicated oscillation courses.
Region of stationary (1) and oscillation (2) state.

Fig. 8. Time change in potential of the Pt redox electrode and the corresponding trajectories in the phase plane (2×10^{-2} M-OA, 3.5 M-H₂SO₄, 2×10^{-3} M-MnSO₄, 10^{-3} M-NaBrO₃, 7×10^{-3} M-NaH₂PO₂, 20 °C, flow rate of N₂ 700 cm³ min⁻¹, 20 cm³).



behaviour of the combined oscillation system would be significantly dependent on concentration of the H₃O⁺ ions. The phase diagram $c(\text{H}_2\text{SO}_4)_0$ —flow rate of nitrogen is represented in Fig. 7. The character of oscillations largely changes with time under constant all initial conditions. Thus we can observe three or even more types of oscillations in one course of oscillations (Fig. 8). Different types of oscillations have been confirmed by recording the limiting cycles in certain time intervals of an oscillation course. We also could record a course in which the oscillations faded and a nonoscillation stage of half an hour or one hour appeared. Afterwards the system started oscillating again and in this way (oscillation in oscillation) the reaction continued for a few hours.

References

1. Bar-Eli, K. and Geiseler, W., *J. Phys. Chem.* 85, 3461 (1981).
2. Marek, M. and Stuchl, I., *Biophys. Chem.* 3, 241 (1975).
3. Stuchl, I. and Marek, M., *J. Chem. Phys.* 77, 2956 (1982).
4. Nakajima, K. and Sawade, Y., *J. Chem. Phys.* 72, 2231 (1980).
5. Crowley, M. F. and Field, R. J., *J. Phys. Chem.* 90, 1907 (1986).
6. Heilweil, E. J., Henschman, M. J., and Epstein, I. R., *J. Am. Chem. Soc.* 101, 3698 (1979).
7. Cooke, D. O., *Int. J. Chem. Kinet.* 12, 683 (1980).
8. Maselko, J., *J. Chem. Phys.* 78, 381 (1983).
9. Alamgir, M. and Epstein, I. R., *J. Phys. Chem.* 88, 2848 (1984).
10. Citri, O. and Epstein, I. R., *J. Phys. Chem.* 92, 1865 (1988).
11. Orbán, M. and Epstein, I. R., *J. Phys. Chem.* 86, 3907 (1982).
12. Noszticzius, Z. and Bódiss, J., *J. Am. Chem. Soc.* 101, 3177 (1979).
13. Ševčík, P. and Adamčíková, L., *Collect. Czechoslov. Chem. Commun.* 47, 891 (1982).
14. Field, R. J. and Burger, M., *Oscillations and Travelling Waves in Chemical Systems*. J. Wiley, New York, 1985.
15. Adamčíková, L. and Ševčík, P., *Int. J. Chem. Kinet.* 14, 735 (1982).
16. Adamčíková, L. and Ševčík, P., *Collect. Czechoslov. Chem. Commun.* 52, 2375 (1987).

17. Maselko, J., *Chem. Phys. Lett.* 73, 194 (1980).
18. Ševčík, P. and Adamčíková, L., *Collect. Czechoslov. Chem. Commun.* 52, 2125 (1987).
19. Kaner, R. J. and Epstein, I. R., *J. Am. Chem. Soc.* 100, 4073 (1978).
20. Cooke, D. O., *Int. J. Chem. Kinet.* 14, 1047 (1982).
21. Field, R. J., Körös, E., and Noyes, R. M., *J. Am. Chem. Soc.* 94, 8649 (1972).
22. Tockstein, A. and Treindl, L., *Pokroky chemie č. 13.* (Progress in Chemistry No. 13.) Academia, Prague, 1986.
23. Wittmann, M., Stirling, P., and Bódiss, J., *React. Kinet. Catal. Lett.*, in press.
24. Försterling, H. D. and Noszticzius, Z., *J. Phys. Chem.* 93, 2740 (1989).

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