Sequential Oscillations in the Uncatalyzed Bromate Oscillator and Their Simple Qualitative Model

L'ubica Adamčíková,*,† Zuzana Farbulová,† Peter Ševčík,† and Andrzej L. Kawczynski‡

Department of Physical Chemistry, Comenius University, 842 15 Bratislava, Slovak Republic, and Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01−224 Warsaw, Poland

Received: May 21, 2002; In Final Form: October 22, 2002

The sequential oscillations of the uncatalyzed Belousov−Zhabotinsky reaction with phenol have been reported. The behavior of this system was found to be remarkably sensitive to stirring in a batch reactor. Oscillations showing identical patterns are obtained in a simple model proposed for a qualitative description of the sequential oscillations observed in uncatalyzed bromate system.

Introduction

The Belousov−Zhabotinsky (BZ) reaction exhibits a variety of dynamic regimes such as periodic oscillations, mixed-mode (MMO) oscillations, bistability, chaos, etc.[1−9] In its classic form, the BZ reaction is the oxidation of an aliphatic organic reactant by acid bromate ions catalyzed by metallic ions or their complexes. Oscillations have been observed also in uncatalyzed systems,[10] which do not contain of metal ions or their complexes but instead of aliphatic reactants contain more reactive aromatic compounds (mainly phenol and aniline derivates).

Sequential oscillations (the oscillations with two oscillatory intervals separated by a no oscillatory one) in a batch reactor have been observed in (a) the "Rácz" system,[11,12] (b) mixed-reactants BZ systems,[13−15] and (c) the BZ systems with aromatic compounds as a single organic reactant[16−18] (with a metal catalyst). In the absence of a catalyst, the sequential oscillations in the two component oscillators have been found so far in BrO_3^-−aniline[19] and BrO_3^-−phenol[20] in aqueous H_2SO_4 solutions.

In this paper, we present examples of sequential oscillations observed in the uncatalyzed bromate−phenol oscillator. The influence of stirring on the sequential oscillations is investigated. Stirring effects on the oscillations of the catalyzed BZ reaction have been studied in a batch reactor by several workers,[2,21−23] but in the uncatalyzed form of bromate oscillator, there are no previous stirring effect studies that can be used for comparison. Moreover, a simple, generic model for sequential oscillations is described. The model quite accurately describes dynamic behavior observed in the uncatalyzed bromate−phenol system.

Experimental Section

Reagents. Sulfuric acid, $NaBrO_3$, and phenol were of commercial analytical quality (Merck, Fluka). All solutions were prepared using double-distilled water.

Apparatus. Measurements have been carried out in a thermostated cylindrical glass reactor (diameter 3.5 cm, height 7.5 cm) at a constant temperature of 25 ± 0.1 °C. The total volume of the reaction mixture was 20 mL. The reactor was closed with a rubber stopper through which a commercial indication platinum macro electrode (0.5 × 0.8 cm) or a bromide-selective electrode (type 35−37) and a reference mercury (I) sulfate electrode were inserted into the reaction mixture. The potentiometric measurements have been carried out using digital multimeter METEX M-4660A and processed by a PC. The solution was stirred magnetically with a Teflon-coated stirrer (length 2.0 cm, diameter 0.8 cm), and the stirring rate has been changed between 50 and 600 rpm.

Procedures. The reactants were introduced into the reactor with rotating stirrer in the following order: first aqueous solution of H_2SO_4, next $NaBrO_3$, and finally the solution of phenol. Simultaneously, the potentiometric measurements have been started. The initial reactant concentrations were equal to 0.025 M $NaBrO_3$, 4×10^{-3} M phenol, and 1.5 M H_2SO_4.

Results

Experimental Results. In addition to simple oscillations,[24,25] the system BrO_3^-−phenol−H_2SO_4 exhibits an astonishing variety of dynamic behaviors including three stationary states and two oscillatory regimes, dual-frequency and dual amplitude oscillations, etc. Typical changes in the potential of the platinum redox electrode and a bromide-selective electrode in the stirred batch experiment are plotted in Figure 1. After a short induction period ∼200 s, the system switches to the oscillatory regime with an apparent period about 65 s. After the series of five oscillations, a nonoscillatory period follows, and next, the second series of 22 oscillations appears, with an apparent period about 165 s. Next oscillations decay and the system approaches a stationary state.

Sequential oscillations are very sensitive to stirring in a batch reactor. Figure 2 illustrates the influence of the rate of stirring on the dynamics of the system. The most reproducible results have been obtained at 50 and 100 rpm. At these rates, a number of oscillations in the second series is maximal. As the stirring rate increases, a number of oscillations in second series decreases from ∼22 (at 50−100 rpm), through ∼6 (at 300 rpm), to ∼0 (at 600 rpm). An increase of the initial phenol concentration increases the sensitivity of the system to the rate of stirring. We have not observed the second oscillatory regime at the stirring rates higher than 150 rpm in the system containing the 2-fold concentration of phenol.

The surprising phenomenon is observed, if the stirring is stopped just at the end of the second oscillatory region, when

---

* To whom correspondence should be addressed.

† Comenius University.

‡ Polish Academy of Sciences.

10.1021/jp0212646 CCC: $25.00

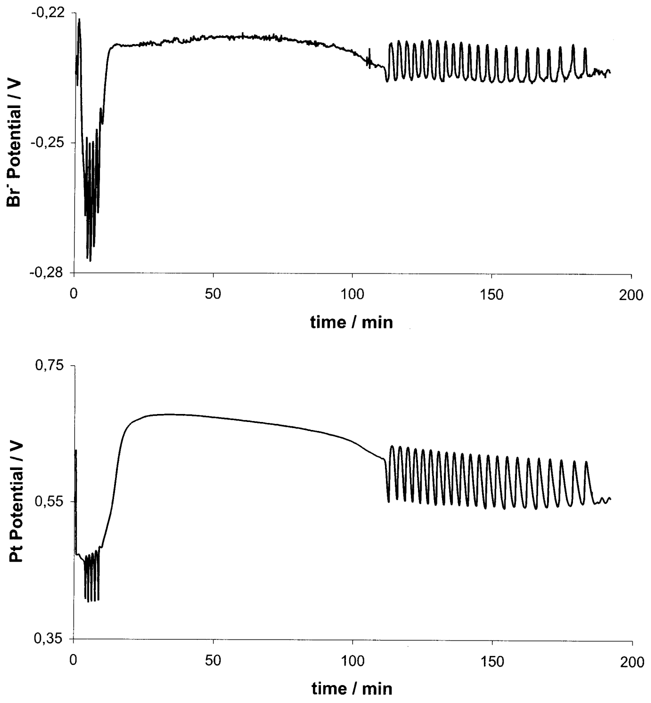

Figure 1. Time oscillations of potentials of Pt (a) and Br$^-$-selective (b) electrodes for initial concentrations of [NaBrO$_3$] = 0.025 M, [H$_2$SO$_4$] = 1.5 M, and [phenol] = 4 × 10^{-3}. Temperature t = 25 °C, 50 rpm.

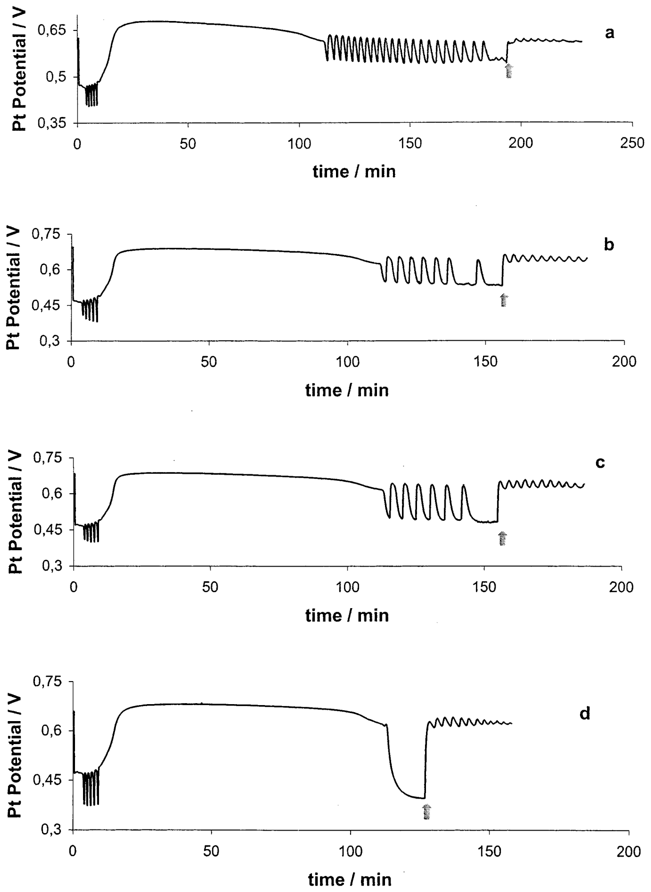

Figure 2. Time dependencies of Pt-electrode potential at stirring rates: (a) 50, (b) 200, (c) 400 and (d) 600 rpm. Initial concentrations as in Figure 1. The arrows indicate where the stirring was stopped.

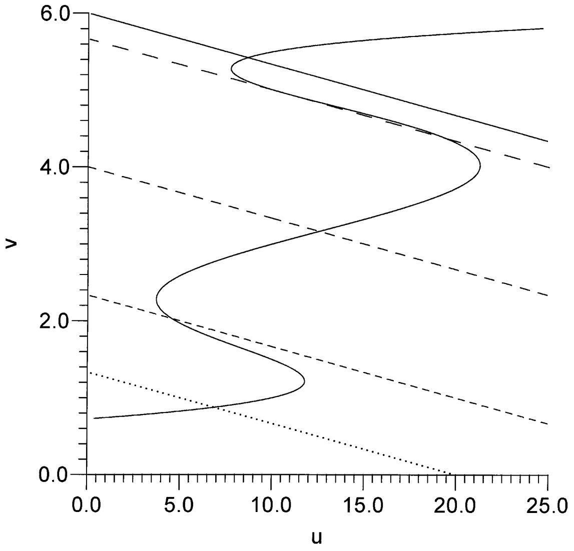

Figure 3. Nullcline for v and changes of the position of the nullcline for u at selected values of q: 0.0, the point line; 15.0, the short dashed line; 25.0, the middle line; 65.0, the long dashed line; and 70.0, the continuous line. The following values of the parameters are assumed: ν_1 = 1.0, ν_2 = 1.5, ν_3 = 3.0, ν_4 = 5.0, ν_5 = 5.5, a = 10.0, b = 20.0, b_1 = 1.0, and b_2 = 15.0.

the systems enters a nonoscillatory low potential steady state (see Figure 2). The third series of very regular but small amplitude oscillations reappears. At the moment, we cannot explain this effect. Let us mention that the extreme cases of ideally mixed, homogeneous systems and of unmixed ones are much better understood than the intermediate case of partially mixed systems. Many systems in nature like oceans, atmosphere, and living cells are important examples in which chemical reactions with nonlinear kinetics occur under conditions of imperfect mixing.

Model. The easiest and the simplest way to ensure the appearance of sequential oscillations may be based on the following general concept. Let us take into account a two-variable (u, v) dynamical system, which nullcline for v consists of five branches and has a shape of two joined and arranged one over another S (see Figure 3). A vector field for the variable v is directed in such a way that the lower and upper branches of the lower S and the lower and the upper branches of upper S are attracting, whereas the two middle branches of both S are repelling. The upper branch of the lower S and the lower branch of the upper S form one attracting branch. A nullcline for u can have arbitrary shape provided it intersects the nullcline for v in one place only giving a position of a stationary state.

Let us assume that a position of the nullcline for u is controlled parametrically by a third variable q in such a way that its changes cause a displacement of the stationary state along all five branches of the nullcline for v. If the intersection point of the nullclines moves along the lower attracting branch of lower S, the subsystem u,v will evolve along a stable stationary state. This interval of time corresponds to an induction period for first sequence of oscillations. Its duration may be controlled by a dynamics of $q(t)$, i.e., by interval of time when q attains a value (say q_a) at which the intersection point of the nullclines shifts from the stable to the unstable branch of the lower S.

At further changes of $q(t)$, the nullcline for u intersects the middle repeling branch of lower S. The intersection point of the nullclines becomes an unstable stationary state, and oscillations in the subsystem u,v start. The variables u,v will oscillate up to a moment of time when $q(t)$ attains a value (say q_b) at which the intersection point of the nullclines reaches the stable branch formed by the upper branch of the lower S and the lower branch of the upper S. A lifetime of these oscillations is controlled by the difference ($q_b - q_a$) at which the nullcline for u intersects the unstable branch. A number of oscillations is controlled by their lifetime and by the dynamics of subsystem u,v.

For $q(t) > q_b$ the nullcline for u intersects the attracting branch formed by the upper branch of the lower S and the lower branch of the upper S giving a stable stationary state for the subsystem u,v moving according to the stationary state. The nonoscillatory period appears. When $q(t)$ attains a value (say q_c), at which the intersection point of the nullclines shifts to the lower, the repelling branch of the upper S the nonoscillatory period finishes. A duration of the nonoscillatory period is controlled by the dynamics of $q(t)$ from the beginning to the end of the branch. During this movement, the subsystem u,v does not oscillate, but u and v change along the moving position of the attracting stationary state. The duration of the nonoscillatory period is controlled by the difference (q_c, q_b) and by a length of the attracting branch of the nullcline of v.

For $q(t) > q_c$, the intersection point of the nullclines shifts to the repelling branch of the upper S and moves along it. The stationary state becomes repelling, and the next series of oscillations of u and v starts. The lifetime of this series is determined by a time interval at which $q(t)$ approaches a value (say q_d), at which the intersection point of nullclines shifts from the repelling to the attracting branch of the upper S.

The stationary state becomes attracting again, and oscillations decay for $q(t) > q_d$. To ensure the appropriate shift of the nullcline for u, it is necessary and sufficient that the variable q evolves from an initial value $q_0 < q_a$ to an asymptotic value $q_\infty > q_d$.

The above scenario can be accomplished for example by the following equations:

$$\frac{dv}{dt} = r[u - (v - v_1)(v - v_2)(v - v_3)(v - v_4)(v - v_5) - a] \tag{1}$$

$$\frac{du}{dt} = b + b_1 q - b_2 v - u \tag{2}$$

$$\frac{dq}{dt} = g(q_\infty - q) \tag{3}$$

where v_1, v_2, v_3, v_4, and v_5 are the parameters which determine lengths of the repelling branches of the lower and upper S, as well as the length of the attracting branch being the connection of the upper branch of the lower S with lower branch of the upper S, r is the parameter which determines a relative rate of the vector field for v as compared with u, a is a parameter allowing to shift a range of changes of u, b_1 determines the influence of q on a position of the nullcline for u, b and b_2 determine the position of the nullcline for u, and g determines the exponential growth of $q(t)$ from the initial value q_0 to the asymptotic value q_∞.

The results of numerical integrations of eqs 1−3 are show in Figure 4. For assumed values of the parameters, the numbers of oscillations in the both sequences are the same as in the experiment shown in Figure 1.

Of course, the qualitative assumptions of the model may be satisfied by many other equations, but eqs 1−3 are the simplest ones. It is noteworthy that only eq 1 is nonlinear and that the dynamics of q does not depend on remaining variables, so the variable q plays a role of the parameter. Moreover, the sequences of oscillations presented in Figure 2a−c may by also modeled. A nullcline for v should consist of four stable branches separated by three unstable ones, and an evolution the variable q shifts the nullcline for u along all branches of the nullcline for v.

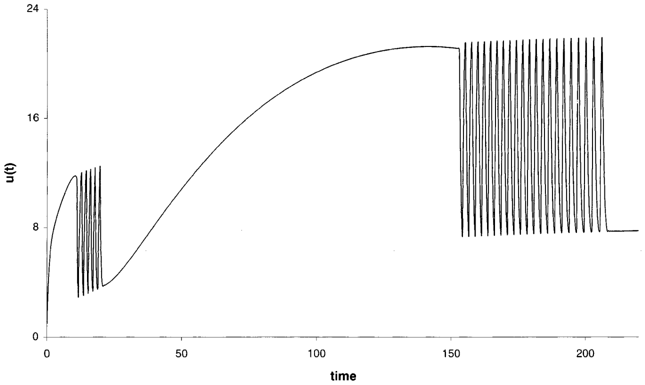

Figure 4. Changes of u in time for the values of the parameters the same as in Figure 3 and $r = 5.0$, $g = 0.015$, and $q_1 = 70.0$ and for the following initial values: $v(0) = 1.0$, $u(0) = 1.0$, and $q(0) = 0.0$.

Discussion

The sequential oscillations in the "Racz" system that is the BZ system with a high malonic acid/bromate ratio in 3 M sulfuric acid have been explained through the consecutive appearance of two oscillators. The first series of oscillations appears to be due to the malonyl radical-controlled oscillator,[11,12] whereas the second series observed after a nonoscillatory period corresponds to the bromide-controlled oscillations.

There are known attempts to model sequential oscillations in the "Racz" system based on realistic schemes (modified Radicalator).[12] The results of numerical solutions of corresponding kinetic equations show the two series of oscillations separated by nonoscillatory period. The first series of oscillations appears without an induction period and is radical-controlled. The next series is bromide-controlled. These results are in qualitative agreement with experiment.

In our uncatalyzed BrO_3^-−phenol system, we assume that we have subsystems (A + B) and (C + B) coupled through the common reactant B (bromate). A is phenol, and C is an oxidation/bromination product or intermediate of the A + B reaction. The product of the first oscillatory subsystem may serve as the substrate for the second oscillatory subsystem. During the nonoscillatory period, phenol is oxidized by bromate, and the product of the oxidation might be pyrocatechol.[25] Pyrocatechol may be a substrate responsible for the second oscillations. We have tested pyrocatechol (1,2-dihydroxybenzene) in order to support our assumption that during the nonoscillatory period phenol and bromophenols are broken down into pyrocatechol and that oscillations in the second oscillatory regime are initiated by the second oscillator containing pyrocatechol as the reductant. The pyrocatechol may behave in an oscillatory manner with bromate, but the conditions are rather different from those applied for phenol. For example, the composition of 0.05 M pyrocatechol, 0.096 M $NaBrO_3$, and 0.9 M H_2SO_4 showed 14 oscillations after above 180 min induction period at temperature of 25 °C and 50 rpm. The oscillations with pyrocatechol as a subtrate were very sensitive to stirring.

Although the presented model has not direct relation to the experimental system studied in the present paper, it may be treated as a generic model for sequential oscillations. However, there are some hints which may be useful in qualitative understanding of chemical mechanism of sequential oscillations. If one assumes that sequential oscillations are generated by two various chemical oscillators, then the variable v in the model can be treated as a some combination (for example sum) of concentrations of autocatalytic components operating in both oscillators. An exhaustion of the activator reacting during the first series of oscillations is accompanied by a delayed production of the activator of the second series. The variable *u* plays the role of an inhibitor for both oscillators. The kinetics the inhibitor depends on concentrations of other phenol derivatives, whose accumulation is described by the variable *q*.

We believe that our model will be useful in qualitative description of sequential oscillations observed in other chemical systems.

Acknowledgment. This work was supported by Grant No. 1/7301/20 from the Scientific Grant Agency of MESR.

References and Notes

(1) *Oscillations and traveling waves in chemical systems;* Field, R. J., Burger, M., Eds.; Wiley-Interscience: New York, 1985.

(2) Epstein, I. R.; Pojman, J. A. *An Introduction to Nonlinear Chemical Dynamics*; Oxford University Press: New York, 1998.

(3) Hudson, J. L.; Hart, M.; Marinko, D. *J. Chem. Phys.* **1999**, *71*, 1601.

(4) Maselko, J.; Swinney, H. L. *J. Chem. Phys.* **1986**, *85*, 6430.

(5) Scott, S. K. *J. Chem. Phys.* **1991**, *94*, 1134.

(6) Wang, J.; Sørensen, P. G.; Hynne, F. *J. Phys. Chem.* **1994**, *98*, 725.

(7) Roux, J. C.; DeKepper, P.; Boissonade, J. *Phys. Lett.* **1983**, *97 A*, 168.

(8) Strizhak, P.; Kawczyński, A. L. *J. Phys. Chem.* **1995**, *99*, 10830.

(9) Rachwalska, M.; Kawczyński, A. L. *J. Phys. Chem. A* **1999**, *103*, 3455.

(10) Körös, E.; Orbán, M. *Nature (London)* **1978**, *273*, 371.

(11) Försterling, H. D.; Murányi, S.; Noszticzius, Z. *J. Phys. Chem.* **1990**, *94*, 2915.

(12) Misra, G. P.; Washington, R. P.; Pojman, J. A. *J. Phys. Chem. A* **1998**, *102*, 612.

(13) Heilweil, J.; Henchman, M. J.; Epstein, I. R. *J. Am. Chem. Soc.* **1979**, *101*, 3698.

(14) Rastogi, R. P.; Misra, G. P.; Das, I.; Sharma, A. *J. Phys. Chem.* **1993**, *97*, 2571.

(15) Wittman, M.; Stirling, P.; Bódiss, J. *Chem. Phys. Lett.* **1987**, *141*, 241.

(16) Srivastava, P. K.; Mori, Y.; Hanazaki, I. *J. Phys. Chem.* **1991**, *95*, 1636.

(17) Li, H.; Huang, X. *Chem. Phys. Lett.* **1996**, *255*, 137.

(18) Pal, S. C.; Banerjee, R. S. *J. Indian Chem. Soc.* **1999**, *76*, 339.

(19) Adamčíková, L'.; Ševčík, P. *React. Kinet. Catal. Lett.* **1995**, *56*, 137.

(20) Adamčíková, L'.; Farbulová, Z.; Ševčík, P. *New J. Chem.* **2001**, *25*, 487.

(21) Hlaváčová, J.; Ševčík, P. *J. Phys. Chem.* **1994**, *98*, 6304.

(22) Ševčík, P.; Adamčíková, L'. *Chem. Phys. Lett.* **1988**, 146, 419.

(23) Pojman, J. A.; Dedeaux, H.; Fortenberry, D. *J. Phys. Chem.* **1992**, *96*, 7331.

(24) Tockstein, A.; Handlířová, M. *Collect. Czech. Chem. Commun.* **1982**, *47*, 2454.

(25) Orbán, M.; Szókán, G. *ACH Model Chem.* **1995**, *132*, 179.