

Dynamic behavior during the oxidation of phenol with bromate in a closed reactor

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The uncatalyzed system BrO_3^- -phenol- H_2SO_4 exhibits an astonishing variety of dynamic behavior including three stationary and two oscillatory states, dual-frequency and dual-amplitude oscillations and aperiodic oscillations in a closed, stirred batch reactor. For an explanation of the sequential oscillations we assume that we have subsystems (A + B) and (C + B) coupled through the common reactant B (bromate). A is phenol and C is the oxidation/bromination product of the A + B reaction. A significant stirring rate and viscosity effect is observed. Stationary complex patterns may spontaneously develop when a solution containing phenol, BrO_3^- and H_2SO_4 is poured into an open Petri dish.

The Belousov-Zhabotinskii (BZ) reaction is one of the best known oscillating chemical reactions.¹ It includes many different chemical systems, all of which contain bromate ion and a substrate in strongly acidic solution and otherwise fall into two major classes: catalyzed and uncatalyzed. Catalyzed systems contain a metal ion catalyst and an aliphatic organic substrate, which is oxidized and brominated by bromate ion as the metal ion cycles between two oxidation states, such as Ce(IV) and Ce(III). Uncatalyzed systems contain no metal ion and substitute more reactive aromatic compounds (mainly phenol and aniline derivatives) for the aliphatic substrate. The source of the redox potential oscillations is not as clear as in catalyzed systems. Uncatalyzed bromate^{2,3} oscillators (UBO) were discovered in 1977–78 and many systems were characterized.⁴ Orbán, Körös and Noyes⁵ proposed a mechanism (OKN) for these uncatalyzed class of oscillations and Herbine and Field⁶ modified and made a computer simulation of the OKN mechanism. In later years an extended mechanism⁷ was suggested, and also, reduced models were published in the literature.⁸ The prototype of the uncatalyzed oscillatory reactions is the bromate-phenol system, which has been investigated in detail.^{9,10} Thin layer chromatography¹⁰ and HPLC techniques¹¹ were used to analyze the reaction intermediates and products.

The opinion that, in general, many fewer oscillations appear in uncatalyzed^{1,7} than in catalyzed systems under batch configuration does not seem to be correct.

We have made a rather unexpected observation: the phenol- BrO_3^- system exhibits a sequential, dual-frequency oscillation regime. After a few oscillations, a nonoscillatory period follows and after that a second series of oscillations appears.

Experimental

Sulfuric acid, NaBrO_3 , phenol, gelatin and hydroquinone were of commercial analytical quality (Merck, Fluka). A sodium silicate solution (Merck) containing 25.5–28.5% SiO_2 was employed. Stock solution containing 4.05 wt% sodium silicate was prepared by dissolving the appropriate volume of the sodium silicate in doubly distilled water. The solution was boiled for several minutes and kept hot while stirring vigorously by means of an ultrasonic compact cleaner for about 30

min. After cooling down to room temperature, the solution was filtered and the evaporated water was replenished.

The experiments were carried out in a thermostatted cylindrical glass reaction vessel (diameter 3.5 cm, height 7.5 cm). It contained 20 ml of reaction solution and was closed with a rubber stopper through which a commercial indication platinum macroelectrode (0.5×0.8 cm) and a $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode as a reference electrode were inserted into the solution. The potentiometric measurements were carried out using a Radelkis OH-105 polarograph. The solution was stirred magnetically with a Teflon-coated stirrer (length 2.0 cm, diameter 0.8 cm). The reactants were introduced into the reaction vessel in the order: aqueous solution of H_2SO_4 , NaBrO_3 and finally the solution of phenol with which the oscillation reaction was started.

Results and discussion

Oscillation behavior

The uncatalyzed BrO_3^- -phenol reaction in aqueous H_2SO_4 exhibits a rich dynamic behavior that has not been reported before in this system. We repeated the experiment of Orbán and Szókán.¹¹ The mentioned authors reported only the first oscillatory regime because they interrupted their measurement after 40 min from the beginning of the reaction. We allowed the reaction to proceed for a longer time and our typical result is shown in Fig. 1. After a short induction period (330 s), the system bifurcates into an oscillatory regime with an average frequency of oscillation of $7.43 \times 10^{-3} \text{ s}^{-1}$. Subsequently the system comes to a nonoscillatory period (95 min) and bifurcates again into another oscillatory regime, which exhibits oscillations with a frequency of $1.91 \times 10^{-3} \text{ s}^{-1}$. The system finally bifurcates to a stable branch once again. During the induction period (IP) the solution is yellow. First oscillations are accompanied by a change of color from yellow to orange and to brown and turbidity is formed. During the nonoscillatory period the turbidity disappears and the transition to the second series of oscillations is accompanied by a change of color from brown to pale yellow.

Characteristics of the system such as the number and frequency of oscillations, nonoscillatory period, *etc.*, are dependent on the initial conditions (concentrations, temperature,

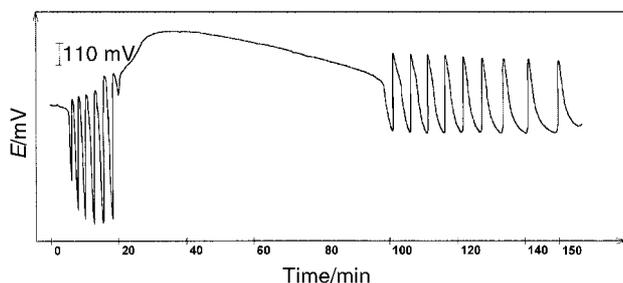


Fig. 1 Plot of redox potential vs. time showing sequential oscillations in a BrO_3^- -phenol- H_2SO_4 system. Conditions are the same as in ref. 11. Initial concentrations: $[\text{phenol}]_0 = 0.003 \text{ M}$, $[\text{BrO}_3^-]_0 = 0.025 \text{ M}$; $[\text{H}_2\text{SO}_4]_0 = 1.0 \text{ M}$, temperature 25°C , 100 rpm.

stirring). Sequential oscillations in the BrO_3^- -phenol- H_2SO_4 system have been obtained in the concentration ranges given in Table 1. The duration of the nonoscillatory period (NP) increases with increasing concentration of H_2SO_4 and BrO_3^- and decreases with increasing concentration of phenol.

Fig. 2 illustrates the influence of different H_2SO_4 concentrations at a stirring rate of 100 rpm. The system is sensitive to changes in the sulfuric acid concentration. The sequential oscillations could be observed only in a certain concentration range of H_2SO_4 , as shown in Table 1. When $[\text{H}_2\text{SO}_4]_0 < 1.2$

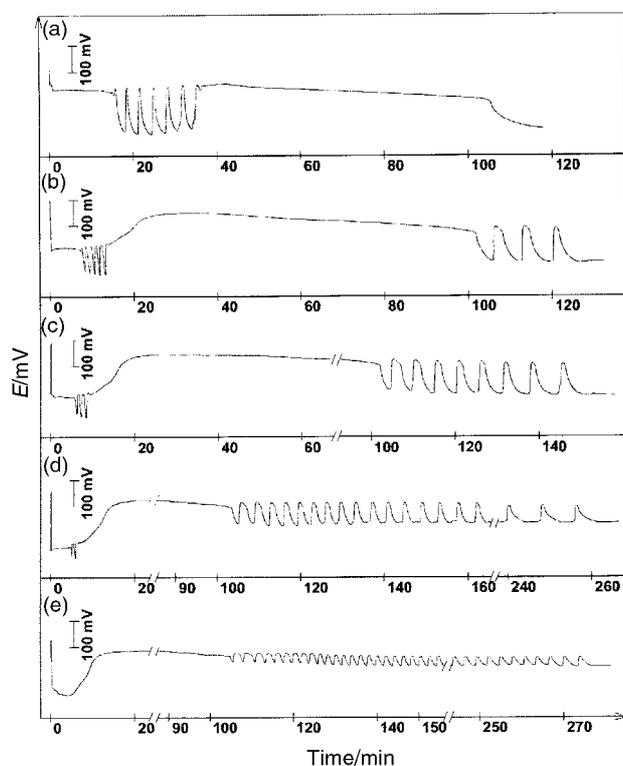


Fig. 2 Dependence of oscillatory characteristics on sulfuric acid concentrations. System: $[\text{phenol}]_0 = 0.008 \text{ M}$, $[\text{BrO}_3^-]_0 = 0.025 \text{ M}$ and $[\text{H}_2\text{SO}_4]_0 \cdot [\text{H}_2\text{SO}_4]_0 =$ (a) 0.8, (b) 1.3, (c) 1.5, (d) 1.7, (e) 2.0 M. $T = 25^\circ\text{C}$, 100 rpm.

Table 1 Dependence of oscillatory characteristics on initial reactant concentrations^a

Concentration/M	IP/min	NP/min	No. of first oscillations	No. of second oscillations
H_2SO_4^b	1.3–1.7	7.23–5.25	86.3–98	5–3
NaBrO_3^c	0.024–0.04	6–2.5	93–107	3–7
Phenol ^d	4.10^{-3} – 8.10^{-3}	3.5–6	100.3–94.3	6–3

^a 25°C ; 100 rpm. ^b 0.025 M NaBrO_3 ; 0.008 M phenol. ^c 1.5 M H_2SO_4 ; 0.008 M phenol. ^d 1.5 M H_2SO_4 ; 0.025 M NaBrO_3 .

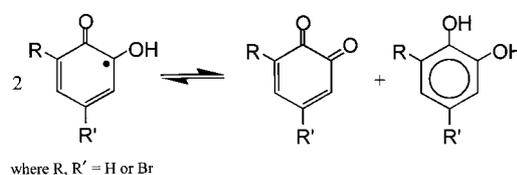
M the second oscillatory regime was completely inhibited and only the first oscillatory regime was found. When $[\text{H}_2\text{SO}_4]_0 > 1.8 \text{ M}$, the first series of oscillations was inhibited and only the second series of oscillations was found with the number of oscillations being 75 and more.

The frequency of oscillation and the duration of the non-oscillatory period are quite sensitive to temperature. The NP decreases and the frequency of oscillation increases with temperature. Plots of $\log(\text{frequency and } 1/\text{NP})$ vs. $1/T$ are straight with apparent activation energies of about 64.5 and 70.7 kJ mol^{-1} , respectively. These activation energies fall within the range for BZ reactions of between 65 and 75 kJ mol^{-1} . Previously¹² it has been found that the activation energy of the classical BZ oscillations was independent of the nature of the catalyst. Later¹³ the influence of substrate composition and initial reagent concentrations on activation energies in closed Ce-ion catalyzed BZ reactions was reported. We suggest that our oscillation parameters are controlled to a significant extent by the rate of reaction between bromide ions and bromate ions to form hypobromous acid and bromous acid and that other reactions that consume bromide ions should be considered too.

The effects of addition of acrylamide, an efficient radical scavenger, to the oscillatory bromate-phenol system have been investigated. Introducing $5 \times 10^{-5} \text{ M}$ acrylamide completely inhibited the first oscillatory regime only. The second oscillatory regime was observed even at high concentration of acrylamide (10^{-3} M). This indicates that the first type of oscillations occurs by a radical mechanism. A possible intermediate of the oxidation is a semiquinone radical (unbrominated or brominated), which may disproportionate to quinone and dihydroxybenzene (Scheme 1).

Of course, the reverse of this reaction is also nearly certain to occur. The semiquinone may be considered to act as a traditional, one-electron-transfer catalyst in the bromate-phenol reaction, like Ce(IV)/Ce(III) and Mn(III)/Mn(II) in the catalyzed BZ-type oscillatory systems.

Sequential or dual-frequency oscillations in a closed reactor were observed in BZ reaction mixtures containing mixed substrates^{14–22} or in the UBO system BrO_3^- -aniline- H_2SO_4 .²³ The system BrO_3^- -phenol- H_2SO_4 exhibits an astonishing variety of dynamic behavior including three stationary and two oscillatory states, dual-frequency and dual-amplitude oscillations, aperiodic oscillations, etc. It is known that coupled oscillators exhibit such behavior. In a chemically coupled system, the subsystems are coupled through chemical reactions between their reactants, products or intermediates. For an explanation of the sequential oscillations in our 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 inter-



Scheme 1

mediate of the A + B reaction. The product of the first oscillatory subsystem may serve as the substrate for the second oscillatory subsystem. Chemical coupling can be extremely difficult to characterize, since it requires a knowledge of all possible reactions between components of the two subsystems.

Orbán *et al.*¹¹ and Tockstein *et al.*¹⁰ thoroughly analyzed the intermediates and products formed during the periodic reaction between phenol and bromate. They concentrated only on the first oscillatory regime and samples for analysis were taken from the mixture before, during and after the first oscillatory regime. They identified 1,2-benzoquinone, 1,2-dihydroxybenzene, 2-bromophenol, 4-bromophenol, 2,4-dibromophenol, 2,4,6-tribromophenol,¹¹ 2,6-dibromo-1,4-benzoquinone, 2-bromo-1,4-benzoquinone, 1,4-benzoquinone, 1,4-dihydroxybenzene and 4-bromo-1,2-benzoquinone.¹⁰

Orbán and Szókán¹¹ tested some of the intermediates to see whether they can also act as oscillatory substrates during their reaction with bromate. The mono- and di-bromophenols were found to oscillate under the same experimental conditions as phenol does. However, a significant shortening of the IP was observed with the bromophenols, indicating that they are intermediates in the bromate-phenol oscillator. Bromination mainly takes place during the IP. The 1,2-dihydroxybenzene may behave in an oscillatory manner with bromate but the conditions are rather different from those applied for phenol.¹¹ We have tested hydroquinone in order to support our assumption that during the nonoscillatory period, phenol and bromophenols are broken down into hydroquinone (H₂Q) and that oscillations in the second oscillatory regime are initiated by the second oscillator containing hydroquinone as the reductant. We were unable to find any set of conditions that gave regular oscillations in the system BrO₃⁻-H₂Q-H₂SO₄. However, Nair *et al.*²⁴ have reported chemical oscillations in this system but the oscillatory reaction was strongly inhibited by stirring of the reaction mixture.

Our sequential oscillations are also very sensitive to stirring. In the absence of stirring, no regular oscillations were recorded. The most reproducible sequential oscillations appear at 100 rpm. The second oscillatory regime was inhibited at stirring rates in excess of 150 rpm. Noszticzus *et al.*²⁵ have interpreted the effects of stirring in terms of diffusion-controlled reactions and hydrodynamic turbulence. Provided that in the UBO system the reaction of PhO[•] with BrO₂[•] radicals or the reaction of HQ[•] with BrO₂[•] ($k = 8 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)²⁶ is diffusion controlled, the change of the turbulent diffusion coefficient will result in a proportional change of the rate constant for that reaction. An increase of the effective diffusion coefficient ($D_{\text{eff}} = D_0 + D_{\text{turb}}$) will result in an increase of the rate constant. The diffusion coefficient is inversely proportional to the viscosity of the solution. Increasing the rate of stirring will increase the rate constant of a diffusion-controlled reaction while increasing the viscosity of the solution will decrease it. One might expect that performing the experiment in a higher viscosity solution would generate oscillations also at higher stirring rates (not only at 100 rpm). This agrees with our experimental observations and the result can be seen in Fig. 3. The viscosity of the UBO system with addition of 1% SiO₂ was changed from 1.14 cP (without SiO₂) to 1.19 cP.

Effect of viscosity

The values of the viscosity of the UBO system with addition of SiO₂ were changed from 1.14 to 1.7 cP (5.8% SiO₂) and with addition of gelatin from 1.14 to 1.26 cP (0.67% gelatin). In this range of viscosities, the effects of added SiO₂ in the initial reaction mixture (Fig. 4) were qualitatively similar to those of added gelatin. The length of the IP and the number of oscillations increase, as [SiO₂]₀ or [gelatin]₀ increase. As [SiO₂]₀ or [gelatin]₀ are increased still further the number of oscillations decreases. The oscillations are suppressed in the

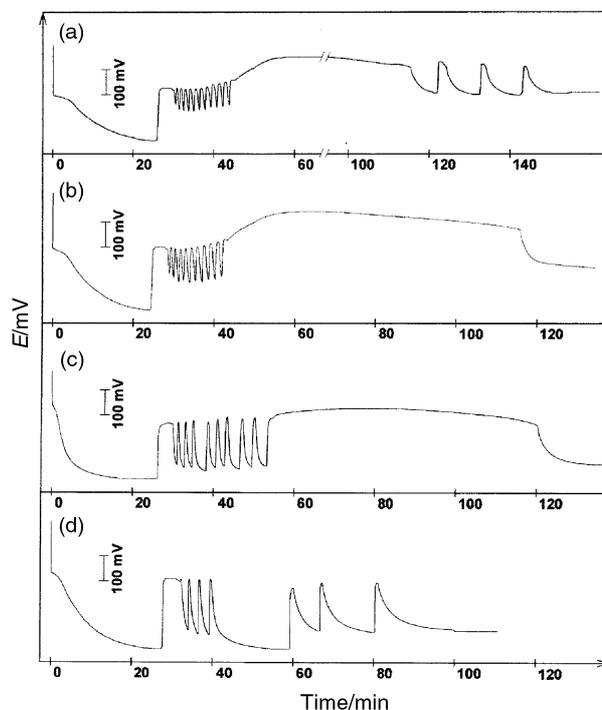


Fig. 3 Potential traces for four different stirring rates with 1% SiO₂ added to the initial reaction mixture: (a) 100, (b) 200, (c) 400, (d) 800 rpm. Initial concentrations: [phenol]₀ = 0.008 M, [BrO₃⁻]₀ = 0.025 M; [H₂SO₄]₀ = 1.5 M, T = 25 °C.

UBO solution containing more than 6% SiO₂ or more than 0.6% gelatin.

Effect of oxygen

The reaction solutions were either open to air or in a nitrogen atmosphere. The solution containing bromate and an aqueous solution of H₂SO₄ was deoxygenated by bubbling with purified nitrogen. N₂ was bubbled through the solution for at least

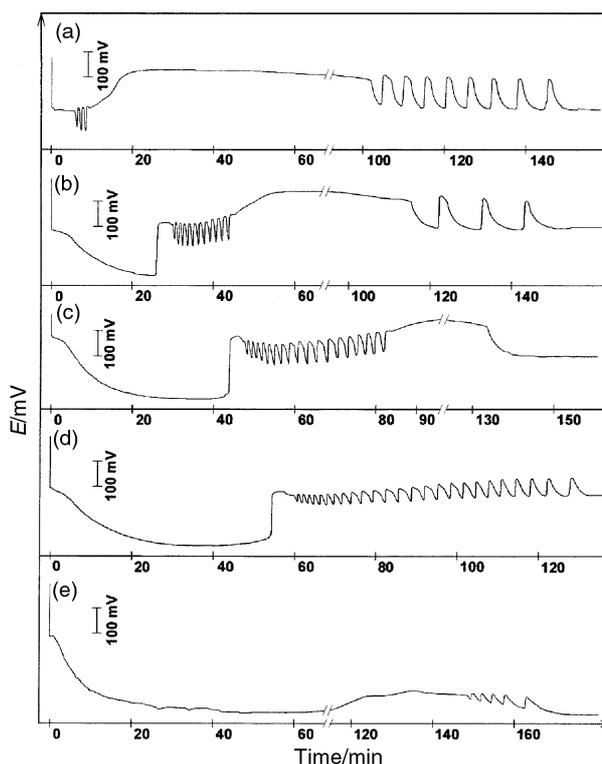


Fig. 4 Dependence of oscillatory characteristics on SiO₂ concentrations. Initial conditions: [phenol]₀ = 0.008 M, [BrO₃⁻]₀ = 0.025 M; [H₂SO₄]₀ = 1.5 M. [SiO₂]₀ = (a) 0, (b) 1.0, (c) 1.74, (d) 2.5, (e) 5.8%. T = 25 °C, 100 rpm.

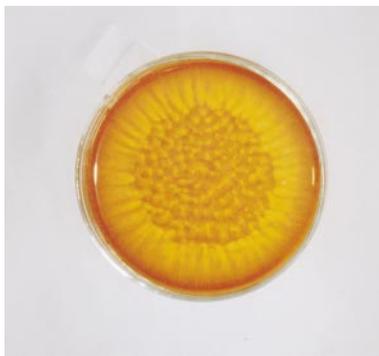


Fig. 5 Pattern formation in the phenol–sulfuric acid–bromate system at 35 min after mixing. Initial reactant concentrations: $[\text{phenol}]_0 = 0.015 \text{ M}$, $[\text{BrO}_3^-]_0 = 0.021 \text{ M}$; $[\text{H}_2\text{SO}_4]_0 = 1.3 \text{ M}$. Thickness of the layer: 1.8 mm.

20 min ($100 \text{ ml of N}_2 \text{ min}^{-1}$). Finally, a previously deoxygenated solution of phenol was injected into the reaction vessel. During the measurements a nitrogen gas flow was fed continuously above the solution. Measurements were done at two different stirring rates. A study of the UBO system in the presence and in the absence of oxygen showed that identical time-courses for the reactions were obtained, thus demonstrating that the bromate–phenol– H_2SO_4 system is not oxygen sensitive.

Pattern formation in the phenol– BrO_3^- system

In some UBO systems with phenol or aniline derivatives as substrates, highly colored intermediates (semiquinones) form periodically during the reaction, allowing visual observation of the pattern formation.^{27,28} In this work, we present spatial pattern formation in a system containing phenol, bromate and H_2SO_4 in aqueous solution and in gel systems (SiO_2 , gelatin). In gel systems the influence of hydrodynamic convection on the pattern formation is usually suppressed. A thoroughly mixed solution containing 1.3 M H_2SO_4 ; 0.021 M NaBrO_3 and 0.015 M phenol was poured into a Petri dish to make a layer of 1.8 mm. After a few minutes, pattern formation became visible in the undisturbed and uncovered solution. The development of the pattern was accompanied by the formation of a precipitate. Three different shapes—dots, lines and circles—are mixed in the same pattern (Fig. 5). After its emergence, the pattern remains stationary for a time of the order of 5 h before it gradually fades.

The optimal composition for generating the patterns in a silica gel system is: 1.3 M H_2SO_4 ; 0.03 M NaBrO_3 ; 0.01 M phenol and 1.7% SiO_2 . The thickness of the fluid layer is 1.5 mm. Typical patterns similar to those in Fig. 5 appeared and developed in the SiO_2 system. The development of the pattern lasted approximately 200 min and did not occur after gelation.

The arising patterns are stationary in time and are generated through hydrodynamic instabilities. If the Petri dish is protected from air with a glass cover, no pattern formation is

seen in the reaction mixture. This indicates that surface effects play a fundamental role in the pattern formation. The patterns are not the result of a purely physical process, but rather arise from a chemically driven convective instability. This instability depends on the chemical generation of Br_2 and appears to be primarily a surface phenomenon.

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