EFFECTS OF CHLORIDE AND BROMIDE IONS ON SEQUENTIAL OSCILLATIONS IN THE UNCATALYZED BROMATE OSCILLATOR

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The uncatalyzed system BrO_3^-–phenol–H_2SO_4 exhibits an astonishing variety of dynamic behaviour, including sequential oscillations in a closed, stirred batch reactor. The effect of initial addition of chloride and bromide ions on a sequential oscillating system has been studied. Various results were obtained, depending on the initial chloride and bromide concentrations. Increasing the concentration of chloride ions (from 5×10^{-5} to 6×10^{-4} mol dm^{-3}), the parameters of sequential oscillations changed. The number of first oscillations increased from 4 to 21 and their amplitude decreased. The duration of the non-oscillatory period and the number of second oscillations decreased from 96 to 26 min and from 8 to 1, respectively. In the concentration range 3.5 mmol dm^{-3} < $[Br^-]_0$ < 8.0 mmol dm^{-3}, the system displays a dual-frequency, dual-amplitude and aperiodic oscillations with a transition period between high- and low-frequency oscillations. The induced oscillations were also observed when the system was perturbed by chloride or bromide ions. The oxidation of pyrocatechol with bromate is an autocatalytic reaction; the rate constants corresponding to the uncatalyzed and catalyzed reactions were evaluated and used in numerical simulations.

Keywords: Uncatalyzed bromate oscillator; Sequential oscillations; Phenol; Pyrocatechol; Autocatalysis.

The Belousov–Zhabotinskii (BZ) reaction is one of the best-known oscillating chemical reactions[1,2]. It includes many different chemical systems, all of them contain bromate ions and a substrate in strongly acidic solution; otherwise, they fall into two major classes: catalyzed and uncatalyzed. The catalyzed systems contain a metal ion catalyst and an aliphatic organic substrate that is oxidized and brominated with bromate ions as the metal ion cycles between two oxidation states, *e.g.*, Ce(IV) and Ce(III). Uncatalyzed systems contain no metal ion and replace more reactive aromatic compounds (mainly phenol and aniline derivatives) with an aliphatic substrate. The source of the redox potential oscillations is not such clear as that in the catalyzed systems. Uncatalyzed bromate oscillators (UBO) were discovered

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in 1977 and 1978; since that time, many systems have been characterized[1,3,4]. The behaviour of the uncatalyzed bromate oscillator has been determined experimentally also in a flow reactor[5,6]. Uncatalyzed oscillators are mechanistically simpler than catalyzed ones. They are not complicated either by the coordination chemistry of the metal-ion catalyst or by degradation of the organic material to CO_2. On the other hand, however, chemical conditions are extremely complex due to parallel oxidation and bromination reactions.

Sequential oscillations (*i.e.* oscillations with two oscillatory intervals separated by a no oscillatory one) in a batch reactor have been observed in (i) the "Rácz" system[7,8], (ii) mixed-reactants BZ systems[9–11] and (iii) the BZ systems with aromatic compounds as a single organic reactant with a metal catalyst[12–14]. We have made a rather unexpected observation: two-component systems, *viz*. phenol–BrO_3^- (refs[15,16]) and aniline–BrO_3^- (ref.[17]), exhibit a sequential dual-frequency oscillation regime. After a few oscillations, a non-oscillatory period follows and, after that, a second series of oscillations appears in a closed, stirred batch reactor.

The effects of Cl^- and Br^- on the oscillations of the catalyzed BZ reaction have been studied in a batch reactor by several workers[13,18–23]. Jacobs and Epstein[18] showed, contrary to the generally accepted belief, that addition of chloride to the BZ system did not permanently suppress the oscillations. In the investigations carried out with chloride added into the classic BZ system (with malonic acid as the organic substrate), only an increase in the induction period could be observed. Chloride was assumed to be an inhibitor of the autocatalytic oxidation of Ce^{3+} with bromate in sulfuric acid solution; an inorganic subset of the BZ reaction. Muranyi and Försterling[19], however, reported chloride-induced oscillations at a high malonic acid/bromate ratio in the presence of added Cl^- ion in a cerium-catalyzed BZ system.

The initial addition of I^- had a dramatic effect on some uncatalyzed BZ oscillators in a well-defined, narrow range of initial concentration of I^- (ref.[24]). Kurin-Csörgei *et al.*[25] investigated the effect of chloride ions on the uncatalyzed bromate oscillators with *para*-substituted phenol derivatives as organic substrates. The high sensitivity of the reacting systems to chloride ion perturbation has been reported. No effects of Cl^- and Br^- on complex sequential oscillations have been described in the literature so far.

In this paper we present examples of sequential oscillations observed in the uncatalyzed bromate–phenol oscillator and the influence of chloride and bromide ions on such type of oscillations.

EXPERIMENTAL

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

The system presented here was studied in batch configuration. Measurements were carried out in a thermostatted cylindrical glass reactor (diameter 3.5 cm, height 7.5 cm). The total volume of the reaction mixture was 20 ml and the mixture was thermostatted to the required temperature ±0.05 °C. The reactor was closed with a rubber stopper, through which a commercial platinum indication macroelectrode (0.5 × 0.8 cm) and a reference mercury(I) sulfate electrode (MSE) were inserted into the reaction mixture. The potentiometric measurements were carried out using a 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); the stirring rate was 100 rpm.

The reactants were introduced into the reactor with a rotating stirrer in the following order: first an aqueous solution of H_2SO_4, next $NaBrO_3$, NaCl or NaBr, and finally a solution of phenol. Simultaneously, the potentiometric measurements were started.

The kinetics of the oxidation of pyrocatechol with the bromate ions was studied polarographically by recording the time dependence of the limiting diffusion current of BrO_3^- ions at –1.0 V against a reference mercury(I) sulfate electrode. The reaction solution was placed in a Kalousek polarographic cell equipped with a thermostatted mantle-piece. The Kalousek cell is two-compartment cell[26] separated by a glass valve with hole diameter 0.5 cm. The solution to be analyzed was placed in the left compartment with a dropping mercury electrode. A reference MSE electrode was situated in the right compartment.

Computer simulations were carried out on a PC Pentium II 400 MHz (Linux operating system) by numerical integration of a differential equation system derived from the model under study. Concentrations of the ten species, Br^-, BrO_3^-, HOBr, $HBrO_2$, pyrocatechol (H_2Q), quinone (Q), Br_2, $BrO_2^•$, $HQ^•$, Br_2O_4, were set as variables. Calculations were performed using the Fortran subroutine LSODE from a systematized collection of ODE solvers – ODEPACK[27] with an absolute error tolerance of 1×10^{-30} and a relative error tolerance of 1×10^{-6}. The initial concentration values of all the species not referred to be present at the beginning of the reaction, were set to zero.

RESULTS AND DISCUSSION

The uncatalyzed phenol–bromate–acid reacting system exhibits some unique features. As we pointed out in our previous paper[15], its sequential oscillatory behaviour can be attributed to coupled oscillators. 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 product of phenol. The oxidation product may be pyrocatechol that is generated continuously and is one of the components of an autocatalytic reaction, a complex process of the chemical oscillator.

There are two main reaction groups in the mechanism. The first one is the reaction of bromate and the starting aromatic compound (phenol), the bromination of phenol and the formation of pyrocatechol (H_2Q) and Br^-. The other one is the autocatalytic reaction of bromate with pyrocatechol.

Kinetics of the Reaction between Pyrocatechol and Bromate Ion in Sulfuric Acid

If the kinetics of the bromate reduction with an excess of pyrocatechol is followed polarographically, a sigmoidal time dependence of the bromate limiting diffusion current is observed, indicating an autocatalytic character of the reaction (Fig. 1). By the Schwartz[28] procedure, we were able to evaluate the rate constants corresponding to the uncatalyzed and catalyzed reactions. According to the literature[29–31] and our results, the following reactions and rate constants were used in the simulation of autocatalysis:

$$Br^- + BrO_3^- + 2\,H^+ \rightleftharpoons HOBr + HBrO_2 \qquad (1)$$

$k_1 = 1.2\ mol^{-3}\ dm^9\ s^{-1}$
$k_{-1} = 3.2\ mol^{-2}\ dm^6\ s^{-1}$

$$H_2Q + BrO_3^- + H^+ \longrightarrow Q + HBrO_2 + H_2O \qquad (2)$$

$k_2 = 1.66 \times 10^{-2}\ mol^{-2}\ dm^6\ s^{-1}$

$$H_2Q + Br_2 \longrightarrow Q + 2\,Br^- + 2\,H^+ \qquad (3)$$

$k_3 = 3 \times 10^4\ mol^{-1}\ dm^3\ s^{-1}$

$$H_2Q + BrO_2^{\bullet} \longrightarrow HQ^{\bullet} + HBrO_2 \qquad (4)$$

$k_4 = 50\ mol^{-1}\ dm^3\ s^{-1}$

$$Br^- + HOBr + H^+ \rightleftharpoons Br_2 + H_2O \qquad (5)$$

$k_5 = 8 \times 10^9\ mol^{-2}\ dm^6\ s^{-1}$
$k_{-5} = 80\ s^{-1}$

$$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons Br_2O_4 + H_2O \qquad (6)$$

$k_6 = 48\ mol^{-2}\ dm^6\ s^{-1}$
$k_{-6} = 3.2 \times 10^3\ s^{-1}$

$$Br_2O_4 \rightleftharpoons 2\ BrO_2^{\bullet} \tag{7}$$

$$k_7 = 7.5 \times 10^4\ s^{-1}$$
$$k_{-7} = 1.4 \times 10^9\ mol^{-1}\ dm^3\ s^{-1}\ ,$$

where Q denotes quinone.

The rate constant values refer to 20 °C. The value of k_2 (Eq. (*2*)) has been estimated in this work; the value of k_4 (Eq. (*4*)) has been modified in this work.

The agreement of the simulated curve with experimental data is acceptable (Fig. 1).

Effects of Chloride Ion in the Bromate–Phenol System

A series of experiments was carried out with chloride present as a component of the original reaction mixture. The initial concentrations of the other species are: $[BrO_3^-]_o$ = 0.025 mol dm^{-3}, $[phenol]_o$ = 8.0 mmol dm^{-3}, $[H_2SO_4]_o$ = 1.5 mol dm^{-3} (25 °C; 100 rpm). Figure 2 shows the effect of the initial addition of various amounts of Cl$^-$. In the absence of chloride (Fig. 2, curve *1*) the system exhibits an induction period (IP) of 375 s. After the IP, the system switches to the oscillatory regime with an apparent period of *ca* 59 s. After the series of 3–4 oscillations, a non-oscillatory period follows

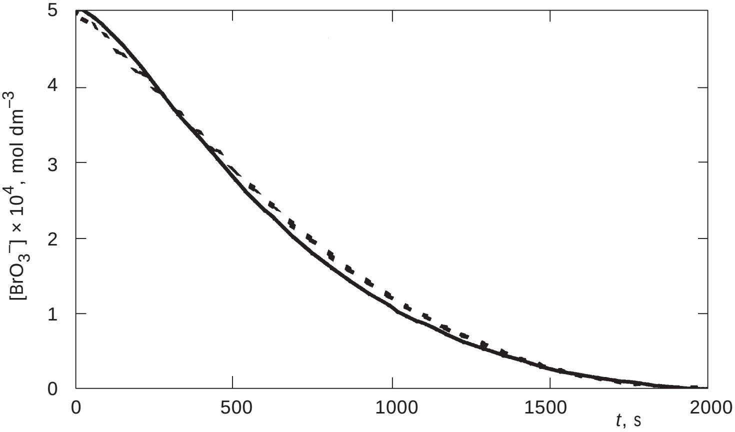

FIG. 1

Autocatalytic character of the reduction of bromate with pyrocatechol (H_2Q). Initial conditions: $[H_2Q]_o$ = 0.04 mol dm^{-3}, $[BrO_3^-]_o$ = 0.5 mmol dm^{-3}, $[H_2SO_4]_o$ = 1.0 mol dm^{-3}; *T* = 20 °C. The solid curve represents experiment and the dots are computer fits

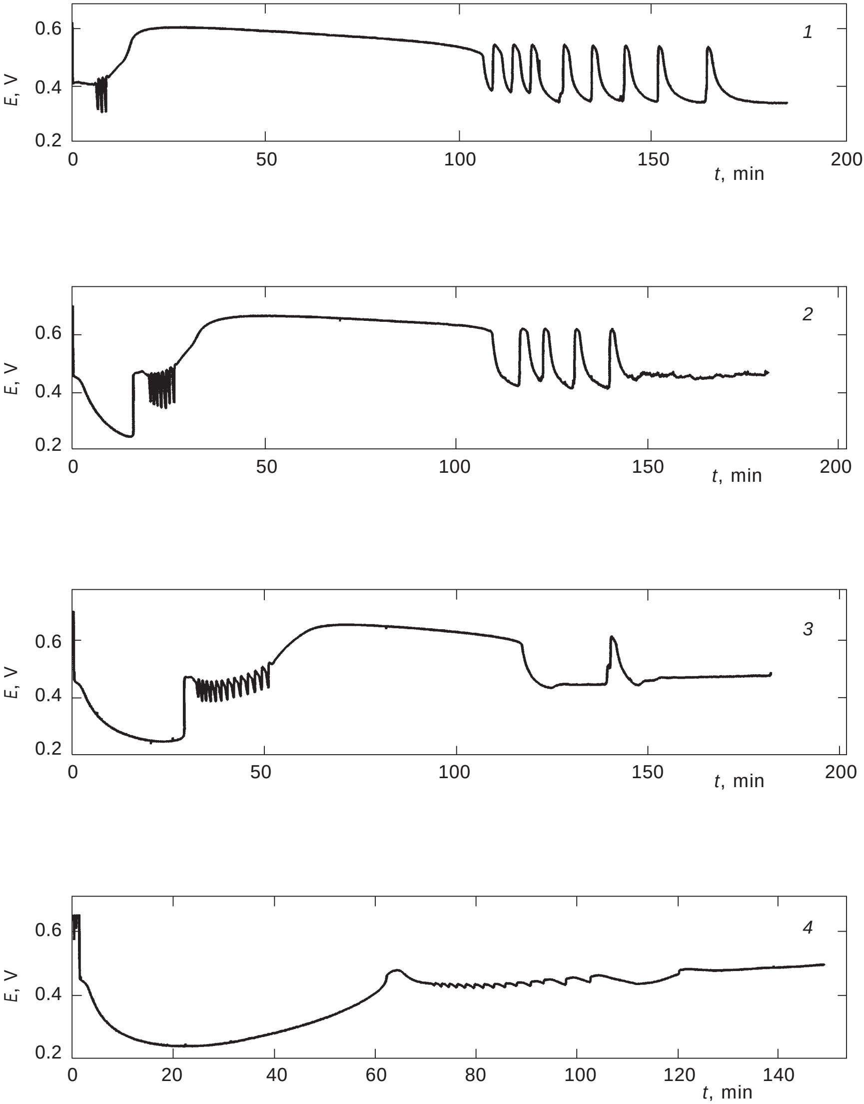

FIG. 2

Dependence of oscillatory characteristics on Cl^- concentration. Initial conditions: $[phenol]_o$ = 8 mmol dm^{-3}, $[BrO_3^-]_o$ = 25 mmol dm^{-3}, $[H_2SO_4]_o$ = 1.5 mol dm^{-3}; $[Cl^-]_o$: 0 (*1*), 0.13 (*2*), 0.3 (*3*), 0.8 mmol dm^{-3} (*4*); T = 25 °C; 100 rpm

(96 min) and next, the second series of 8 oscillations appears, with an apparent period of *ca* 280 s. It was found that for $[Cl^-]_o < 3 \times 10^{-5}$ mol dm^{-3} no changes were observed. The result of the added chloride was the prolonged IP, and division of that period into two parts. The duration of the first part varied significantly with the Cl^- concentration (Fig. 2, curves *2*–*4*), while the second part was relatively invariant. The general characteristics of the second part resemble those of the unperturbed IP, though the second part is always somewhat shorter in agreement with the observation in the classic BZ system[18]. The effect of initially added Cl^- on the IP is shown in Fig. 3. With increasing concentration of chloride ions (from 0.05 to 0.6 mmol dm^{-3}) the parameters of sequential oscillations changed: the number of first oscillations increased from 4 to 21 and their amplitude decreased; the duration of the non-oscillatory period (NP) and the number of second oscillations decreased from 96 to 26 min and from 8 to 1, respectively (Fig. 2, curves *2*, *3*). The sequential oscillations could be only observed in a certain concentration range of Cl^-. For $[Cl^-]_o > 0.7$ mmol dm^{-3}, the second oscillatory regime was completely inhibited and only the first oscillatory regime was found (Figs 2, 4). When $[Cl^-]_o > 1.3$ mmol dm^{-3}, the oscillatory behaviour was totally suppressed.

In our perturbed system, kinetically active chlorinated aromatics are formed. They serve as a transient pool, protecting chlorine from further oxidation with BrO_3^- to ClO_3^-. The chlorinated organics apparently decrease the amplitude of the oscillations by inhibiting the $HBrO_2$ autocatalysis.

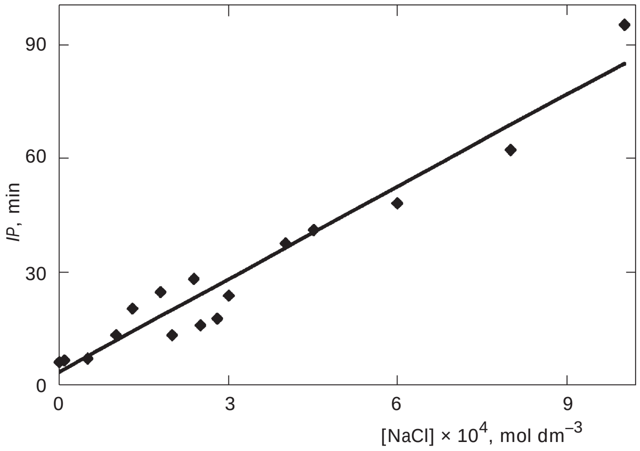

FIG. 3
The effect of initially added Cl^- on the induction period (IP). Initial conditions: $[phenol]_o = 8$ mmol dm^{-3}, $[BrO_3^-]_o = 25$ mmol dm^{-3}, $[H_2SO_4]_o = 1.5$ mol dm^{-3}; *T* = 25 °C; 100 rpm

Thus, a single oscillatory step consumes less of the initial materials and their important derivatives, leading to more oscillations in a Cl^--perturbed system than in an unperturbed one.

The sequential oscillations in the BrO_3^-–phenol–acid system could be observed only in a certain temperature range (T > 23 °C). Our reacting chloride-free system below 19 °C was not oscillatory at given concentrations (Fig. 4, curve *1*). However, an addition of Cl^- triggered a transition from the non-oscillatory to oscillatory states (Fig. 4, curve *2*).

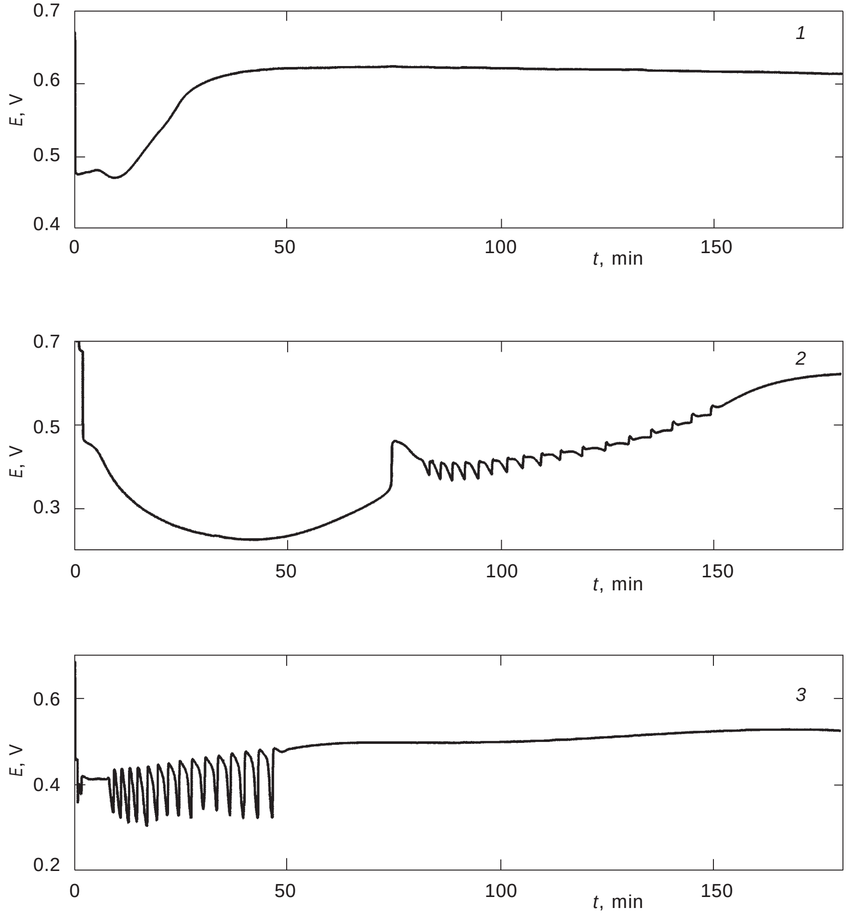

FIG. 4

Chloride- and bromide-induced oscillations. The same initial concentrations of phenol, BrO_3^- and H_2SO_4 as in Fig. 2. In addition, $[\text{halide}]_o = 0$ (*1*), $[Cl^-]_o = 0.3$ (*2*), $[Br^-]_o = 5.0$ mmol dm^{-3} (*3*); T = 18 °C

In our previous paper[15], we studied the effect of viscosity. The viscosity of the phenol–bromate–acid system changed with addition of SiO_2 and oscillatory courses were very similar to those resulting from the initial addition of $Cl^–$. Increasing the viscosity of the solution decreases the rate constant of a diffusion-controlled reaction. The effect of addition of $Cl^–$ can be also interpreted on the basis of diffusion-controlled radical reaction[32]. Provided the reaction of $PhO^•$ with $BrO_2^•$ radicals or the reaction of $HQ^•$ with $BrO_2^•$ ($k = 8 \times 10^9$ mol$^{–1}$ dm^3 s$^{–1}$) in our UBO system are diffusion-controlled, the change of the rate constant for these reactions will result in a proportional change of the turbulent diffusion coefficient.

Effects of Bromide Ions in the Bromate–Phenol System

Initial addition of bromide ions to the oscillatory uncatalyzed bromate–phenol system produces a variety of phenomena, depending on the initial bromide concentration.

At low $[Br^–]_o$ values (0.5 to 2.5 mmol dm$^{–3}$), sequential oscillations are still observed. The IP remains unaltered, the number of first oscillations increases (from 5 to 12) and the non-oscillatory period and the number of second oscillations decrease with increasing concentration of $Br^–$.

In the concentration range 3.5 mmol dm$^{–3}$ < $[Br^–]_o$ < 8.0 mmol dm$^{–3}$, the system displays dual-frequency, dual-amplitude and aperiodic oscillations, with a transition period between high- and low-frequency oscillations. When $[Br^–]_o$ reaches 5.0 mmol dm$^{–3}$, the NP disappears and the small first oscillations grow directly into the second oscillations, as is shown in Fig. 5, curve *3*. When the initial bromide concentration exceeds 12 mmol dm$^{–3}$, no oscillations appear.

Similar to addition of $Cl^–$, also added $Br^–$ ions triggered a transition from the non-oscillatory to oscillatory states (Fig. 4, curve *3*).

According to the Field–Körös–Noyes mechanism[1], the controlling intermediate of the bromate-driven oscillators is the bromide; it has the advantage of being a real intermediate in the system. Thus, after the injection of the perturbing agent, the system evolves along a “natural” trajectory because no new chemical component is present as a result of the perturbation. The UBO system, phenol–bromate–acid, although similar in some characteristic to other bromate-driven oscillators, exhibits some unique freatures also in the presence of added $Br^–$. As we pointed out in our previous paper[15], its oscillatory behaviour can be attributed to phenol and to an intermediate, a rather stable oxidation product of phenol. Probably it is the pyrocatechol that is generated continuously during the non-oscillating pe-

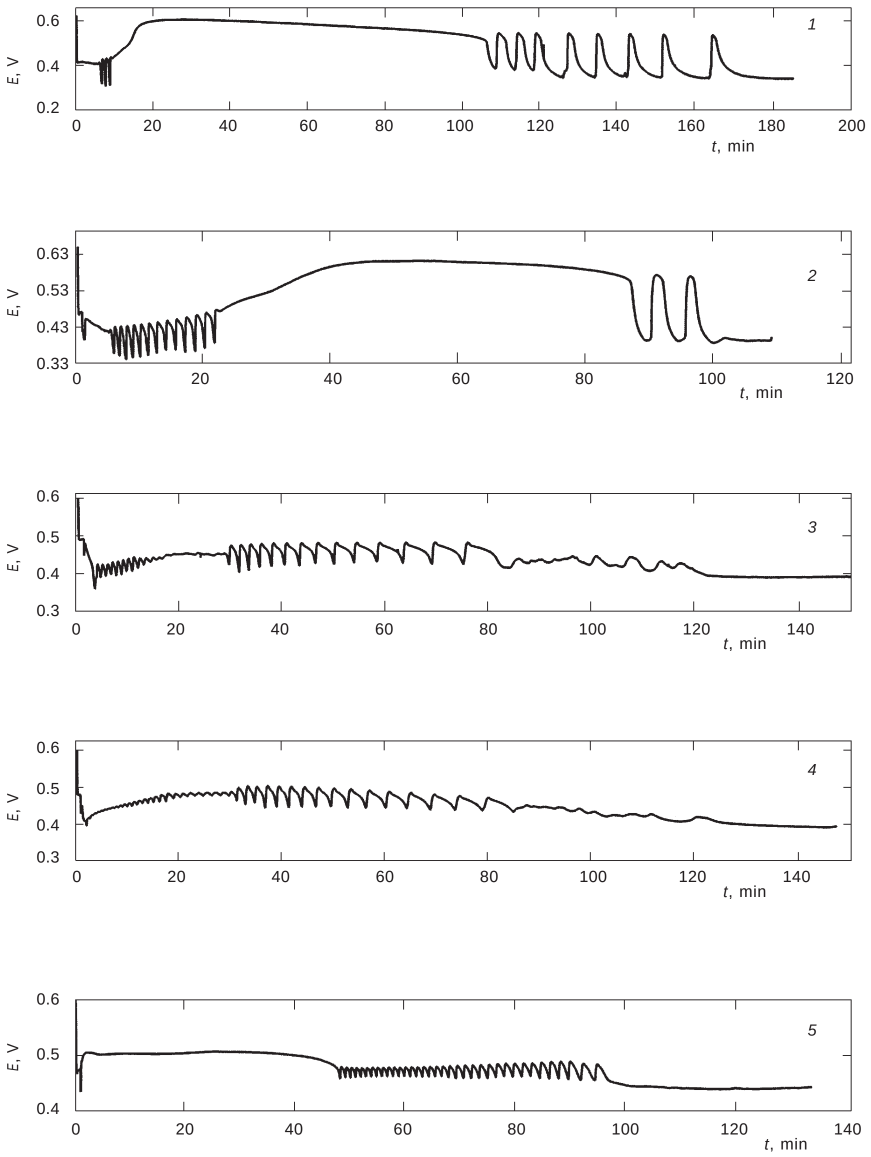

FIG. 5

Dependence of oscillatory characteristics on Br^- concentrations. The same initial conditions of phenol, BrO_3^- and H_2SO_4 as in Fig. 2. In addition, $[Br^-]_o$ = 0 (*1*), 2.5 (*2*), 5.0 (*3*), 6.5 (*4*), 10 mmol dm^{-3} (*5*); *T* = 25 °C riod, being one of the components of an autocatalytic reaction, a complex process of the chemical oscillation. We may assume that in our UBO system, the production of both bromide ions and pyrocatechol is responsible for the chemical control. Szalai, Körös and Györgyi[30], who studied the UBO system with cyclohexa-1,3-diene as substrate, suggested a similar behaviour. We may assume control by a synergetic process involving both Br^- and $PhO^\bullet$ or $HQ^\bullet$ radicals.

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