INTRODUCTION

The oscillatory Belousov–Zhabotinsky (BZ) reaction is the oxidation of malonic acid (MA), by bromate ions in water solutions of mineral acids, catalyzed by Ce^{3+} or Ce^{4+} metal ions \([1, 2]\). Under various conditions in a open and closed reactor, this reaction exhibits simple periodic oscillations, multiple steady states, multiply periodic oscillations, mixed-mode oscillations, chaos and spatially propagating waves \([3–19]\).

Wanting to explain the experimental results, numerous models of the mechanism of the BZ reaction and modification of these models were proposed \([16, 17, 20, 21]\). So, the numerical calculations of some complex dynamic behavior of BZ oscillatory reaction under different initial concentrations of the malonic acid were earlier successfully carried out by the known model \([21]\), including the Br_2O species \([22]\) (table). This model was derived from the GF model referred to as model B \([17]\). Four reactions were added to the model B as a consequence of including the species Br_2O: (R2), (R3), (R-3), and (R11). Formally, the second step of the basic model B was replaced by three reactions (R2), (R3), and (R-3). Such introducing of Br_2O species as an intermediate is appropriate for the fine regulation of the HOBr concentration in the reaction system, since Br_2O species reacts with malonic acid to yield bromomalonic acid (BrMA) and HOBr in the reaction (R11).

The reduction of the bromine concentration caused by bromine evaporation from the system would influence the reaction between bromine and malonic acid, and consequently lead to the change of the malonic acid and bromomalonic acid concentrations and time evolutions of the BZ reaction. BrMA has been suggested to play an essential role in the development of complex oscillations in the cerium-BZ reaction \([17, 23]\), in which transient complex oscillations would not occur until the concentration of BrMA has reached a certain level \([12–14]\). In order to investigate the effect of bromine on the oscillatory evolutions of BZ reaction in the closed reactor, reaction due to evaporation of bromine \([24, 25]\) was included in the model:

\[
\text{Br}_2\text{(sol)} \xrightarrow{k_{\text{evap}}} \text{Br}_2\text{(g)}.
\]  

In this context, a detailed simulation based on this extended model (table) has been done to include various initial concentrations of malonic acid and the rate constant of bromine evaporation. Here, our attention is particularly focused on searching for transient complex oscillations in the above system, because complex oscillations are extremely susceptible to variations of reaction parameters and thus have particular advantages in characterizing the underlying reaction mechanism.

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**Numerical Evidence of Complex Nonlinear Phenomena of the Belousov–Zhabotinsky Oscillatory Reaction under Batch Conditions**


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**Abstract** — By numerical calculations based on our previously proposed model with Br_2O intermediate species we were able to simulate complex evolution of the Belousov–Zhabotinsky (BZ) reaction under batch conditions. In the defined region of initial malonic acid concentration \([\text{MA}_0](1.00 \times 10^{-3} \text{ mol dm}^{-3} \leq \text{MA}_0 \leq 1.50 \text{ mol dm}^{-3})\) different sequences of regular and complex periodic and aperiodic oscillations were obtained. It is noticed that the bromine evaporation significantly affects the dynamics of the reaction.

**Keywords:** Belousov–Zhabotinsky reaction, oscillating reactions, mixed-mode oscillations, chaotic behavior.

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Concentration of intermediate species was \([\text{HOBr}]_0 = 1.00 \times 10^{-3}\) mol dm\(^{-3}\) in all the simulations. In all simulations, the initial concentration of water \([\text{H}_2\text{O}]_0 = 55\) mol dm\(^{-3}\), the initial concentrations of other species (in mol dm\(^{-3}\)) are presented in the table. The rate constant of the reaction of bromine evaporation, \(k_{12}\), varied from \(1.00 \times 10^{-4}\) to \(5.50 \times 10^{-1}\) s\(^{-1}\), and all other rate constants (table) were taken from earlier publication [21].

**Numerical Simulations**

The simulated results were obtained using the MATLAB program package. The differential equations derived from the model were integrated using the ode15s solver. Relative and absolute error tolerance values of \(3 \times 10^{-14}\) and \(1 \times 10^{-20}\) were used in all simulations. Since under the batch conditions, concentrations of reactants decrease with time, for implementing the chosen model for simulating the evolution of BZ reaction in closed reactor, the concentrations of the reactants were treated as dynamical variables, and only the concentration of water \([\text{H}_2\text{O}]_0 = 55\) mol dm\(^{-3}\), was included in the rate constants of corresponding reactions [16, 17].

We examined a narrow part of the phase space where the initial concentration of malonic acid varied \((1.00 \times 10^{-3} \leq [\text{MA}]_0 \leq 1.50 \text{ mol dm}^{-3})\) under isothermal conditions at 30°C, with constant values of the initial concentrations of other species (in mol dm\(^{-3}\)):

\[
\begin{align*}
[\text{H}_2\text{SO}_4]_0 & = 1.05, \\
[\text{KBrO}_3]_0 & = 6.20 \times 10^{-2}, \\
[\text{KBr}]_0 & = 1.50 \times 10^{-5}, \\
[\text{Ce}_5(\text{SO}_4)_3]_0 & = 2.50 \times 10^{-3}.
\end{align*}
\]

According to Clegg et al. [26], \([\text{H}_2\text{SO}_4]_0 = 1.05 \text{ mol dm}^{-3}\) gives \([\text{H}^+]_0 = 1.29\) mol dm\(^{-3}\), and this value was used in all the simulations. In the all simulations, the initial concentration of intermediate species was \([\text{HOBr}]_0 = 1.50 \times 10^{-8}\) mol dm\(^{-3}\). The initial concentrations of the other intermediate species at time zero are considered as \(1.00 \times 10^{-20}\) mol dm\(^{-3}\).

The rate constant of the reaction of bromine evaporation, namely, \(k_{12}\), was varied from \(1.00 \times 10^{-4}\) to \(5.50 \times 10^{-1}\) s\(^{-1}\), and all other rate constants (table) were taken from earlier publication [21].

**RESULTS AND DISCUSSION**

The numerical results of some of the mentioned complex phenomena in the closed Belousov–Zhabotinsky reaction system as a function of the initial malonic acid concentration are presented in Fig. 1. These time dependences of \([\text{Br}^-]\) were obtained by the numerical simulation of the kinetic scheme presented in the table, with eleven reactions (R1)—(R11) without the reaction of bromine evaporation (R12). Dependence of the observed transient complex oscillations on concentrations of malonic acid was characterized systematically. In very low concentration range \((1.00 \times 10^{-3} \leq [\text{MA}]_0 \leq 3.12 \times 10^{-3}\) mol dm\(^{-3}\) during the time evolution of the system, occurred only stable steady state and no appearance of oscillatory evolution (Fig. 1a).

With further increase of the initial concentration of malonic acid, in the system, the two dynamic forms were observed: a stable steady state and oscillatory evolution. In the middle and high range of the initial malonic acid concentration \((3.13 \times 10^{-3} \leq [\text{MA}]_0 \leq 3.37 \times 10^{-2}\) mol dm\(^{-3}\) different sequences of regular and complex periodic and aperiodic oscillations were obtained and presented in Figs. 1b—1f. Obviously, in the concentration range \((3.13 \times 10^{-3} \leq [\text{MA}]_0 \leq 3.37 \times 10^{-2}\) mol dm\(^{-3}\) the oscillatory sequence with different number of regular oscillations appeared (Fig. 1b). At the end of