Numerical simulation of oscillation reaction of the Belousov—Zhabotinskii type in the presence of oxalic acid

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

The behaviour of oscillating system of the Belousov—Zhabotinskii type in the presence of oxalic acid has been simulated on the basis of the BHC Oregonator, the GNF model, the Sasaki mechanism and their modifications. The numerical simulations show that the present models involving substrates incapable of bromination allow to interpret the oscillations in a system containing oxalic acid only if the arising bromine is removed from the reaction solution by a continuous stream of inert gas, "the rate constant" being of 10^{-3}—10^{-2} s^{-1} decimal order. We have not succeeded in elucidating the behaviour if bromine is removed by bromination of acetone in real concentrations or is not removed at all.

Поведение осцилляционной системы типа Белоусова—Жаботинского с щавелевой кислотой было симулировано на основании BHC Орегонатора, GNF модели, механизма Сасаки и их видоизменений. Численные симуляции показывают, что современные модели с небромирующими субстратами позволяют объяснить осцилляции в системе с щавелевой кислотой тогда, если образующийся бром устраняется из реакционного раствора непрерывно током инертного газа с «константной скоростью» порядка 10^{-3}—10^{-2} c^{-1}. Не удалось получить осцилляционное решение, если бром устраняется бромированием реальных концентраций ацетона или вообще не устраняется.

The classical Belousov—Zhabotinskii (BZ) reaction is an oxidation of organic substrate disposed to bromination by the BrO_3^- ions in strongly acid medium which is catalyzed by the Ce(IV) ions. Field, Körös, and Noyes (FKN) have proposed a detailed mechanism of the BZ reaction with malonic acid [1] which can be simplified in a model called Oregonator [2] where $HBrO_2$, Br^-, and catalyst are variables. In this mechanism and model the Br^- ions are regarded as regulating intermediate. This model has proved to be very useful and successful in simulating the oscillation reactions with brominable substrates [3].

However, some modifications of the BZ reaction do not fit in the framework of the FKN mechanism or Oregonator. First of all, it is the discovery of oscillations in the system containing oxalic acid if an inert gas [4, 5], acetone

[6, 7] or continuously stirred flow reactor (CSTR) [7, 8] is used for continuous removal of the generated bromine. These experiments cannot be interpreted by assuming the existence of the reactions analogous to those taking place in the system containing malonic acid because oxalic acid is not able to give brominated derivatives.

This fact initiated the creation of a new model, the so-called Explodator [9] in which $HBrO_2$, HOBr, and Br_2 are variables. The response to its creation was the revised Oregonator [10] ($HBrO_2$, HOBr, and Br^-) and later the extended Oregonator [11] involving $HBrO_2$, HOBr, Br^-, and catalyst as variables. These models have also made possible to solve the problem of the stoichiometric factor in the fifth step of the original Oregonator [2] in which the regulating intermediate arises as a product of the oxidation of bromomalonic acid by the oxidized form of catalyst. It has been evident that the reaction of the brominated organic substrate cannot be the source of the Br^- ions if the oscillations in the system containing oxalic acid are controlled by concentration of the Br^- ions. At a later time, it appeared that bromomalonic acid could not be regarded as a source of the Br^- ions in the classical BZ reaction either [12].

Bódiss and *Field* [3] successfully simulated the oscillations in the system containing oxalic acid when the generated bromine was removed only physically at a convenient rate while *Gáspár* and *Galambosi* [8] had to use a high flow rate of Br_2 removal in CSTR for successful simulation. *Field* and *Boyd* [13] consider the oscillations in the BrO_3^-—Ce(IV)—$(COOH)_2$—acetone system to be controlled by the hydrolysis of bromine because the regulating intermediate, *i.e.* the Br^- ions also come from the hydrolysis of bromine. They proposed a new model, BHC Oregonator with five concentration variables in which Br_2 was removed by bromination of acetone. *Sasaki* [14] simulated the oscillating behaviour of the BrO_3^-—Ce(IV)—$(COOH)_2$ system on the basis of the BHC Oregonator taking into account the $HCO_2^\bullet$, $BrO_2^\bullet$, and $Br^\bullet$ radicals as well as the physical process in which bromine was removed from the system.

It is assumed in all proposed models that the concentration of bromine in the oscillating system containing oxalic acid must be reduced by some process and the rate of this removal is a bifurcation parameter. The publication of *Blume* and *Bader* [15] suggested the possibility of oscillations at low values of this parameter. Recently, oscillations were also observed in the closed BrO_3^-—Mn(II)—$(COOH)_2$ system without any mechanism in which bromine could be removed from the solution [16]. Besides, the rate constants resulting from the FKN mechanism [1] have been hitherto used in models and simulations, but *Field* and *Försterling* (FF) prepared a newer set of rate constants [17].

The aim of this study has been to find out on the basis of those new facts by using numerical simulation to which extent the present models are able to reproduce the oscillating behaviour of the BZ system containing oxalic acid.

Models and calculations

We investigated three latest models of oscillation reaction of the BZ type with oxalic acid:

1. Field—Boyd (FB) BHC Oregonator [13] which comprises these steps

$BrO_3^- + Br^- \rightarrow HBrO_2 + HOBr$ (FB1)
$HBrO_2 + Br^- \rightarrow 2\,HOBr$ (FB2)
$BrO_3^- + HBrO_2 \rightarrow 2\,HBrO_2 + Ce(IV)$ (FB3)
$2\,HBrO_2 \rightarrow HOBr + BrO_3^-$ (FB4)
$Ce(IV) \rightarrow$ inert products (FB5)
$HOBr \rightarrow Br^-$ (FB6)
$HOBr + Br^- \rightleftarrows Br_2$ (FB7)
$Br_2 \rightarrow Br^-$ (FB8)

The corresponding rate parameters are given in Table 1. Step FB8 represents the removal of bromine by acetone.

Table 1

Rate parameters of the BHC Oregonator [13]

Step	Defining equation	Rate parameter
FB1	$5\,[H^+]^2$	$5\ dm^3\ mol^{-1}\ s^{-1}$
FB2	$2 \times 10^9\,[H^+]$	$2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$
FB3	$10^4\,[H^+]$	$10^4\ dm^3\ mol^{-1}\ s^{-1}$
FB4	4×10^7	$4 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$
FB5	$27.5\,[(COOH)_2]/[H^+]$	$0.825\ s^{-1}$
FB6	$150\,[(COOH)_2]$	$4.5\ s^{-1}$
FB7	$8 \times 10^9\,[H^+]$	$8 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$
FB−7	110	$110\ s^{-1}$
FB8	8.3×10^{-6} [acetone] $[H^+]$	$5.8 \times 10^{-5}\ s^{-1}$

FB−7 — reverse reaction.

2. Gáspár—Noszticzius—Farkas (GNF) model [18]

$BrO_3^- + HBrO_2 \rightarrow 2\,HBrO_2$ (GNF1)
$HBrO_2 + Br^- \rightarrow 2\,HOBr$ (GNF2)
$(COOH)_2 + HOBr \rightarrow Br^-$ + inert products (GNF3)
$HOBr + Br^- \rightleftarrows Br_2$ (GNF4)
$Br_2(sol) \rightarrow Br_2(g)$ (inert) (GNF5)
$BrO_3^- + Br^- \rightarrow HBrO_2 + HOBr$ (GNF6)
$2\,HBrO_2 \rightarrow HOBr + BrO_3^-$ (GNF7)
$BrO_3^- + (COOH)_2 \rightarrow HBrO_2$ + inert products (GNF8)

Table 2

Rate parameters of the GNF model [18]

Step	Defining equation	Rate parameter
GNF1	$10[H^+][BrO_3^-]$	$6 \times 10^{-1}\ s^{-1}$
GNF2	$10^6[H^+]$	$1.5 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$
GNF3	$220\ [(COOH)_2]$	$8.8\ s^{-1}$
GNF4	$8 \times 10^9\ [H^+]$	$1.2 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$
GNF−4	100	$100\ s^{-1}$
GNF5		bifurcation parameter
GNF6	$2\ [H^+]^2\ [BrO_3^-]$	$1.8 \times 10^{-1}\ s^{-1}$
GNF7		$4 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$
GNF8	$6 \times 10^{-4}\ [H^+]\ [BrO_3^-]\ [(COOH)_2]$	$1.44 \times 10^{-6}\ mol\ dm^{-3}\ s^{-1}$

The corresponding rate parameters are given in Table 2. Step GNF5 corresponds to physical removal of bromine and is governed by the equation

$$-\frac{d[Br_2(sol)]}{dt} = k_5[Br_2(sol)]$$

3. Sasaki mechanism (S) [14]

$$Br^- + BrO_3^- + 2\,H^+ \rightarrow HOBr + HBrO_2 \tag{S1}$$
$$Br^- + HBrO_2 + H^+ \rightarrow 2\,HOBr \tag{S2}$$
$$Br^- + HOBr + H^+ \rightleftarrows Br_2 + H_2O \tag{S3}$$
$$BrO_3^- + HBrO_2 + H^+ \rightleftarrows 2\,BrO_2^{\bullet} + H_2O \tag{S4}$$
$$BrO_2^{\bullet} + Ce(III) + H^+ \rightleftarrows Ce(IV) + HBrO_2 \tag{S5}$$
$$2\,HBrO_2 \rightarrow HOBr + BrO_3^- + H^+ \tag{S6}$$
$$HOBr + (COOH)_2 \rightarrow HCO_2^{\bullet} + Br^{\bullet} + H_2O + CO_2 \tag{S7}$$
$$Ce(IV) + (COOH)_2 \rightarrow Ce(III) + HCO_2^{\bullet} + CO_2 + H^+ \tag{S8}$$
$$HCO_2^{\bullet} + HOBr \rightarrow Br^{\bullet} + CO_2 + H_2O \tag{S9}$$
$$Br^{\bullet} + (COOH)_2 \rightarrow HCO_2^{\bullet} + Br^- + CO_2 + H^+ \tag{S10}$$
$$Br^{\bullet} + Br^{\bullet} \rightarrow Br_2 \tag{S11}$$
$$HCO_2^{\bullet} + HCO_2^{\bullet} \rightarrow (COOH)_2 \tag{S12}$$
$$Br_2(sol) \rightarrow Br_2(g) \tag{S13}$$

The corresponding rate constants are given in Table 3. Step S13 is analogous to step GNF5.

The numerical integration of the differential equations describing steps FB1—FB8, GNF1—GNF8, and S1—S13 was performed on a computer JS 1033 by using the *Gear* algorithm [19]. The program was tested by the systems of differential equations made up according to the published models [14, 18, 20].

Table 3

Rate constants in the Sasaki mechanism [14]

Step	Rate constant	Step	Rate constant $dm^3\ mol^{-1}\ s^{-1}$
S1	$2.1\ dm^9\ mol^{-3}\ s^{-1}$	S6	4×10^7
S2	$2 \times 10^9\ dm^6\ mol^{-2}\ s^{-1}$	S7	25
S3	$8 \times 10^9\ dm^6\ mol^{-2}\ s^{-1}$	S8	27.5
S−3	$110\ s^{-1}$	S9	2×10^7
S4	$10^4\ dm^6\ mol^{-2}\ s^{-1}$	S10	2×10^3
S−4	$2 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$	S11	10^8
S5	$6 \times 10^5\ dm^6\ mol^{-2}\ s^{-1}$	S12	1.2×10^9
S−5	$5 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$	S13	bifurcation parameter

The results of our simulations were consistent with the published data. An example of numerical simulation of GNF model solved by means of our program is represented in Fig. 1.

Results

The original Oregonator [2] does not comprise the reversible hydrolysis of bromine though the reaction of the bromide ions with hypobromous acid may

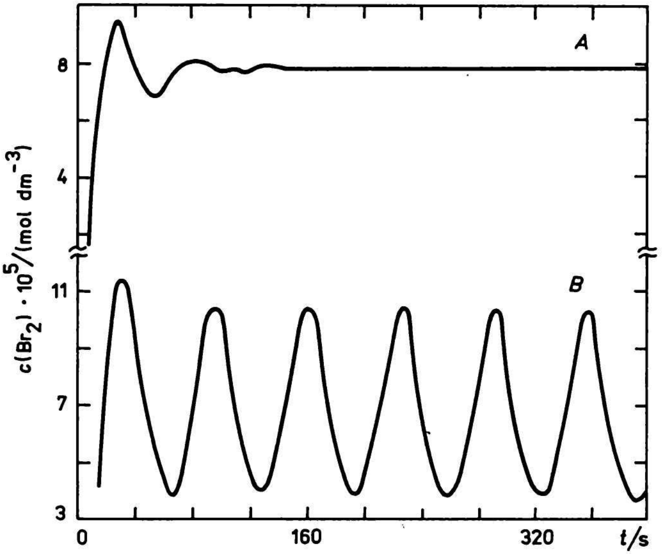

Fig. 1. Numerical simulation of the GNF model for $k_5 = 9 \times 10^{-2}\ s^{-1}$ (*A*) and $k_5 = 6 \times 10^{-2}\ s^{-1}$ (*B*).

be as far as thousand times more rapid under oscillation conditions than other reactions of the bromide ions. The introduction of this reversible reaction into the modification of Oregonator with the FF rate constants [20] resulted in nonoscillating course (Fig. 2).

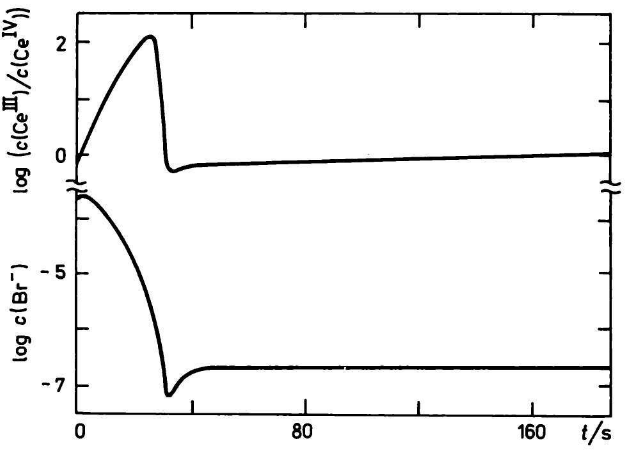

Fig. 2. Simulation of Oregonator [20] after introducing the hydrolysis of Br_2.

Simulations based on BHC Oregonator

Field and *Boyd* [13] consider the rate of formation of the enol form of acetone to be the rate-determining step of bromination of acetone (FB8). The reversibility of enolization was neglected or the value of k_8 in Table 1 was adjusted. Then the rate of step FB8 ought to be independent of bromine concentration and the following system of differential equations (*I*) may be devised

$$\frac{dc_1}{dt} = -k_1c_1c_3 - k_3c_1c_2 + k_4c_2^2$$

$$\frac{dc_2}{dt} = k_1c_1c_3 - k_2c_2c_3 + k_3c_1c_2 - 2k_4c_2^2$$

$$\frac{dc_3}{dt} = -k_1c_1c_3 - k_2c_2c_3 + k_6c_4 - k_7c_3c_4 + k_{-7}c_5 + k_8$$

$$\frac{dc_4}{dt} = k_1c_1c_3 + k_4c_2^2 + 2k_2c_2c_3 - k_6c_4 - k_7c_3c_4 + k_{-7}c_5 \qquad (I)$$

$$\frac{\mathrm{d}c_5}{\mathrm{d}t} = k_7 c_3 c_4 - k_{-7} c_5 - k_8$$

$$\frac{\mathrm{d}c_6}{\mathrm{d}t} = k_8$$

where c_1, c_2, c_3, c_4, c_5, and c_6 stand for concentration of BrO_3^-, $HBrO_2$, Br^-, HOBr, Br_2, and bromoacetone, respectively. The initial concentrations were: 1 M-H^+ (constant), 0.02 M-BrO_3^-, 0.03 M-$(COOH)_2$, 0.07 M acetone, and 10^{-8} M-$HBrO_2$. According to BHC Oregonator, bromoacetone does not affect the kinetics of oscillation reaction, it is only a product. It is enough only to solve the system of differential equations $\mathrm{d}c_1/\mathrm{d}t$ to $\mathrm{d}c_5/\mathrm{d}t$. Because of inconsistency of the parameters in Tables 1 and 2 [13] we used three values of k_8/s^{-1}: 5.8×10^{-7}, 5.8×10^{-6}, and 5.8×10^{-5}.

The unit of k_8 (s^{-1}) corresponds to a first-order reaction, which is in contradiction with the assumption that the rate of enolization of acetone is rate-determining for FB8. Then the rate parameter k_8 should be expressed in mol $\mathrm{dm}^{-3}\,\mathrm{s}^{-1}$, *i.e.* in units of a zero-order reaction. Unit s^{-1} would correspond to the system of differential equations (*II*) where it would be valid in contrast to (*I*)

$$\frac{\mathrm{d}c_3}{\mathrm{d}t} = -k_1 c_1 c_3 - k_2 c_2 c_3 + k_6 c_4 - k_7 c_3 c_4 + k_{-7} c_5 + k_8 c_5$$

$$\frac{\mathrm{d}c_5}{\mathrm{d}t} = k_7 c_3 c_4 - k_{-7} c_5 - k_8 c_5 \qquad (II)$$

$$\frac{\mathrm{d}c_6}{\mathrm{d}t} = k_8 c_5$$

It suffices to solve for c_1—c_5 again.

In order to avoid the ambiguity of step FB8, we can make up a system of differential equations (*III*) where step FB8 is replaced by two reactions

keto form + H^+ $\rightleftarrows$ enol form + H^+ (FB8″)
enol form + Br_2 $\rightarrow$ Br^- + bromoacetone (FB9)

where $k''_8 = 8.3 \times 10^{-5}\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$, $k''_{-8} = 21.3\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$, and $k_9 = 1.03 \times 10^7\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ [13].

System *I* of differential equations is to be modified as follows

$$\frac{\mathrm{d}c_3}{\mathrm{d}t} = -k_1 c_1 c_3 - k_2 c_2 c_3 + k_6 c_4 - k_7 c_3 c_4 + k_{-7} c_5 + k_9 c_5 c_7$$

$$\frac{\mathrm{d}c_5}{\mathrm{d}t} = k_7 c_3 c_4 - k_{-7} c_5 - k_9 c_5 c_7$$

and the following two equations are to be added

$$\begin{aligned}\frac{\mathrm{d}c_6}{\mathrm{d}t} &= -k''_8 c_6 + k''_{-8} c_7 \\ \frac{\mathrm{d}c_7}{\mathrm{d}t} &= k''_8 c_6 - k''_{-8} c_7 - k_9 c_5 c_7\end{aligned} \qquad (III)$$

where c_6 and c_7 are concentration of keto and enol form of acetone, respectively. As the concentration of bromoacetone does not affect the kinetics, the pertinent equation is omitted by reason of better survey.

The simulations with systems *I* and *II* for all three values of k_8 and with system *III* for conditions [13] did not result in a solution involving oscillations.

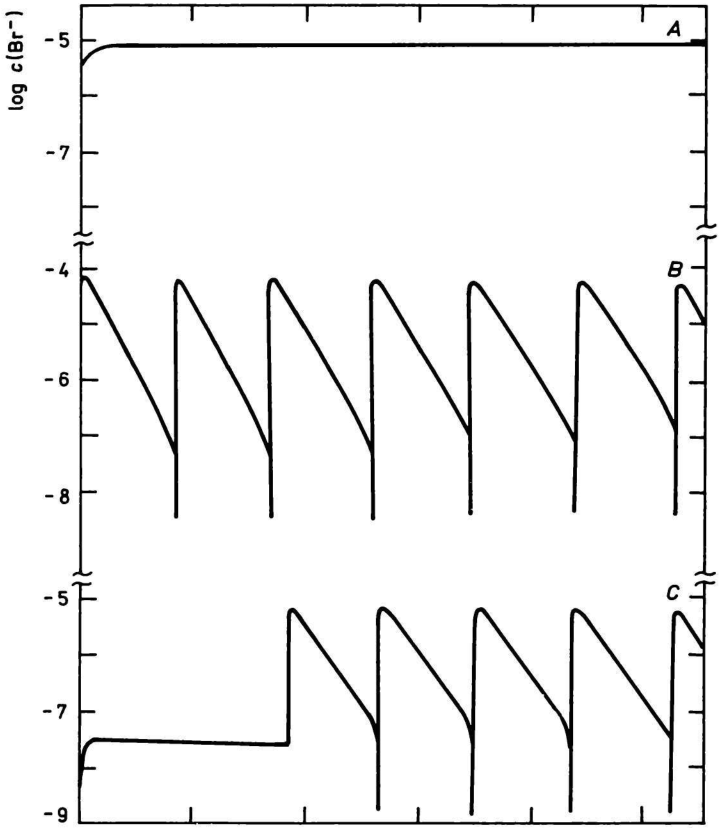

Fig. 3. Simulation of the BHC Oregonator for $k_8 = 5.8 \times 10^{-5}\ \mathrm{s}^{-1}$, $5.8 \times 10^{-6}\ \mathrm{s}^{-1}$ or $5.8 \times 10^{-7}\ \mathrm{s}^{-1}$ (*A*), $k_8 = 5.8 \times 10^{-1}\ \mathrm{s}^{-1}$ (*B*), and $k_8 = 3\ \mathrm{s}^{-1}$ (*C*). Other parameters like in paper [13].

Systems *I* and *III* afforded a negligible concentration of $HBrO_2$ and excess formation of Br^-. Even the introduction of dibromoacetone formation did not give a solution involving oscillations in system *III*.

The results of simulation obtained for system *II* are represented in Fig. 3. Provided k_8 exceeds 0.3 s^{-1}, a solution indicating oscillations can be obtained. If the value of k_8 increases, an induction period appears.

No solution involving oscillations was obtained for system *II* ($k_8 = 5.8 \times \times 10^{-6}\ s^{-1}$) and for system *III* ($k_6 = 15.5\ dm^3\ mol^{-1}\ s^{-1}$ [21], $k_6 = 25\ dm^3\ mol^{-1}\ s^{-1}$ [22] or $k_6 = 220\ dm^3\ mol^{-1}\ s^{-1}$ [23]) even if the FF rate constants were used. System *II* with the FF rate constants did not give any oscillations for k_8 varying in the range from $5.8 \times 10^{-7}\ s^{-1}$ to 10 s^{-1}. At least three values of k_8 were used in simulations for every decimal order.

The simulation with the BHC Oregonator was also carried out for experimental conditions under which bromine was removed physically ($k_8 = 2 \times \times 10^{-2}\ s^{-1}$, process GNF5, in the text called heterogeneous system [5]). Provided steps FB1—FB7 and the mentioned k_8 were used, the system did not manifest any oscillations. If the rate constants for FB7 taken from Table 1 were replaced by the latest values for bromine hydrolysis [24], a solution involving oscillations was obtained for $k_8 = 2 \times 10^{-2}\ s^{-1}$ and for parameters similar to those used in work [5] (Fig. 4).

The homogeneous closed oscillating system was established by experimental conditions [16]. The numerical integration of the system of differential equations of the BHC Oregonator was carried out for $k_8 = 0\ s^{-1}$. The values of rate constants published by *Eigen* and *Kustin* [25] or *Kshirsagar* and *Field* [24] were used for FB7. In both cases we obtained solution without oscillations even if the FF values were used for steps FB1—FB4.

Simulations with modifications of the GNF model

The original value of k_3 of the reaction GNF3 in the defining expression was replaced by 15.5 $dm^3\ mol^{-1}\ s^{-1}$ [22], which gave the rate parameter of 0.62 s^{-1} instead of 8.8 s^{-1}. The oscillating behaviour was obtained for $2 \times 10^{-3}\ s^{-1} < < k_5 < 9 \times 10^{-3}\ s^{-1}$, which approximately corresponded to a decrease in the parameter k_5 of physical removal of bromine from solution by one decimal order.

The use of complete rate equation [26] for oxidation of oxalic acid by the bromate ions (GNF8) brings the rate parameter $k_8 = 4 \times 10^{-6}\ mol\ dm^{-3}\ s^{-1}$ instead of $k_8 = 1.44 \times 10^{-6}\ mol\ dm^{-3}\ s^{-1}$. The system did not oscillate for $k_5 = 2 \times 10^{-2}\ s^{-1}$ but a solution indicating oscillations was obtained for $k_5 =$

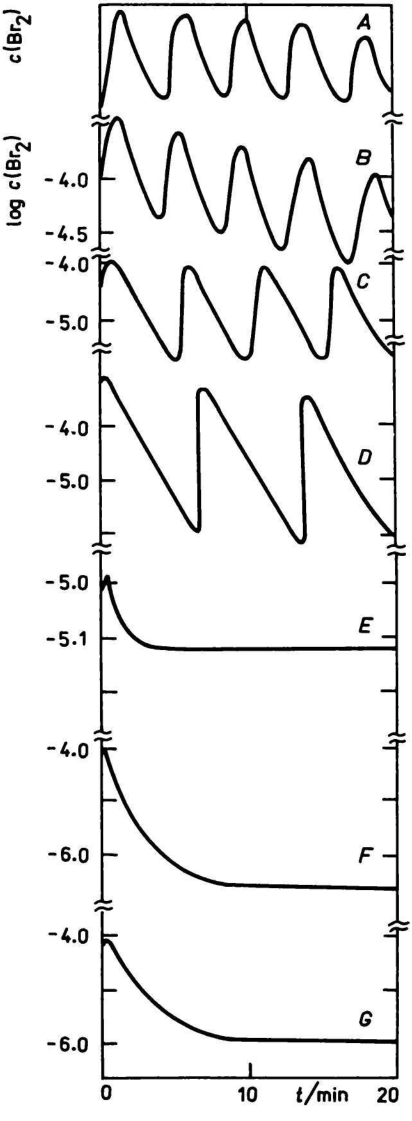

Fig. 4. Numerical simulations under conditions of heterogeneous system [5]. Experimental record of Br_2 oscillations (*A*). Simulation No. 4 in modifications of the Sasaki mechanism (Table 4) (*B*). Simulation of the Sasaki mechanism with the FF values of rate constants (*C*). Simulation of the BHC Oregonator with the rate constants according to [24] for the hydrolysis of Br_2 and replacement of FB8 by process GNF5 with $k_8 = 2 \times 10^{-2}\ s^{-1}$ (*D*). Simulation of the original GNF model (*E*). Simulation of the original Sasaki mechanism (*F*). Simulation of the original BHC Oregonator (*G*).

$= 6 \times 10^{-2}\ s^{-1}$ or $0.1\ s^{-1}$. An increase in k_8 produced a decrease in period and amplitude of oscillations (Fig. 5).

The application of the GNF model to experimental conditions of the heterogeneous system with bromine removal and $k_5 = 2 \times 10^{-2}\ s^{-1}$ [5] did not afford oscillating behaviour (Fig. 4*E*) nor did its modifications for $k_5 = 0\ s^{-1}$ under conditions of the homogeneous closed system.

Simulations with the modified Sasaki model

For simulation calculation we used the new FF values of rate constants [17] and $k_7 = 15.5\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [22]. However, the value $k_{13} = 5 \times 10^{-2}\ \mathrm{s^{-1}}$ did not give any oscillations for the Sasaki concentrations. Oscillations the period of which was equal to 3.5 min were obtained with $k_{13} = 2 \times 10^{-2}\ \mathrm{s^{-1}}$.

Other modifications consisted in inserting and omitting the following reactions

$\mathrm{BrO_3^- + (COOH)_2 \rightarrow HBrO_2}$ + inert products (S14)
$\mathrm{BrO_2^{\bullet} + HCO_2^{\bullet} \rightarrow HBrO_2 + CO_2}$ (S15)
$\mathrm{2\,HCO_2^{\bullet} \rightarrow (COOH)_2}$ (S12)
$\mathrm{HCO_2^{\bullet} + Ce(IV) \rightarrow CO_2 + Ce(III) + H^+}$ (S16)
$\mathrm{Ce(IV) + (COOH)_2 \rightarrow HCO_2^{\bullet} + Ce(III) + CO_2 + H^+}$ (S8)
$\mathrm{HBrO_2 + Ce(IV) \rightarrow BrO_2^{\bullet} + Ce(III) + H^+}$ (S−5)

while the FF rate constants were used for other reactions. The results of simulation obtained for heterogeneous conditions are given in Figs. 4, 6 and Table 4. If we use the latest values of rate constants [24] for reaction S3, we do not obtain oscillations in the original Sasaki mechanism, not even in its modi-

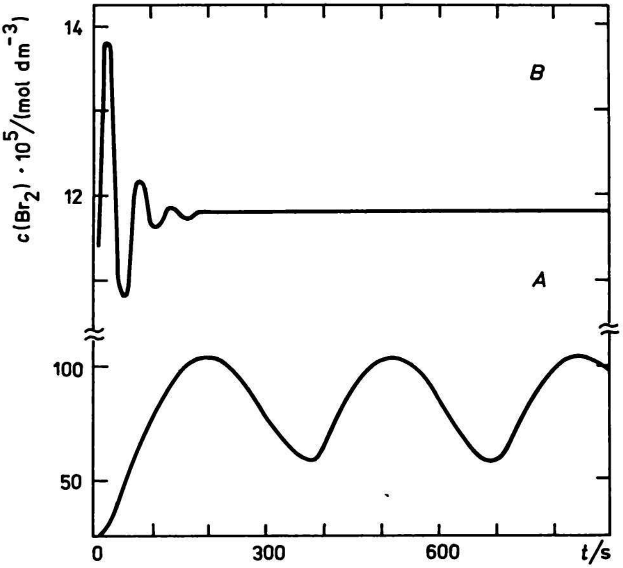

Fig. 5. Simulations with modifications of the GNF model. $k_3 = 0.62\ \mathrm{s^{-1}}$, $k_5 = 6 \times 10^{-3}\ \mathrm{s^{-1}}$, $k_8 = 1.44 \times 10^{-6}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ (*A*). $k_3 = 8.8\ \mathrm{s^{-1}}$, $k_5 = 6 \times 10^{-2}\ \mathrm{s^{-1}}$, $k_8 = 4 \times 10^{-6}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ (*B*). Other parameters like in paper [18].

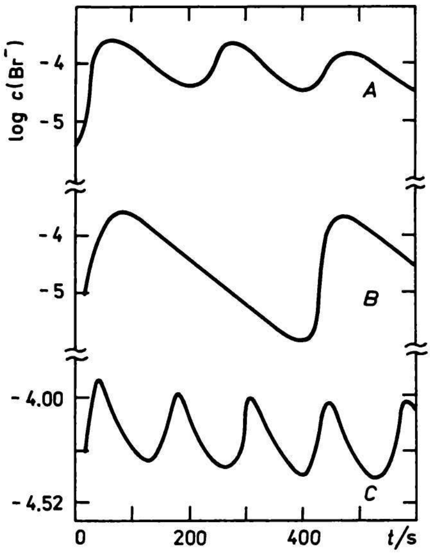

Fig. 6. Simulation of modifications of the Sasaki mechanism under conditions of heterogeneous system [5]. Simulation No. 3 (*A*), simulation No. 2 (*B*), simulation No. 1 (Table 4) (*C*).

fication with the Sasaki concentrations or under conditions of heterogeneous system [5].

As the Sasaki mechanism with original rate constants did not afford oscillations under conditions of heterogeneous system (Fig. 4*F*), we used the FF values

Table 4

Simulation of the modified Sasaki mechanism

Simulation	Reaction	Rate constant / $dm^3\ mol^{-1}\ s^{-1}$	Note
1	S14	2.5×10^{-3}	Fig. 6*C*
2	S15	5×10^9	Fig. 6*B*
3	S14	2.5×10^{-3}	
	S15	5×10^9	Fig. 6*A*
4	S14	2.5×10^{-3}	
	S15	1.6×10^{10}	Fig. 4*B*
5	S12	0	2 damped oscillations
6	S16	10^6	2 damped oscillations
7	S12	0	
	S16	10^6	No oscillations
8	S8	*a*	Oscillations with the period 90 s
9	S−5	0	Oscillations with the period 130 s

a) $0.1\ s^{-1}$.

and $k_7 = 15.5\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$. We obtained oscillations with a period of about 5 min. The introduction of further two reactions (simulation 3 and 4 in Table 4) giving rise to $HBrO_2$ afforded oscillations with the first period of 3.53 min and subsequent oscillations with the period of 4.29 min. Recently, *Försterling* and *Noszticzius* [27] pointed out the importance of reaction of the S15 type. If we raised the rate constant of reaction S15 to $1.6 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, we obtained oscillations with a period approaching the experimental value.

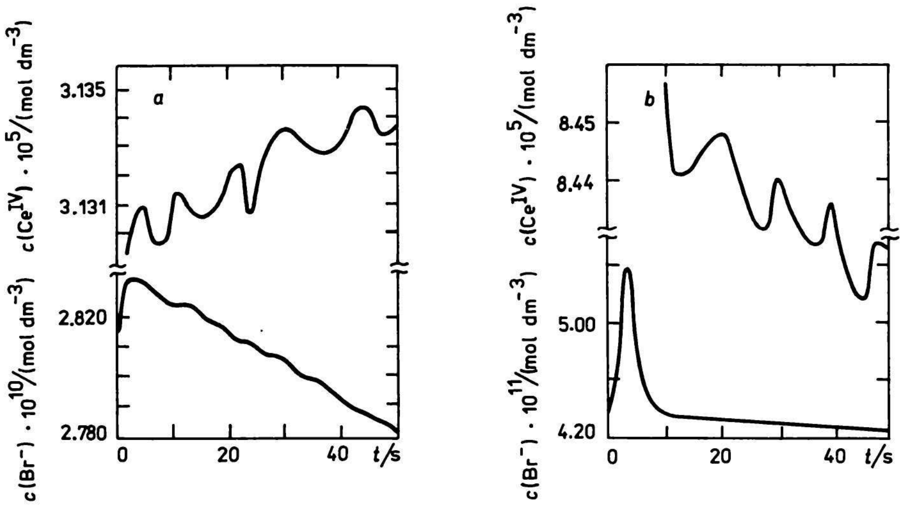

Fig. 7. Numerical simulations of the Sasaki mechanism in homogeneous closed system for k_{-3} and $k_{13} = 0\ \mathrm{s^{-1}}$. Concentrations according to [14] (*a*). Concentrations according to [16] (*b*).

The simulations concerning the Sasaki mechanism and its modifications did not afford any oscillations for the conditions of homogeneous closed system [16] with $k_{13} = 0\ \mathrm{s^{-1}}$. If we do not take into consideration the reversible hydrolysis of bromine ($k_{-3} = 0\ \mathrm{s^{-1}}$) in the original Sasaki mechanism, we obtain a periodic behaviour for catalyst concentration with short period (10 s) and amplitude of oscillations of 10^{-8}—$10^{-7}\ \mathrm{mol\ dm^{-3}}$ decimal order (Fig. 7) which, however, does not correspond to experiment.

Neither the Sasaki mechanism nor its modifications afforded oscillations for the FB conditions [13] and $k_{13} = 5.8 \times 10^{-6}\ \mathrm{s^{-1}}$ or $k_{13} = 5.8 \times 10^{-5}\ \mathrm{s^{-1}}$ which corresponded to the removal of bromine from solution by the bromination of acetone.

Discussion

The long-termed aim to find a convenient mechanism or at least a model for oscillations in a homogeneous closed system with nonbrominable substrate stimulated us to apply some modifications concerning the BHC Oregonator, the GNF model and the Sasaki mechanism. No modification and not a single one simulation with original model gave a solution involving oscillations for concentrations according to [16] and the rate constant corresponding to the removal of bromine from the reaction system which was equal to 0 s^{-1}. Only if the rate of the hydrolysis of bromine was neglected in the original Sasaki mechanism, we obtained a nonmonotonous course of catalyst concentrations in the course of time. In this case, the concentration of the Br^- ions was reduced and the accumulating bromine was prevented to affect the kinetics.

In order to find out to what extent the above-mentioned models are able to reproduce experiment, we also simulated oscillations under heterogeneous conditions [5]. We obtained a solution indicating oscillations for the Sasaki mechanism with the FF values of rate constants, for some its modifications as well as for the BHC Oregonator with the latest value of the rate constants of bromine hydrolysis. In the last case, the oscillations were obtained owing to reduction of the rate of decay of the Br^- ions in reaction FB7 and to fifty-fold reduction of the rate of bromine hydrolysis.

The problem of accumulation of hypobromous acid in the original Oregonator (where the consumption of the Br^- ions in the reaction with HOBr giving rise to Br_2 was neglected) also appeared in its modification, *i.e.* in the BHC Oregonator. The authors allege that they were obliged to raise the rate constant of the oxidation of oxalic acid by hypobromous acid (FB6) six times when compared with the experimental value [22] for obtaining oscillations conformable with experiment. However, owing to this increase the concentration of HOBr and Br^- decreases. On the other hand, a too high concentration of bromine brings about that a too great number of the Br^- ions is generated by bromine hydrolysis. Then bromous acid preferentially reacts with Br^- and its autocatalytic formation does not take place (FB3). Therefore our simulations necessitated to increase the rate constant of bromine removal (FB8) as much as by five decimal orders for obtaining a solution involving oscillations. An increase in this rate constant brings about an increase in concentration of the Br^- ions. For this reason, step FB3 is retarded and an induction period appears in simulations. The length of this induction period increases with the increasing value of the rate constant for FB8.

The GNF model as well as the Explodator does not take into account the influence of catalyst on the kinetics of the BZ reaction. It comprises similar steps at the BHC Oregonator. If the rate constant equal to 15.5 $dm^3\ mol^{-1}\ s^{-1}$ is applied in the reaction of oxalic acid with HOBr instead of the too high value given in [23], the rate constant of bromine removal must be reduced by one decimal order for obtaining oscillations in the GNF model. Thus the loss of the Br^- ions is compensated. The rate constant of reduction of oxalic acid was made fourteen times smaller and so much the possible limit for the rate of GNF5 process was cut down. Reaction GNF8 is important from the viewpoint of induction period. Owing to this reaction the GNF model does not require nonzero initial concentrations of intermediates. The use of the complete rate equation for GNF8 increases the concentration of bromous acid in simulation and shortens the period of oscillations. Simultaneously the disproportionation of $HBrO_2$, too, proceeds faster and the amplitude of oscillations decreases. The use of new rate constants for reactions GNF6 and GNF8 simultaneously reduces the possible range of rate of bromine removal (GNF5) in oscillation solution because this process affects the formation not only of Br^- ions but also of $HBrO_2$.

The simulations applying the Sasaki mechanism and the FF values of rate constants confirm the rightness of using these constants because they are able to reproduce experiment. The introduction of the reaction of the $BrO_2^{\bullet}$ and $HCO_2^{\bullet}$ radicals with the rate constant of 1.6×10^{10} dm^3 mol^{-1} s^{-1} led to oscillations with a period agreeing with experiment, but only for one set of concentrations. The introduction of the reaction of oxalic acid with the BrO_3^- ions into the Sasaki mechanism affects the period as well as the amplitude of oscillations, which indicates the kinetic importance of this reaction.

The numerical simulations show that the use of the FF rate constants in present models of oscillation reactions of the BZ type with nonbrominable substrate enables us to interpret oscillations in a heterogeneous system with oxalic acid in case the arising bromine is continuously removed from the reaction solution by a stream of inert gas, the rate constant of this process being 10^{-3}—10^{-2} s^{-1}. We failed in striving to obtain a solution with oscillations in the BZ system with oxalic acid if bromine was removed by bromination of the acetone present in real concentrations or was not removed at all.

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