

# Modeling of a Silver Ion Perturbed Belousov–Zhabotinskii Oscillator

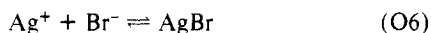
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There has been much recent study of the reaction  $\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}$  (reaction O6) and its relevance to the silver ion perturbed Belousov–Zhabotinskii reaction; the mechanistic interpretation of the so-called non-bromide-controlled oscillations, and the refutation of that interpretation, depend quite strongly on whether this reaction effectively removes bromide from the solution. Our work examines the effect of silver bromide precipitation on two modified Oregonator models, with a variety of rate constants of (O6). We show that, if the reaction O6 is assumed slow, bromide control can be maintained, but at the expense of having very high supersaturation of AgBr monomers. If reaction O6 is fast, no bromide-controlled oscillations occur while there is a significant concentration of silver ion. A more involved precipitation model with recent experimentally determined rate constants also shows that the Oregonator will not give bromide-controlled oscillations during the time when silver ion is in high concentration. Furthermore, the simulations indicate that the relatively high rate of the bromide production reaction O5 predicts a fast disappearance of the silver ions which contradicts the experimental results. It is concluded that models which include the “non-bromide-controlled” oscillations as perturbed bromide-controlled oscillations are thus far incomplete and that modification of these models should be considered.

## Introduction

In a recent paper Noyes et al.<sup>1</sup> reviewed the controversial interpretations of  $\text{Ag}^+$  perturbation of the Belousov–Zhabotinskii (BZ) reaction. One source of the controversy is the mechanistic interpretation of the oscillations observed by Noszticzius<sup>2</sup> in the classical BZ system<sup>3</sup> in the presence of  $10^{-3}$  M silver ions. While at first all authors<sup>2–4</sup> agreed that these oscillations are non-bromide-controlled in their nature, opinions have been divided since the publication of two interesting papers by Ruoff and Schwitters.<sup>5,6</sup> These authors assumed that bromide control prevails even in the presence of silver ions. Their crucial hypothesis is that the reversible bromide ion removing reaction—often designated as (O6)—is a relatively slow one



Due to the slowness of (O6) enough free bromide can accumulate in the BZ system via other bromide-producing reactions to reach its critical concentration even in the presence of  $10^{-3}$  M silver ions. Whenever the bromide concentration reaches its critical value it “turns off” the autocatalytic bromous acid production. Consequently, if (O6) is slow, bromide is able to control relaxation oscillations even in the presence of silver ions. Thus, the controversy has focused on the rate of (O6). The conflicting views and experiments can be read in the refs 1 and 7–13. As Kshirsagar et al.<sup>11</sup> and Noyes et al.<sup>1</sup> emphasize, the whole process of silver bromide precipitation is a rather complicated one. Nevertheless, according to ref 1,  $v_{\text{O6}}$ , the net rate of (O6), can be estimated at sufficiently long times by an expression of the form

$$v_{\text{O6}} = k_{\text{O6}}\{[\text{Ag}^+][\text{Br}^-] - [\text{Ag}^+]_{\text{eq}}[\text{Br}^-]_{\text{eq}}\} \quad (1)$$

where

$$[\text{Ag}^+]_{\text{eq}}[\text{Br}^-]_{\text{eq}} = S \quad (2)$$

is the product of the silver and bromide ion concentrations in the final equilibrium, i.e., the solubility product  $S$ . Ruoff and Schwitters<sup>5,6</sup> presented model calculations which generated oscillations of approximately the observed frequency and amplitude while assuming that  $k_{\text{O6}}$  was about  $10^4 \text{ M}^{-1} \text{ s}^{-1}$ . Noszticzius and McCormick<sup>10</sup> performed experiments suggesting that  $k_{\text{O6}}$  is greater than  $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . As Noyes et al.<sup>1</sup> point out correctly “Noszticzius has not yet attempted to counter the Ruoff claims by making computations with the large  $k_{\text{O6}}$  he believes is more appropriate”. Thus the aim of the present work is to study the effect of  $k_{\text{O6}}$  on the modeling. This is especially timely because new estimates and measurements for  $k_{\text{O6}}$  are now available. Ruoff et al.<sup>9</sup> estimated that  $k_{\text{O6}}$  is  $5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . According to Försterling et al.,<sup>13</sup>  $k_{\text{O6}}$  is  $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , while according to Marek et al.<sup>14</sup>  $k_{\text{O6}}$  is probably greater than  $10^6 \text{ M}^{-1} \text{ s}^{-1}$ . Most recently some direct measurements on O6 were also made by Meisel et al.<sup>15</sup> They found a diffusion-limited forward rate constant for reaction O6.

## Model Calculations

The rate constants of the BZ reaction were revised recently by Field and Försterling.<sup>16</sup> Consequently, for a realistic comparison we started with the Oregonator model used by Kshirsagar et al.<sup>11</sup> in their studies of the silver-perturbed BZ system; these authors applied the Field–Försterling rate constants in their calculations. Unlike Kshirsagar et al.,<sup>11</sup> however, we did not assume any direct reactions between silver bromide oligomers and oxybromine species. Instead, following Ruoff and Schwitters,<sup>5,6</sup> we assume that only free (i.e., uncomplexed) bromide ions can take part in direct reactions with the oxybromine molecules. The mechanism, the original Oregonator plus the reversible precipitation reaction, is given in Table I together with the rate constants and initial conditions that were used.

Our program of model calculations involved four basic steps: 1. First we performed calculations assuming that  $k_{\text{O6}} = 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , as originally suggested by Ruoff and Schwitters. The results are shown in Figure 1. In addition to the usual  $\log [\text{Br}^-]$

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**TABLE I: Reactions, Rate Constants, and Initial Conditions Used in Our Simulations<sup>a</sup>**

	$A + Y \rightarrow X + P$ $X + Y \rightarrow 2P$ $A + X + C \rightarrow 2X + Z$ $2X \rightarrow A + P$ $Z \rightarrow fY + C$ $Ag^+ + Y \rightleftharpoons AgBr$ $2AgBr \rightarrow Ag_2Br_2$
	Initial Conditions
A	$5.0 \times 10^{-2} \text{ M}$
Y	$3.6 \times 10^{-6} \text{ M}$
X	$1.6 \times 10^{-7} \text{ M}$
C	$1.0 \times 10^{-3} \text{ M}$
Z	$1.3 \times 10^{-6} \text{ M}$
Ag <sup>+</sup>	$2.0 \times 10^{-3} \text{ M}$ (Figure 1, Figure 2a-d), $2.0 \times 10^{-2} \text{ M}$ (Figure 2e-g)
	Rate Constants
$k_{O1}$	$2.1 \text{ M}^{-1} \text{ s}^{-1}$
$k_{O2}$	$1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
$k_{O3}$	$4.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$
$k_{O4}$	$2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$
$k_{O5}$	$0.2 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 1, Figure 2e-g), $0.02 \text{ s}^{-1}$ (Figure 2a-d)
$k_{O6}$	$1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ to $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
$k_{O6b}$ (used only for Figure 1g-h, Figure 2)	$4.6 \times 10^5 \text{ s}^{-1}$
$k_{M7}$ (used only for Figure 1g-h, Figure 2)	$1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
	Other Constants
f	1
S	$7.7 \times 10^{-13} \text{ M}^2$
	Sources of Species
Ag <sup>+</sup> (Figure 1a-f)	$k_{O6}S$
Br <sup>-</sup> (Figure 1a-f)	$k_{O6}S$
AgBr (Figure 1g,h)	$2k_{M7} [k_{O6f}/k_{O6b}]^2 S^2$

<sup>a</sup>The sources mentioned refer to an approximation in which the backward reaction of either (O6) or (M7) is treated as a steady source of bromide and silver (for (O6)) or AgBr (for (M7)) (cf. eqs 2 and 3).

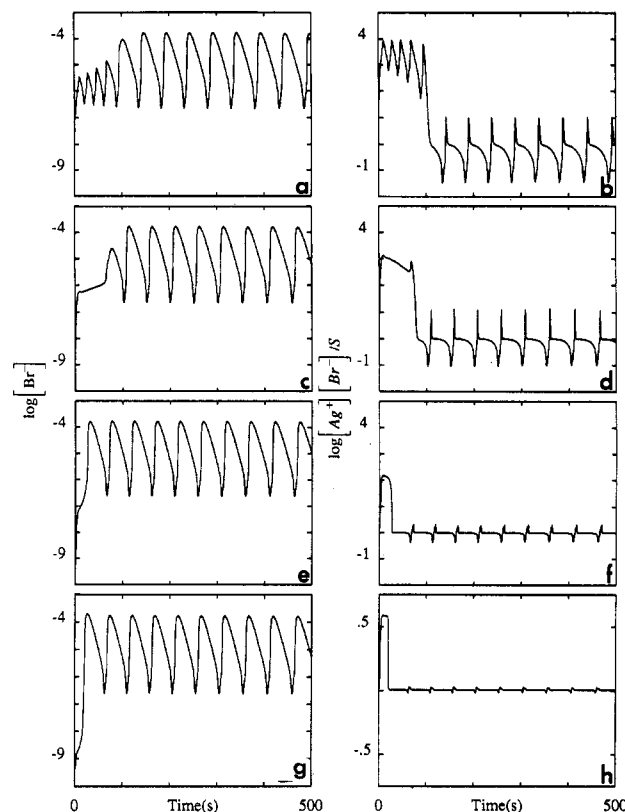
trace in Figure 1a, we have included a trace of the logarithm of the supersaturation ratio,  $\log R$ , in Figure 1b:

$$\log R = \log \frac{[Ag^+][Br^-]}{S}$$

2. We repeated the above calculation with  $k_{O6} = 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  as was proposed by Ruoff et al.<sup>9</sup>

3. We ran simulations with  $k_{O6} = 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . This value is in accordance with the findings of Marek et al.<sup>14</sup>

4. Lastly, we made some model calculations incorporating the recent results of Meisel et al.<sup>15</sup> These authors generated supersaturated solutions of silver and halide ions using a pulse radiolysis technique. We shall cite their work for the case of bromide only. They concluded that the initial reaction between Ag<sup>+</sup> and Br<sup>-</sup> ions proceeds at a diffusion-controlled rate, rapidly establishing an equilibrium between AgBr molecules and the ions. According to their results the rate constant of the forward reaction of (O6) is  $k_{O6f} = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , while the rate constant of the backward reaction is  $k_{O6b} = 4.6 \times 10^5 \text{ s}^{-1}$ . Moreover, they have shown that the subsequent growth of AgBr molecules to colloidal particles is an agglomeration process with diffusion-controlled rate constants. Unfortunately, the dissociation rates of the different oligomers participating in the growth process are not known. What is known, however, is that these rates are relatively small because an irreversible model of the growth<sup>17</sup> gives a fairly good description of the whole process.<sup>15</sup> On the basis of these results we tried to



**Figure 1.** Plots of  $\log [Br^-]$  and  $\log [Ag^+][Br^-]/S$  for the simulations we performed. (a-f) Simulations of the Oregonator with perturbation by (O6). (a, b)  $k_{O6f} = 1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . (c, d)  $k_{O6f} = 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . (e, f)  $k_{O6f} = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . (g, h) Perturbation by (O6) and (M7).  $k_{O6f} = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{O6b} = 4.6 \times 10^5 \text{ s}^{-1}$ . Note the vertical scale has changed in (h).

model the process of precipitation with a two-step model consisting of (O6) and (M7):



The rate law for (M7) was written in a form similar to  $v_{O6}$

$$v_{M7} = k_{M7}([AgBr]^2 - [AgBr]_{eq}^2) \quad (3)$$

where  $[AgBr]_{eq}$  is the concentration of the monomeric silver bromide molecules in the final thermodynamic equilibrium, i.e.

$$[AgBr]_{eq} = \frac{k_{O6f}}{k_{O6b}} S$$

The logic behind the actual form of  $v_{M7}$  is similar to the case of  $v_{O6}$ : the concentration of the AgBr molecules should reach its equilibrium value as an asymptotic state. The problems of such a simplified description are obvious. In the real process there are many oligomers besides the dimer, and within the first second of the precipitation the aggregation numbers already range up to 1000.<sup>15</sup> All of these oligomers are reacting simultaneously with each other and with the monomers with diffusion-controlled rates. Nevertheless, neglecting all of these reactions can give a lower limit for the rate of the disappearance of the monomeric species at least far from equilibrium, when back reactions are unimportant. The results of our model calculations are depicted in Figure 1g-h.

In all cases, the differential equations were integrated by using DEBDF, a variable-order, variable-time-step, backward differentiation formula integrator<sup>22</sup> on a Silicon Graphics 4 Server 8. The

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initial conditions and rate constants we used are given in Table I. The initial conditions are those used by Kshirsagar et al.<sup>11</sup> and are obtained by integrating an unperturbed Oregonator for some time.

### Discussion

Figure 1a shows that the Ruoff-Schwitters model with the original, low  $k_{O6}$  value works well with the Field-Försterling<sup>16</sup> rate constants. Five silver-perturbed oscillations can be observed with a higher frequency and a lower amplitude in a semiquantitative agreement with the experimental results of Noszticzius.<sup>2</sup> After about 100 s, when most of the silver ions have been precipitated, oscillations with the regular frequency and amplitude resume. Figure 1b reveals, however, a peculiar feature of these oscillations. Assuming a relatively low  $k_{O6}$  results in a surprisingly high oversaturation of the AgBr monomer over an extended period of time. During the first 100 s the supersaturation ratio (i.e., the actual AgBr monomer concentration divided by its equilibrium value) oscillates around 1000, reaching a peak value of nearly 10 000.

Figure 1c shows that only a single silver-perturbed oscillation can be observed in the Ruoff-Schwitters model if  $k_{O6} = 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  as it was suggested by Ruoff et al.<sup>9</sup> Nevertheless, according to Figure 1d the supersaturation ratio is still unusually high; it reaches a peak value of more than 1000.

In Figure 1e, analogous calculations can be seen for  $k_{O6} = 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . No silver-perturbed oscillations were found in this case. After an initial transient regime of 20 s (with a supersaturation ratio above 100; see Figure 1f) the usual oscillations appear.

Finally, Figure 1g shows that no silver-perturbed oscillations can be observed in the calculations if we apply the simplified two-step precipitation model incorporating the rate constants found by Meisel et al.<sup>15</sup> Figure 1h shows that the initial high supersaturation rapidly decreases and after the first second it settles down to a value of 4. After 20 s this drops further to a value near unity.

It is interesting to remark that the high supersaturation ratio displayed in Figure 1b is a prerequisite of oscillations if we want to maintain the bromide control in the BZ system even in the presence of  $2 \times 10^{-3} \text{ M}$  silver ions. Bromide control can switch off the autocatalytic reaction only if its concentration surpasses a critical value<sup>23</sup>

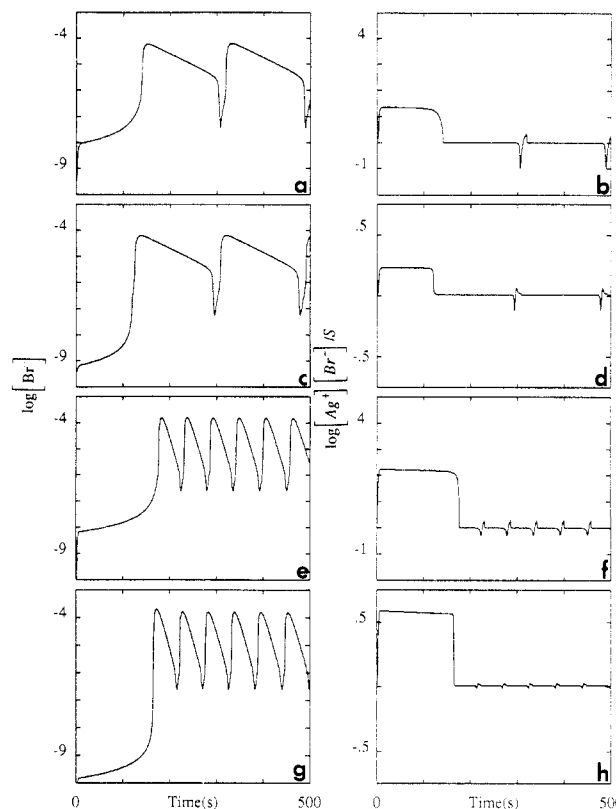
$$[\text{Br}^-]_{\text{crit}} = [\text{BrO}_3^-] \cdot 18 \times 10^{-6}$$

In our case  $[\text{BrO}_3^-] = 5 \times 10^{-2} \text{ M}$ ; thus  $[\text{Br}^-]_{\text{crit}} = 9 \times 10^{-7} \text{ M}$ . The nonequilibrium ionic product in the presence of  $2 \times 10^{-3} \text{ Ag}^+$  at the critical bromide concentration is

$$[\text{Ag}^+][\text{Br}^-]_{\text{crit}} = 1.8 \times 10^{-9} \text{ M}^2$$

This is more than 3 orders of magnitude higher than the equilibrium ionic product of  $S = 7.7 \times 10^{-13} \text{ M}^2$ . To maintain this nonequilibrium situation we need an AgBr monomer concentration which is proportionately higher than its equilibrium value.

Another problem inherent in the simulations is that, due to the relatively high rate of the bromide production reaction (O5), silver ions disappear from the system too soon in the model calculations, in contradiction with experimental results. In fact, for realistic values of  $k_{O6}$  the length of the silver-rich, oscillation-free regime is less than one time period in the oscillatory regime (see Figure 1e-h). If we decrease  $k_{O5}$  by 1 order of magnitude, both the oscillation-free regime and the time period of the oscillations are increased (see Figure 2a-d). Thus decreasing  $k_{O5}$  does not help. If the initial silver concentration is increased by 1 order of magnitude, as it is in the simulations of Figure 2e-h, the silver-rich



**Figure 2.** Plots of  $\log [\text{Br}^-]$  and  $\log [\text{Ag}^+][\text{Br}^-]/S$ . (a-d)  $k_{O5} = 0.02 \text{ s}^{-1}$ ,  $[\text{Ag}^+]_0 = 2 \times 10^{-3} \text{ M}$ . (a, b) Reactions O1 through O5 with O6 perturbation and  $k_{O6} = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . (c, d) Perturbation by (O6) and (M7),  $k_{O6f} = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{O6b} = 4.6 \times 10^5 \text{ s}^{-1}$ . (e-h)  $k_{O5} = 0.2 \text{ s}^{-1}$ ,  $[\text{Ag}^+]_0 = 2 \times 10^{-2} \text{ M}$ . (e, f) Perturbation by (O6),  $k_{O6} = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . (g, h) Perturbation by (O6) and (M7),  $k_{O6f} = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{O6b} = 4.6 \times 10^5 \text{ s}^{-1}$ . Note that the scales in (a, b) and (e, f) differ from those in (c, d) and (g, h).

regime can be increased without affecting the time period of the oscillating regime. The problem with this result is that still no silver ion perturbed oscillations can be seen in this increased silver-rich regime.

### Conclusions

Our calculations show that silver-perturbed oscillations can be reproduced with the Ruoff-Schwitters model if  $k_{O6}$  is  $10^4 \text{ M}^{-1} \text{ s}^{-1}$  or lower. This is much smaller than the recently found experimental values.<sup>9,10,13-15</sup> There are three possible resolutions to this contradiction.

1. If we want to maintain that the silver-perturbed BZ oscillator is really controlled by free bromide ion as proposed by Ruoff and Schwitters,<sup>5,6</sup> then we must modify the rate laws describing the precipitation process in order to achieve the required high supersaturation ratios.

2. We can assume that the reaction is controlled by some oligomers as proposed by Kshirsagar et al.<sup>11</sup>

3. Finally, it is possible that, in the presence of silver ions, BZ oscillations are not controlled by free or complexed bromide ions. In this case we have to find another control intermediate. Organic free radicals are good candidates for the role of an additional control intermediate as proposed by several authors.<sup>18-21</sup>

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